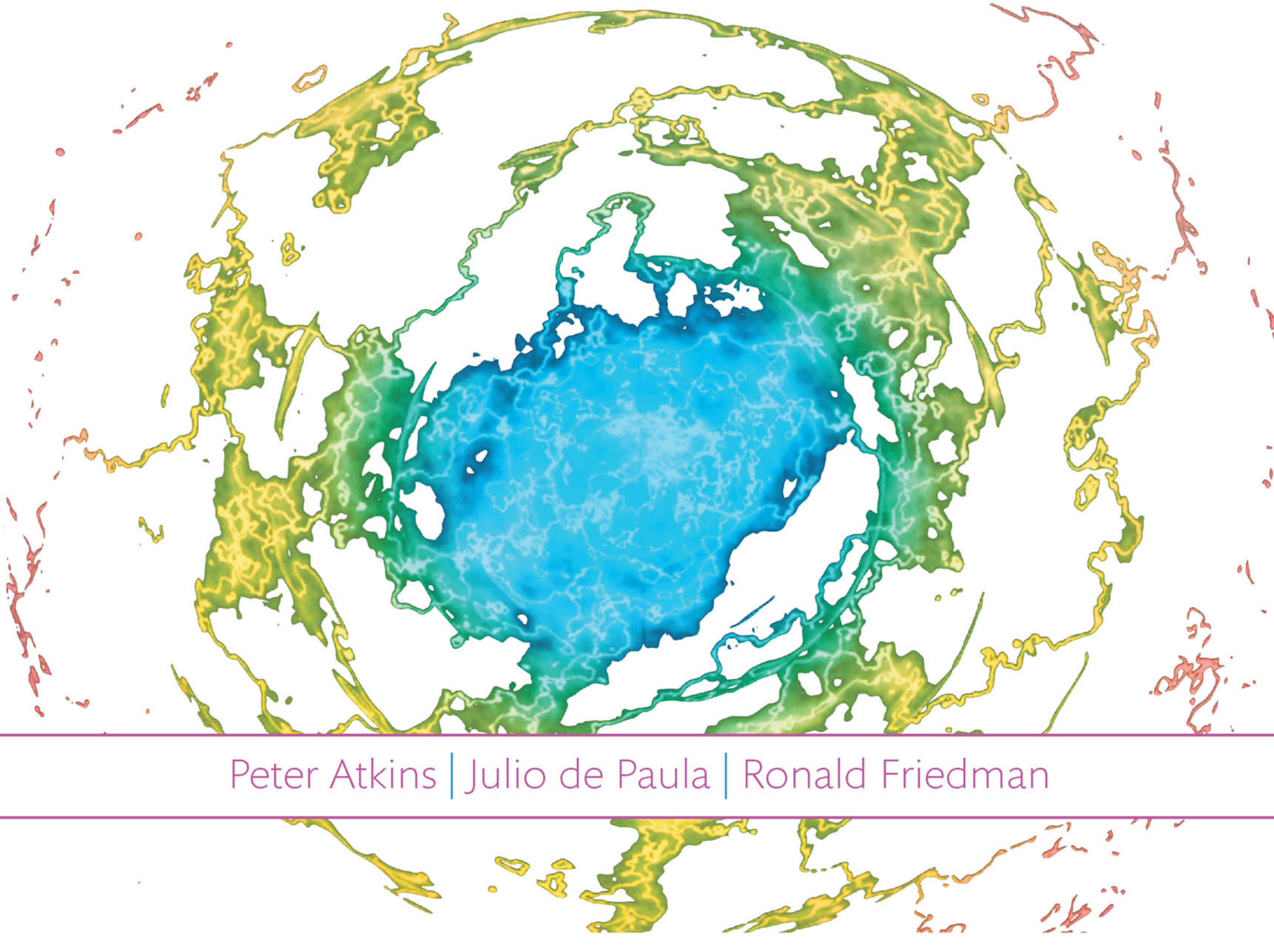
Physical Chemistry

Quanta, Matter, and Change

Second Edition



Peter Atkins | Julio de Paula | Ronald Friedman

FUNDAMENTAL CONSTANTS

Constant	Symbol	Value		
			Power of 10	Units
Speed of light	c	2.997 924 58*	10^{8}	m s^{-1}
Elementary charge	e	1.602 176 565	10^{-19}	C
Planck's constant	h	6.626 069 57	10^{-34}	J s
	$\hbar = h/2\pi$	1.054 571 726	10^{-34}	J s
Boltzmann's constant	k	1.380 6488	10^{-23}	J K^{-1}
Avogadro's constant	N_A	6.022 141 29	10^{23}	mol^{-1}
Gas constant	$R = N_\mathrm{A}k$	8.314 4621		J K^{-1} mol^{-1}
Faraday's constant	$F = N_\mathrm{A}e$	9.648 533 65	10^{4}	C mol^{-1}
Mass				
electron	m_e	9.109 382 91	10^{-31}	kg
proton	m_p	1.672 621 777	10^{-27}	kg
neutron	m_n	1.674 927 351	10^{-27}	kg
atomic mass constant	m_u	1.660 538 921	10^{-27}	kg
Vacuum permeability	μ_0	4π*	10^{-7}	J s^{2} C^{-2} m^{-1}
Vacuum permittivity	$\varepsilon_0 = 1/\mu_0 c^2$	8.854 187 817	10^{-12}	J^{-1} C^{2} m^{-1}
	$4\pi\varepsilon_0$	1.112 650 056	10^{-10}	J^{-1} C^{2} m^{-1}
Bohr magneton	$\mu_\mathrm{B} = e\hbar/2m_\mathrm{e}$	9.274 009 68	10^{-24}	J T^{-1}
Nuclear magneton	$\mu_\mathrm{N} = e\hbar/2m_\mathrm{p}$	5.050 783 53	10^{-27}	J T^{-1}
Proton magnetic moment	μ_p	1.410 606 743	10^{-26}	J T^{-1}
g-Value of electron	g_e	2.002 319 304		
Magnetogyric ratio				
electron	$\gamma_\mathrm{e} = -g_\mathrm{e}e/2m_\mathrm{e}$	−1.001 159 652	10^{10}	C kg^{-1}
proton	$\gamma_\mathrm{p} = 2\mu_\mathrm{p}/\hbar$	2.675 222 004	10^{8}	C kg^{-1}
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/e^2 m_\mathrm{e}$	5.291 772 109	10^{-11}	m
Rydberg constant	$\tilde{R}_\infty = m_\mathrm{e}e^4/8h^3 c\varepsilon_0^2$	1.097 373 157	10^{5}	cm^{-1}
	$hc\tilde{R}_\infty/e$	13.605 692 53		eV
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	7.297 352 5698	10^{-3}	
	α^{-1}	1.370 359 990 74	10^{2}	
Second radiation constant	$c_2 = hc/k$	1.438 777 0	10^{-2}	m K
Stefan–Boltzmann constant	$\sigma = 2\pi^5 k^4/15h^3 c^2$	5.670 373	10^{-8}	W m^{-2} K^{-4}
Standard acceleration of free fall	g	9.806 65*		m s^{-2}
Gravitational constant	G	6.673 84	10^{-11}	N m^{2} kg^{-2}

* Exact value. For current values of the constants, see the National Institute of Standards and Technology (NIST) website.

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PHYSICAL CHEMISTRY

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Second edition

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ABOUT THE BOOK

This new edition follows the approach of the first edition in so far as it puts quantum theory in the forefront of the development, but we have transformed the presentation. Instead of the chapters of conventional texts, we have presented the material as a series of short *Topics* arranged into thematic groups we call *Focuses*. Our aim is to present reader and instructor with maximum flexibility. Although we had in mind a particular sequence when writing the book, we acknowledge that instructors might have different ideas. The division into many Topics will allow the instructor to tailor the text within the time constraints of the course as omissions will be much easier to make. The student should also find the Topics easier to assimilate and review. No longer is it necessary to take a linear path through chapters. Instead, students and instructors can match the choice of Topics to their learning objectives. Indeed, we have carefully avoided language that suggests the Topics have been read in the order they appear in the book.

We did consider avoiding any implication of structure, but came to the view that because the Topics do fall into thematic groups it would be sensible to acknowledge that fact. Moreover, we wanted the student, if not the instructor, to appreciate the intellectual coherence of the subject and to understand the context of each Topic. Each Focus therefore begins with a brief discussion of how its Topics cover a shared theme and how that theme links to others in the book. This contextual relationship is also captured by the 'Road Map' that lies at the head of each Focus. These maps also indicate not only how the Topics relate to each other but how certain Topics can be discarded and how each one draws on and feeds into other Focus groups. We wanted to convey the intellectual structure of the subject without imposing our will on its order of presentation.

We have focused on helping students master this sometimes daunting material. Thus, each Topic opens with three questions a student typically asks: 'Why do you need to know this material?', 'What is the key idea?', and 'What do you need to know already?'. The answers to the third question point to other Topics that we consider appropriate to have studied or at least to refer to as background to the current Topic.

This edition has more *Examples,* which require readers to collect and organize their thoughts about how to proceed, and more *Brief illustrations*, which show how to use an equation in a straightforward way. Both have *Self-tests* to enable the reader to assess their grasp of the material. In response to requests from students and reviewers, we have added more steps to many of the derivations of equations and solutions of Examples and have added hints about how to go from one expression to the next. Furthermore, we bring to this edition a new feature: *The chemist's toolkit*, which offers quick and immediate help on a concept from mathematics or physics. The *Mathematical background* sections provide more support and appear where we judge they are most needed. We have structured the end-of-Focus *Discussion questions*, *Exercises*, and *Problems* to match the grouping of the Topics, but have added Topic- and Focus-crossing *Integrated activities* to emphasize that no Topic is an island. We have added new material throughout the text and have incorporated as Topics sections that were previously 'Further information' sections.

Teaching and learning are being transformed by technology, and this edition of the text incorporates several web-based resources that enhance learning: they are identified in the *How to use this book* section that follows this preface.

We hope that you will enjoy using this text as much as we have enjoyed writing it. As ever, we hope that you will contact us with your suggestions for its continued improvement.

PWA
JdeP
RSF

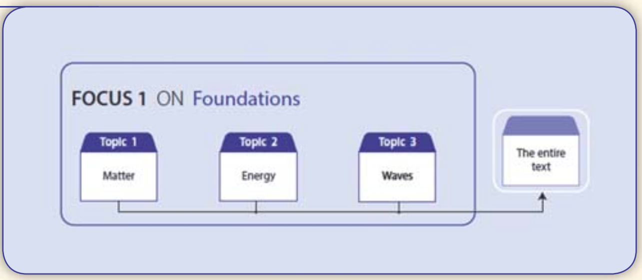
USING THE BOOK

For the second edition of *Physical Chemistry: Quanta, Matter, and Change* we have tailored the text even more closely to meet the needs of students. First, it has been radically reorganized to improve its accessibility, clarity, and flexibility. Second, in addition to the variety of learning features already present in the first edition, we have significantly enhanced the mathematics support by adding new 'Chemist's toolkit' boxes, equation annotations and labels, and checklists of key equations at the end of each Topic.

Organizing the information

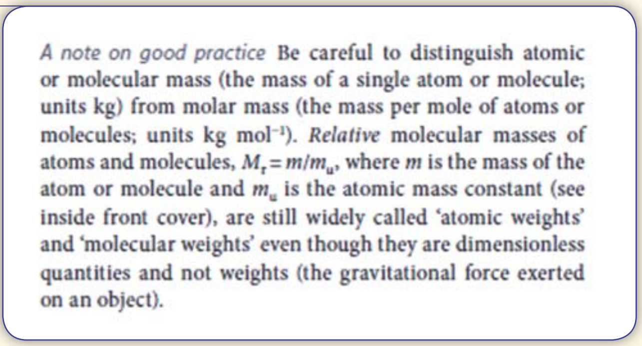
➤ Innovative new structure

Instead of being organized into chapters, the material is presented as 97 short Topics grouped into 20 Focus sections. The Roadmaps at the beginning of each Focus group show you the connections between the different Topics. Then each Topic opens with a comment on why it is important, a statement of the key idea, and a short summary of the background needed.



➤ Notes on good practice

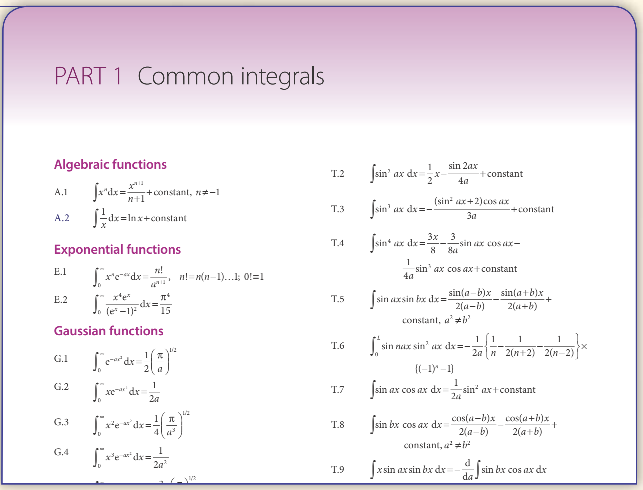
Our Notes on good practice will help you avoid making common mistakes. They encourage conformity to the international language of science by setting out the language and procedures adopted by the International Union of Pure and Applied Chemistry (IUPAC).



A note on good practice Be careful to distinguish atomic or molecular mass (the mass of a single atom or molecule; units kg) from molar mass (the mass per mole of atoms or molecules; units kg mol^{-1}). *Relative* molecular masses of atoms and molecules, $M_r = m/m_u$, where m is the mass of the atom or molecule and m_u is the atomic mass constant (see inside front cover), are still widely called 'atomic weights' and 'molecular weights' even though they are dimensionless quantities and not weights (the gravitational force exerted on an object).

➤ Resource section

The comprehensive 'Resource section' at the end of the book contains a table of integrals, operators, quantum numbers, and data, a summary of conventions about units, and character tables. Short extracts of these tables often appear in the Topics themselves principally to give an idea of the typical values of the physical quantities we are introducing.



PART 1 Common integrals

Algebraic functions

A.1 $\int x^n \mathrm{d}x = \frac{x^{n+1}}{n+1} + \text{constant},\ n \neq -1$

A.2 $\int \frac{1}{x}\mathrm{d}x = \ln x + \text{constant}$

Exponential functions

E.1 $\int_0^\infty x^n \mathrm{e}^{-ax}\mathrm{d}x = \frac{n!}{a^{n+1}},\quad n! = n(n-1)\ldots 1;\ 0! \equiv 1$

E.2 $\int_0^\infty \frac{x^4 \mathrm{e}^x}{(\mathrm{e}^x - 1)^2}\mathrm{d}x = \frac{\pi^4}{15}$

Gaussian functions

G.1 $\int_0^\infty \mathrm{e}^{-ax^2}\mathrm{d}x = \frac{1}{2}\left(\frac{\pi}{a}\right)^{1/2}$

G.2 $\int_0^\infty x\mathrm{e}^{-ax^2}\mathrm{d}x = \frac{1}{2a}$

G.3 $\int_0^\infty x^2\mathrm{e}^{-ax^2}\mathrm{d}x = \frac{1}{4}\left(\frac{\pi}{a^3}\right)^{1/2}$

G.4 $\int_0^\infty x^3\mathrm{e}^{-ax^2}\mathrm{d}x = \frac{1}{2a^2}$

T.2 $\int \sin^2 ax\,\mathrm{d}x = \frac{1}{2}x - \frac{\sin 2ax}{4a} + \text{constant}$

T.3 $\int \sin^3 ax\,\mathrm{d}x = -\frac{(\sin^2 ax + 2)\cos ax}{3a} + \text{constant}$

T.4 $\int \sin^4 ax\,\mathrm{d}x = \frac{3x}{8} - \frac{3}{8a}\sin ax \cos ax - \frac{1}{4a}\sin^3 ax \cos ax + \text{constant}$

T.5 $\int \sin ax \sin bx\,\mathrm{d}x = \frac{\sin(a-b)x}{2(a-b)} - \frac{\sin(a+b)x}{2(a+b)} + \text{constant},\ a^2 \neq b^2$

T.6 $\int_0^L \sin nax \sin^2 ax\,\mathrm{d}x = -\frac{1}{2a}\left\{\frac{1}{n} - \frac{1}{2(n+2)} - \frac{1}{2(n-2)}\right\} \times \{(-1)^n - 1\}$

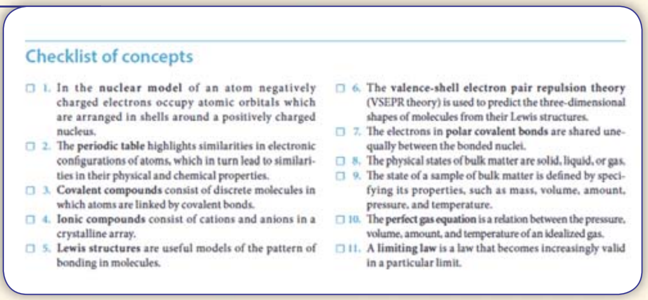
T.7 $\int \sin ax \cos ax\,\mathrm{d}x = \frac{1}{2a}\sin^2 ax + \text{constant}$

T.8 $\int \sin bx \cos ax\,\mathrm{d}x = \frac{\cos(a-b)x}{2(a-b)} - \frac{\cos(a+b)x}{2(a+b)} + \text{constant},\ a^2 \neq b^2$

T.9 $\int x \sin ax \sin bx\,\mathrm{d}x = -\frac{\mathrm{d}}{\mathrm{d}a}\int \sin bx \cos ax\,\mathrm{d}x$

➤ Checklist of concepts

A checklist of key concepts is provided at the end of each Topic, so that you can tick off those concepts which you feel you have mastered.



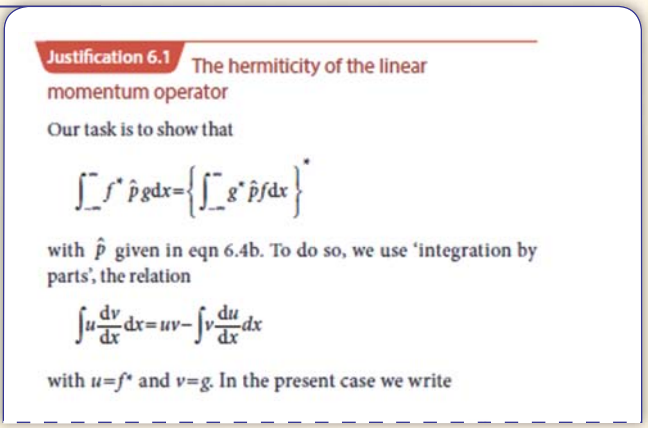
Checklist of concepts

☐ 1. In the **nuclear model** of an atom negatively charged electrons occupy atomic orbitals which are arranged in shells around a positively charged nucleus.
☐ 2. The **periodic table** highlights similarities in electronic configurations of atoms, which in turn lead to similarities in their physical and chemical properties.
☐ 3. **Covalent compounds** consist of discrete molecules in which atoms are linked by covalent bonds.
☐ 4. **Ionic compounds** consist of cations and anions in a crystalline array.
☐ 5. **Lewis structures** are useful models of the pattern of bonding in molecules.
☐ 6. The **valence-shell electron pair repulsion theory** (VSEPR theory) is used to predict the three-dimensional shapes of molecules from their Lewis structures.
☐ 7. The electrons in **polar covalent bonds** are shared unequally between the bonded nuclei.
☐ 8. The physical states of bulk matter are solid, liquid, or gas.
☐ 9. The state of a sample of bulk matter is defined by specifying its properties, such as mass, volume, amount, pressure, and temperature.
☐ 10. The **perfect gas equation** is a relation between the pressure, volume, amount, and temperature of an idealized gas.
☐ 11. A **limiting law** is a law that becomes increasingly valid in a particular limit.

Presenting the mathematics

➤ Justifications

Mathematical development is an intrinsic part of physical chemistry, and to achieve full understanding you need to see how a particular expression is obtained and if any assumptions have been made. The Justifications are set off from the text to let you adjust the level of detail that you require to your current needs and make it easier to review material.



Justification 6.1 The hermiticity of the linear momentum operator

Our task is to show that

$$\int_{-\infty}^{\infty} f^* \hat{p} g \mathrm{d}x = \left\{\int_{-\infty}^{\infty} g^* \hat{p} f \mathrm{d}x\right\}^*$$

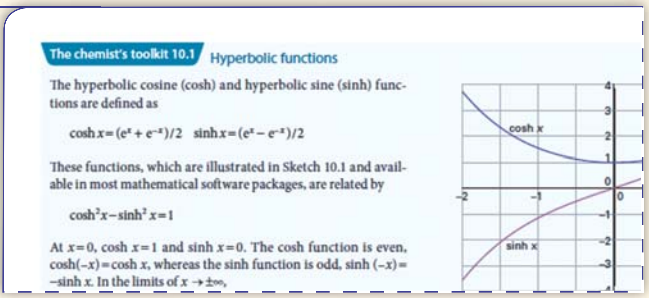
with $\hat{p}$ given in eqn 6.4b. To do so, we use 'integration by parts', the relation

$$\int u \frac{\mathrm{d}v}{\mathrm{d}x}\mathrm{d}x = uv - \int v \frac{\mathrm{d}u}{\mathrm{d}x}\mathrm{d}x$$

with $u=f^*$ and $v=g$. In the present case we write

➤ Chemist's toolkits

New to this edition, the Chemist's toolkits are succinct reminders of the mathematical concepts and techniques that you will need in order to understand a particular derivation being described in the main text.



The chemist's toolkit 10.1 Hyperbolic functions

The hyperbolic cosine (cosh) and hyperbolic sine (sinh) functions are defined as

$$\cosh x = (\mathrm{e}^x + \mathrm{e}^{-x})/2 \quad \sinh x = (\mathrm{e}^x - \mathrm{e}^{-x})/2$$

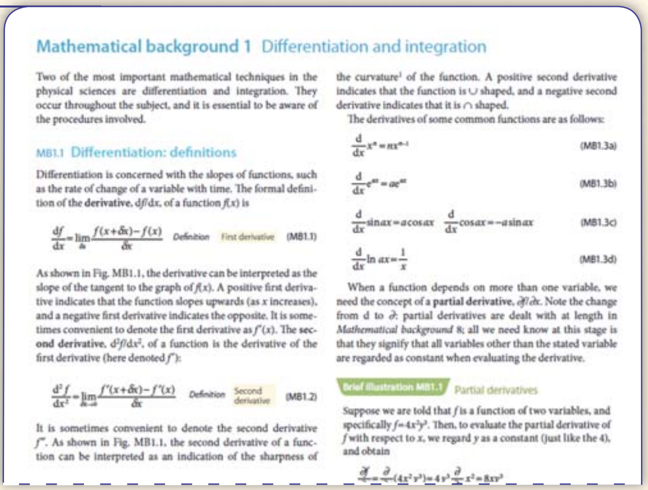
These functions, which are illustrated in Sketch 10.1 and available in most mathematical software packages, are related by

$$\cosh^2 x - \sinh^2 x = 1$$

At $x=0$, $\cosh x=1$ and $\sinh x=0$. The cosh function is even, $\cosh(-x)=\cosh x$, whereas the sinh function is odd, $\sinh(-x)=-\sinh x$. In the limits of $x \to \pm\infty$,

➤ Mathematical backgrounds

There are eight Mathematical background sections dispersed throughout the text. They cover in detail the main mathematical concepts that you need to understand in order to be able to master physical chemistry. Each one is located at the end of the Focus where it is first needed.



Mathematical background 1 Differentiation and integration

Two of the most important mathematical techniques in the physical sciences are differentiation and integration. They occur throughout the subject, and it is essential to be aware of the procedures involved.

MB1.1 Differentiation: definitions

Differentiation is concerned with the slopes of functions, such as the rate of change of a variable with time. The formal definition of the **derivative**, $\mathrm{d}f/\mathrm{d}x$, of a function $f(x)$ is

$$\frac{\mathrm{d}f}{\mathrm{d}x} = \lim_{\delta x \to 0} \frac{f(x+\delta x)-f(x)}{\delta x} \quad \text{Definition} \quad \text{First derivative} \quad \text{(MB1.1)}$$

As shown in Fig. MB1.1, the derivative can be interpreted as the slope of the tangent to the graph of $f(x)$. A positive first derivative indicates that the function slopes upwards (as x increases), and a negative first derivative indicates the opposite. It is sometimes convenient to denote the first derivative as $f'(x)$. The **second derivative**, $\mathrm{d}^2f/\mathrm{d}x^2$, of a function is the derivative of the first derivative (here denoted f'):

$$\frac{\mathrm{d}^2 f}{\mathrm{d}x^2} = \lim_{\delta x \to 0} \frac{f'(x+\delta x)-f'(x)}{\delta x} \quad \text{Definition} \quad \text{Second derivative} \quad \text{(MB1.2)}$$

It is sometimes convenient to denote the second derivative f''. As shown in Fig. MB1.1, the second derivative of a function can be interpreted as an indication of the sharpness of the curvature[1] of the function. A positive second derivative indicates that the function is ∪ shaped, and a negative second derivative indicates that it is ∩ shaped.

The derivatives of some common functions are as follows:

$$\frac{\mathrm{d}}{\mathrm{d}x}x^n = nx^{n-1} \quad \text{(MB1.3a)}$$

$$\frac{\mathrm{d}}{\mathrm{d}x}\mathrm{e}^{ax} = a\mathrm{e}^{ax} \quad \text{(MB1.3b)}$$

$$\frac{\mathrm{d}}{\mathrm{d}x}\sin ax = a\cos ax \quad \frac{\mathrm{d}}{\mathrm{d}x}\cos ax = -a\sin ax \quad \text{(MB1.3c)}$$

$$\frac{\mathrm{d}}{\mathrm{d}x}\ln ax = \frac{1}{x} \quad \text{(MB1.3d)}$$

When a function depends on more than one variable, we need the concept of a **partial derivative**, $\partial f/\partial x$. Note the change from d to ∂: partial derivatives are dealt with at length in *Mathematical background* 8; all we need know at this stage is that they signify that all variables other than the stated variable are regarded as constant when evaluating the derivative.

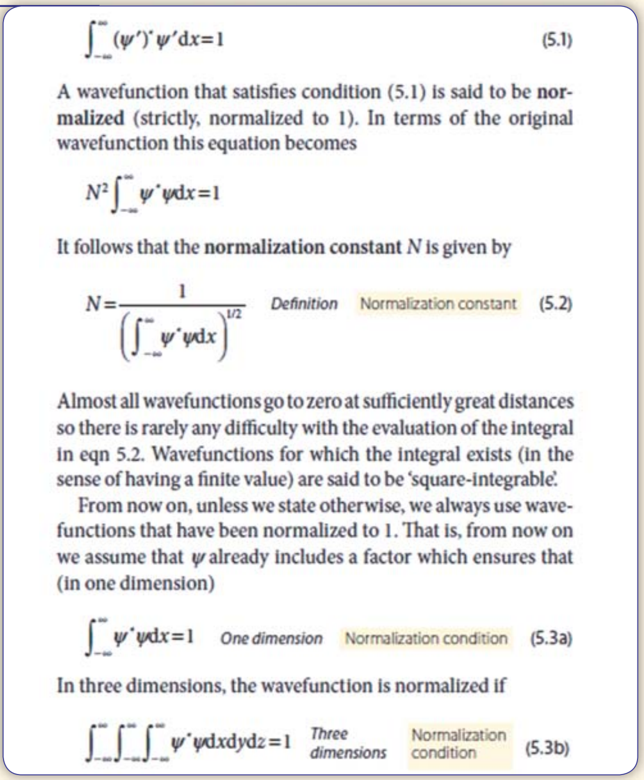
Brief illustration MB1.1 Partial derivatives

Suppose we are told that f is a function of two variables, and specifically $f=4x^2y^3$. Then, to evaluate the partial derivative of f with respect to x, we regard y as a constant (just like the 4), and obtain

$$\frac{\partial f}{\partial x} = \frac{\partial}{\partial x}(4x^2y^3) = 4y^3\frac{\partial}{\partial x}x^2 = 8xy^3$$

➤ Annotated equations and equation labels

We have annotated many equations to help you follow how they are developed. An annotation can take you across the equals sign: it is a reminder of the substitution used, an approximation made, the terms that have been assumed constant, the integral used, and so on. An annotation can also be a reminder of the significance of an individual term in an expression. We sometimes color a collection of numbers or symbols to show how they carry from one line to the next. Many of the equations are labeled to highlight their significance.



$$\int_{-\infty}^{\infty}(\psi')^*\psi'\mathrm{d}x=1 \qquad (5.1)$$

A wavefunction that satisfies condition (5.1) is said to be **normalized** (strictly, normalized to 1). In terms of the original wavefunction this equation becomes

$$N^2\int_{-\infty}^{\infty}\psi^*\psi\mathrm{d}x=1$$

It follows that the **normalization constant** N is given by

$$N=\frac{1}{\left(\int_{-\infty}^{\infty}\psi^*\psi\mathrm{d}x\right)^{1/2}} \qquad \textit{Definition} \quad \text{Normalization constant} \qquad (5.2)$$

Almost all wavefunctions go to zero at sufficiently great distances so there is rarely any difficulty with the evaluation of the integral in eqn 5.2. Wavefunctions for which the integral exists (in the sense of having a finite value) are said to be 'square-integrable'.

From now on, unless we state otherwise, we always use wavefunctions that have been normalized to 1. That is, from now on we assume that ψ already includes a factor which ensures that (in one dimension)

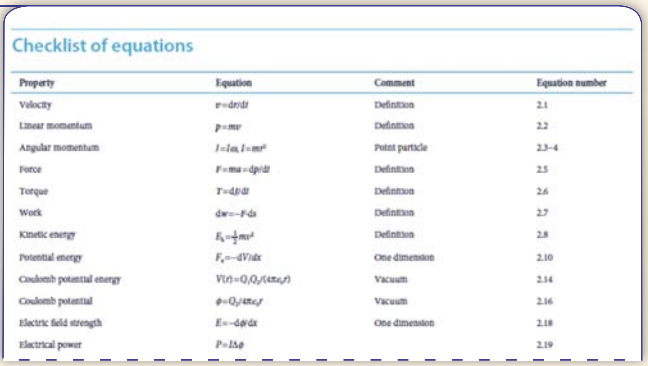
$$\int_{-\infty}^{\infty}\psi^*\psi\mathrm{d}x=1 \qquad \textit{One dimension} \quad \text{Normalization condition} \qquad (5.3a)$$

In three dimensions, the wavefunction is normalized if

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^*\psi\mathrm{d}x\mathrm{d}y\mathrm{d}z=1 \qquad \textit{Three dimensions} \quad \text{Normalization condition} \qquad (5.3b)$$

➤ Checklists of equations

You don't have to memorize every equation in the text. A checklist at the end of each Topic summarizes the most important equations and the conditions under which they apply.



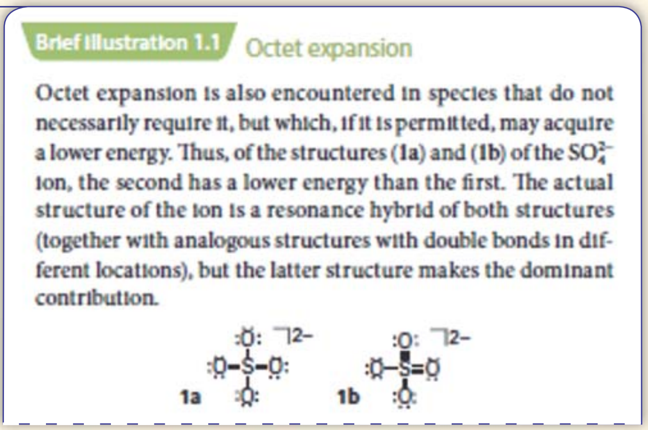
Checklist of equations

Property	Equation	Comment	Equation number
Velocity	$v=\mathrm{d}r/\mathrm{d}t$	Definition	2.1
Linear momentum	$p=mv$	Definition	2.2
Angular momentum	$J=I\omega,\ I=mr^2$	Point particle	2.3–4
Force	$F=ma=\mathrm{d}p/\mathrm{d}t$	Definition	2.5
Torque	$T=\mathrm{d}J/\mathrm{d}t$	Definition	2.6
Work	$\mathrm{d}w=-F\cdot\mathrm{d}s$	Definition	2.7
Kinetic energy	$E_k=\frac{1}{2}mv^2$	Definition	2.8
Potential energy	$F_x=-\mathrm{d}V/\mathrm{d}x$	One dimension	2.10
Coulomb potential energy	$V(r)=Q_1Q_2/(4\pi\varepsilon_0 r)$	Vacuum	2.14
Coulomb potential	$\phi=Q_2/4\pi\varepsilon_0 r$	Vacuum	2.16
Electric field strength	$E=-\mathrm{d}\phi/\mathrm{d}x$	One dimension	2.18
Electrical power	$P=I\Delta\phi$		2.19

Setting up and solving problems

➤ Brief illustrations

A Brief illustration shows you how to use equations or concepts that have just been introduced in the text. They will help you to learn how to use data, manipulate units correctly, and become familiar with the magnitudes of properties. They are all accompanied by a Self-test which you can use to monitor your progress.

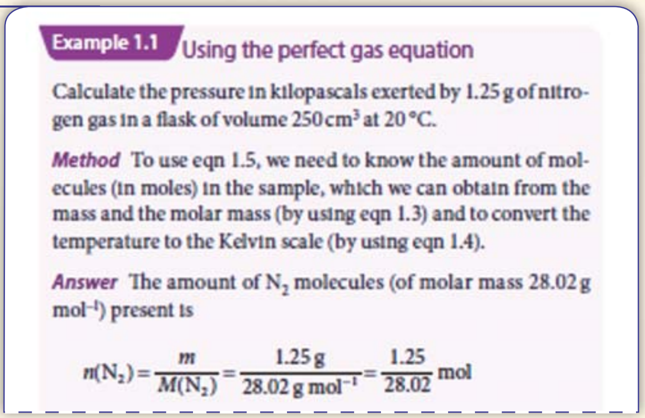


Brief illustration 1.1 Octet expansion

Octet expansion is also encountered in species that do not necessarily require it, but which, if it is permitted, may acquire a lower energy. Thus, of the structures (1a) and (1b) of the SO_4^{2-} ion, the second has a lower energy than the first. The actual structure of the ion is a resonance hybrid of both structures (together with analogous structures with double bonds in different locations), but the latter structure makes the dominant contribution.

➤ Worked examples

Worked examples are more detailed illustrations of the application of the material, which require you to assemble and develop concepts and equations. We provide a suggested method for solving the problem and then implement it to reach the answer. Worked examples are also accompanied by Self-tests.



Example 1.1 Using the perfect gas equation

Calculate the pressure in kilopascals exerted by 1.25 g of nitrogen gas in a flask of volume 250 cm³ at 20 °C.

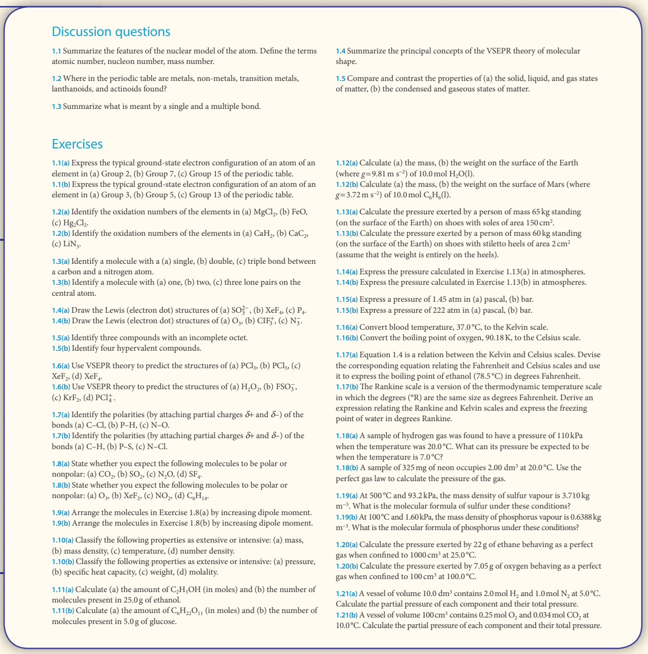
Method To use eqn 1.5, we need to know the amount of molecules (in moles) in the sample, which we can obtain from the mass and the molar mass (by using eqn 1.3) and to convert the temperature to the Kelvin scale (by using eqn 1.4).

Answer The amount of N_2 molecules (of molar mass 28.02 g mol⁻¹) present is

$$n(\mathrm{N_2})=\frac{m}{M(\mathrm{N_2})}=\frac{1.25\,\mathrm{g}}{28.02\,\mathrm{g\,mol^{-1}}}=\frac{1.25}{28.02}\,\mathrm{mol}$$

➤ Discussion questions

Discussion questions appear at the end of every Focus, where they are organized by Topic. These questions are designed to encourage you to reflect on the material you have just read, and to view it conceptually.



Discussion questions

1.1 Summarize the features of the nuclear model of the atom. Define the terms atomic number, nucleon number, mass number.

1.2 Where in the periodic table are metals, non-metals, transition metals, lanthanoids, and actinoids found?

1.3 Summarize what is meant by a single and a multiple bond.

1.4 Summarize the principal concepts of the VSEPR theory of molecular shape.

1.5 Compare and contrast the properties of (a) the solid, liquid, and gas states of matter, (b) the condensed and gaseous states of matter.

Exercises

1.1(a) Express the typical ground-state electron configuration of an atom of an element in (a) Group 2, (b) Group 7, (c) Group 15 of the periodic table.
1.1(b) Express the typical ground-state electron configuration of an atom of an element in (a) Group 3, (b) Group 5, (c) Group 13 of the periodic table.

1.2(a) Identify the oxidation numbers of the elements in (a) $MgCl_2$, (b) FeO, (c) Hg_2Cl_2.
1.2(b) Identify the oxidation numbers of the elements in (a) CaH_2, (b) CaC_2, (c) LiN_3.

1.3(a) Identify a molecule with a (a) single, (b) double, (c) triple bond between a carbon and a nitrogen atom.
1.3(b) Identify a molecule with (a) one, (b) two, (c) three lone pairs on the central atom.

1.4(a) Draw the Lewis (electron dot) structures of (a) SO_3^{2-}, (b) XeF_4, (c) P_4.
1.4(b) Draw the Lewis (electron dot) structures of (a) O_3, (b) ClF_3^+, (c) N_3^-.

1.5(a) Identify three compounds with an incomplete octet.
1.5(b) Identify four hypervalent compounds.

1.6(a) Use VSEPR theory to predict the structures of (a) PCl_3, (b) PCl_5, (c) XeF_2, (d) XeF_4.
1.6(b) Use VSEPR theory to predict the structures of (a) H_2O_2, (b) FSO_3^-, (c) KrF_2, (d) PCl_4^+.

1.7(a) Identify the polarities (by attaching partial charges δ+ and δ–) of the bonds (a) C–Cl, (b) P–H, (c) N–O.
1.7(b) Identify the polarities (by attaching partial charges δ+ and δ–) of the bonds (a) C–H, (b) P–S, (c) N–Cl.

1.8(a) State whether you expect the following molecules to be polar or nonpolar: (a) CO_2, (b) SO_2, (c) N_2O, (d) SF_4.
1.8(b) State whether you expect the following molecules to be polar or nonpolar: (a) O_3, (b) XeF_2, (c) NO_2, (d) C_6H_{14}.

1.9(a) Arrange the molecules in Exercise 1.8(a) by increasing dipole moment.
1.9(b) Arrange the molecules in Exercise 1.8(b) by increasing dipole moment.

1.10(a) Classify the following properties as extensive or intensive: (a) mass, (b) mass density, (c) temperature, (d) number density.
1.10(b) Classify the following properties as extensive or intensive: (a) pressure, (b) specific heat capacity, (c) weight, (d) molality.

1.11(a) Calculate (a) the amount of C_2H_5OH (in moles) and (b) the number of molecules present in 25.0 g of ethanol.
1.11(b) Calculate (a) the amount of $C_6H_{22}O_{11}$ (in moles) and (b) the number of molecules present in 5.0 g of glucose.

1.12(a) Calculate (a) the mass, (b) the weight on the surface of the Earth (where $g=9.81\,m\,s^{-2}$) of 10.0 mol $H_2O(l)$.
1.12(b) Calculate (a) the mass, (b) the weight on the surface of Mars (where $g=3.72\,m\,s^{-2}$) of 10.0 mol $C_6H_6(l)$.

1.13(a) Calculate the pressure exerted by a person of mass 65 kg standing (on the surface of the Earth) on shoes with soles of area 150 cm².
1.13(b) Calculate the pressure exerted by a person of mass 60 kg standing (on the surface of the Earth) on shoes with stiletto heels of area 2 cm² (assume that the weight is entirely on the heels).

1.14(a) Express the pressure calculated in Exercise 1.13(a) in atmospheres.
1.14(b) Express the pressure calculated in Exercise 1.13(b) in atmospheres.

1.15(a) Express a pressure of 1.45 atm in (a) pascal, (b) bar.
1.15(b) Express a pressure of 222 atm in (a) pascal, (b) bar.

1.16(a) Convert blood temperature, 37.0 °C, to the Kelvin scale.
1.16(b) Convert the boiling point of oxygen, 90.18 K, to the Celsius scale.

1.17(a) Equation 1.4 is a relation between the Kelvin and Celsius scales. Devise the corresponding equation relating the Fahrenheit and Celsius scales and use it to express the boiling point of ethanol (78.5 °C) in degrees Fahrenheit.
1.17(b) The Rankine scale is a version of the thermodynamic temperature scale in which the degrees (°R) are the same size as degrees Fahrenheit. Derive an expression relating the Rankine and Kelvin scales and express the freezing point of water in degrees Rankine.

1.18(a) A sample of hydrogen gas was found to have a pressure of 110 kPa when the temperature was 20.0 °C. What can its pressure be expected to be when the temperature is 7.0 °C?
1.18(b) A sample of 325 mg of neon occupies 2.00 dm³ at 20.0 °C. Use the perfect gas law to calculate the pressure of the gas.

1.19(a) At 500 °C and 93.2 kPa, the mass density of sulfur vapour is 3.710 kg m⁻³. What is the molecular formula of sulfur under these conditions?
1.19(b) At 100 °C and 1.60 kPa, the mass density of phosphorus vapour is 0.6388 kg m⁻³. What is the molecular formula of phosphorus under these conditions?

1.20(a) Calculate the pressure exerted by 22 g of ethane behaving as a perfect gas when confined to 1000 cm³ at 25.0 °C.
1.20(b) Calculate the pressure exerted by 7.05 g of oxygen behaving as a perfect gas when confined to 100 cm³ at 100.0 °C.

1.21(a) A vessel of volume 10.0 dm³ contains 2.0 mol H_2 and 1.0 mol N_2 at 5.0 °C. Calculate the partial pressure of each component and their total pressure.
1.21(b) A vessel of volume 100 cm³ contains 0.25 mol O_2 and 0.034 mol CO_2 at 10.0 °C. Calculate the partial pressure of each component and their total pressure.

➤ Exercises and problems

Exercises and problems are also provided at the end of every Focus and organized by Topic. They prompt you to test your understanding of the Topics in that Focus group. Exercises are designed as relatively straightforward numerical tests whereas the problems are more challenging. The Integrated activities, which are problems that cross several Topics, also appear at the end of each Focus.

➤ Integrated activities

At the end of most Focus sections, you will find questions designed to help you use your knowledge creatively in a variety of ways. Some of the questions refer to the ‘Living graphs’ on the Book Companion Site, which you will find helpful for answering them.

➤ Solutions manuals

Two solutions manuals have been written by Charles Trapp, Marshall Cady, and Carmen Giunta to accompany this book.

The *Student Solutions Manual* (ISBN 1-4641-2442-6) provides full solutions to the ‘a’ exercises and to the odd-numbered problems.

The *Instructor’s Solutions Manual* provides full solutions to the ‘b’ exercises and to the even-numbered problems (available to registered adopters of the book only). The Instructor’s Solutions Manual is available online only and can be accessed on the Book Companion Site.

THE BOOK COMPANION SITE

The Book Companion Site to accompany *Physical Chemistry: Quanta, Matter, and Change*, second edition provides a number of useful teaching and learning resources for students and instructors.

The Book Companion Site can be accessed by visiting:
www.whfreeman.com/qmc2e

Instructor resources are available only to regisered adopters of the textbook. To register, simply visit www.whfreeman.com/qmc2e and follow the appropriate links.

Student resources are openly available to all, without registration.

Materials on the Book Companion Site include:

Online Impact sections

Impact sections place the subject of physical chemistry in context by showing how it has been applied in a variety of modern contexts. New for this edition, the Impacts are linked from the text by QR codes. Alternatively, visit the URL displayed next to the QR code.

Group theory tables

Comprehensive group theory tables are available to download.

Figures and tables from the book

Instructors can find the artwork and tables from the book online in ready-to-download format. These may be used for lectures without charge (but not for commercial purposes without specific permission).

Molecular modelling problems

PDFs containing molecular modelling problems can be downloaded, designed for use with the Spartan Student™ software. However they can also be completed using any modeling software program that allows Hartree–Fock, density functional, and MP2 calculations.

Living graphs

These interactive graphs can be used to explore how a property changes as various parameters are changed. Living graphs are sometimes referred to in the 'Integrated activities' section of a Focus group.

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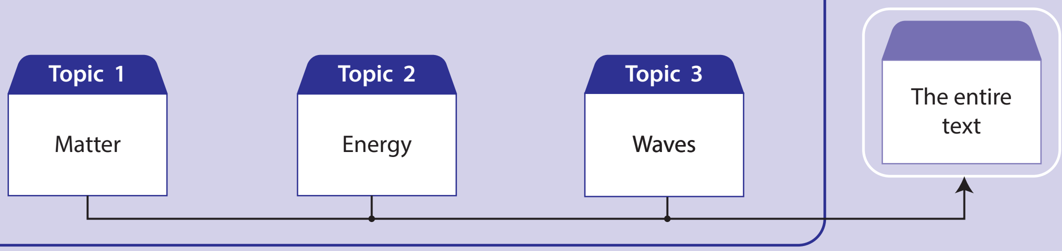
FOCUS 1 ON Foundations



Chemistry is the science of matter and the changes it can undergo. Physical chemistry is the branch of chemistry that establishes and develops the principles of the subject in terms of the underlying concepts of physics and the language of mathematics. It provides the basis for developing new spectroscopic techniques and their interpretation, for understanding the structures of molecules and the details of their electron distributions, and for relating the bulk properties of matter to their constituent atoms. Physical chemistry also provides a window on to the world of chemical reactions, and allows us to understand in detail how they take place.

Throughout the text we draw on a number of concepts that should already be familiar from introductory chemistry, such as the 'nuclear model' of the atom, 'Lewis structures' of molecules, and the 'perfect gas equation'. **Topic 1** reviews these and other concepts of chemistry that appear at many stages of the presentation.

Because physical chemistry lies at the interface between physics and chemistry, we also need to review some of the concepts from elementary physics that we need to draw on in the text. **Topic 2** begins with a brief summary of 'classical mechanics', our starting point for discussion of the motion and energy of particles. Then it reviews concepts of 'thermodynamics' that should already be part of your chemical vocabulary. Finally, we introduce the 'Boltzmann distribution' and the 'equipartition theorem', which help to establish connections between the bulk and molecular properties of matter.

Topic 3 describes waves, with a focus on 'harmonic waves', which form the basis for the classical description of electromagnetic radiation. The classical ideas of motion, energy, and waves in **Topics 2** and **3** are then expanded with *The principles of quantum mechanics*, setting the stage for the treatment of electrons, atoms, and molecules. From quantum mechanics we develop through the text principles of chemical structure and change, and the basis of many techniques of investigation.

TOPIC 1

Matter

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➤ Why do you need to know this material?

Because chemistry is about matter and the changes that it can undergo, both physically and chemically, the properties of matter underlie the entire discussion in this book.

➤ What is the key idea?

The bulk properties of matter are related to the identities and arrangements of atoms and molecules in a sample.

➤ What do you need to know already?

This Topic reviews material commonly covered in introductory chemistry.

The presentation of physical chemistry in this text is based on the experimentally verified fact that matter consists of atoms. In this Topic, which is a review of elementary concepts and language widely used in chemistry, we begin to make connections between atomic, molecular, and bulk properties. Most of the material is developed in greater detail later in the text.

1.1 Atoms

The atom of an element is characterized by its **atomic number**, Z, which is the number of protons in its nucleus. The number of neutrons in a nucleus is variable to a small extent, and the **nucleon number** (which is also commonly called the *mass number*), A, is the total number of protons and neutrons in the nucleus. Protons and neutrons are collectively called **nucleons**. Atoms of the same atomic number but different nucleon number are the **isotopes** of the element.

(a) The nuclear model

According to the **nuclear model**, an atom of atomic number Z consists of a nucleus of charge $+Ze$ surrounded by Z electrons each of charge $-e$ (e is the fundamental charge: see inside the front cover for its value and the values of the other fundamental constants). These electrons occupy **atomic orbitals**, which are regions of space where they are most likely to be found, with no more than two electrons in any one orbital. The atomic orbitals are arranged in **shells** around the nucleus, each shell being characterized by the **principal quantum number**, $n=1, 2, \ldots$. A shell consists of n^2 individual orbitals, which are grouped together into n **subshells**; these subshells, and the orbitals they contain, are denoted s, p, d, and f. For all neutral atoms other than hydrogen, the subshells of a given shell have slightly different energies.

(b) The periodic table

The sequential occupation of the orbitals in successive shells results in periodic similarities in the **electronic configurations**, the specification of the occupied orbitals, of atoms when they are arranged in order of their atomic number. This periodicity of structure accounts for the formulation of the **periodic table** (see inside the back cover). The vertical columns of the periodic table are called **groups** and (in the modern convention) numbered from 1 to 18. Successive rows of the periodic table are called **periods**, the number of the period being equal to the principal quantum number of the **valence shell**, the outermost shell of the atom.

Some of the groups also have familiar names: Group 1 consists of the **alkali metals**, Group 2 (more specifically, calcium, strontium, and barium) of the **alkaline earth metals**, Group 17 of the **halogens**, and Group 18 of the **noble gases.** Broadly speaking, the elements towards the left of the periodic table are **metals** and those towards the right are **non-metals**; the two classes of substance meet at a diagonal line running from boron to polonium, which constitute the **metalloids**, with properties intermediate between those of metals and non-metals.

The periodic table is divided into s, p, d, and f **blocks**, according to the subshell that is last to be occupied in the formulation of the electronic configuration of the atom. The members of the d block (specifically the members of Groups 3–11 in the d block) are also known as the **transition metals**; those of the f block (which is not divided into numbered groups) are sometimes called the **inner transition metals**. The upper row of the f block (Period 6) consists of the **lanthanoids** (still commonly the 'lanthanides') and the lower row (Period 7) consists of the **actinoids** (still commonly the 'actinides').

(c) Ions

A monatomic **ion** is an electrically charged atom. When an atom gains one or more electrons it becomes a negatively charged **anion**; when it loses one or more electrons it becomes a positively charged **cation**. The charge number of an ion is called the **oxidation number** of the element in that state (thus, the oxidation number of magnesium in Mg^{2+} is +2 and that of oxygen in O^{2-} is −2). It is appropriate, but not always done, to distinguish between the oxidation number and the **oxidation state**, the latter being the physical state of the atom with a specified oxidation number. Thus, the oxidation number *of* magnesium is +2 when it is present as Mg^{2+}, and it is present *in* the oxidation state Mg^{2+}.

The elements form ions that are characteristic of their location in the periodic table: metallic elements typically form cations by losing the electrons of their outermost shell and acquiring the electronic configuration of the preceding noble gas atom. Non-metals typically form anions by gaining electrons and attaining the electronic configuration of the following noble gas atom.

1.2 Molecules

A **chemical bond** is the link between atoms. Compounds that contain a metallic element typically, but far from universally, form **ionic compounds** that consist of cations and anions in a crystalline array. The 'chemical bonds' in an ionic compound are due to the Coulombic interactions between all the ions in the crystal, and it is inappropriate to refer to a bond between a specific pair of neighbouring ions. The smallest unit of an ionic compound is called a **formula unit**. Thus $NaNO_3$, consisting of a Na^+ cation and a NO_3^- anion, is the formula unit of sodium nitrate. Compounds that do not contain a metallic element typically form **covalent compounds** consisting of discrete molecules. In this case, the bonds between the atoms of a molecule are **covalent**, meaning that they consist of shared pairs of electrons.

> *A note on good practice* Some chemists use the term 'molecule' to denote the smallest unit of a compound with the composition of the bulk material regardless of whether it is an ionic or covalent compound and thus speak of 'a molecule of NaCl'. We use the term 'molecule' to denote a discrete covalently bonded entity (as in H_2O); for an ionic compound we use 'formula unit'.

(a) Lewis structures

The pattern of bonds between neighbouring atoms is displayed by drawing a **Lewis structure**, in which bonds are shown as lines and **lone pairs** of electrons, pairs of valence electrons that are not used in bonding, are shown as dots. Lewis structures are constructed by allowing each atom to share electrons until it has acquired an **octet** of eight electrons (for hydrogen, a *duplet* of two electrons). A shared pair of electrons is a **single bond**, two shared pairs constitute a **double bond**, and three shared pairs constitute a **triple bond**. Atoms of elements of Period 3 and later can accommodate more than eight electrons in their valence shell and 'expand their octet' to become **hypervalent**, that is, form more bonds than the octet rule would allow (for example, SF_6), or form more bonds to a small number of atoms (see *Brief illustration* 1.1). When more than one Lewis structure can be written for a given arrangement of atoms, it is supposed that **resonance**, a blending of the structures, may occur and distribute multiple-bond character over the molecule (for example, the two Kekulé structures of benzene). Examples of these aspects of Lewis structures are shown in Fig. 1.1.

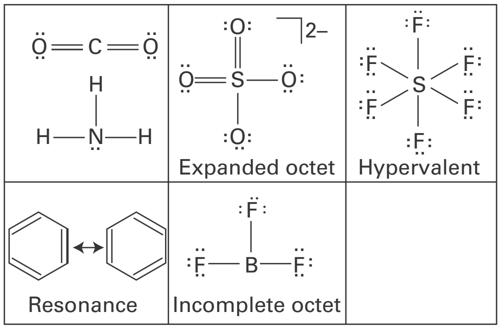
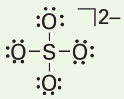


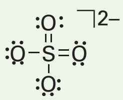
Figure 1.1 Examples of Lewis structures.

Brief illustration 1.1 Octet expansion

Octet expansion is also encountered in species that do not necessarily require it, but which, if it is permitted, may acquire a lower energy. Thus, of the structures (**1a**) and (**1b**) of the SO_4^{2-} ion, the second has a lower energy than the first. The actual structure of the ion is a resonance hybrid of both structures (together with analogous structures with double bonds in different locations), but the latter structure makes the dominant contribution.



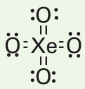
1a



1b

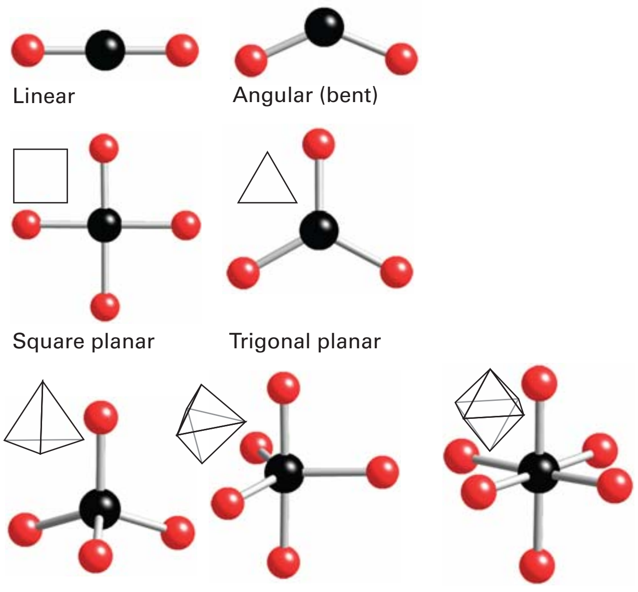
Self-test 1.1 Draw the Lewis structure for XeO_4.

Answer: **2**



(b) VSEPR theory

Except in the simplest cases, a Lewis structure does not express the three-dimensional structure of a molecule. The simplest approach to the prediction of molecular shape is **valence-shell electron pair repulsion theory** (VSEPR theory). In this approach, the regions of high electron density, as represented by bonds—whether single or multiple—and lone pairs, take up orientations around the central atom that maximize their separations. Then the position of the attached atoms (not the lone pairs) is noted and used to classify the shape of the molecule. Thus, four regions of electron density adopt a tetrahedral arrangement; if an atom is at each of these locations (as in CH_4), then the molecule is tetrahedral; if there is an atom at only three of these locations (as in NH_3), then the molecule is trigonal pyramidal, and so on. The names of the various shapes that are commonly found are shown in Fig. 1.2. In a refinement of the theory, lone pairs are assumed to repel bonding pairs more strongly than bonding pairs repel each other. The shape a molecule then adopts, if it is not determined fully by symmetry, is such as to minimize repulsions from lone pairs.



Linear

Angular (bent)

Square planar

Trigonal planar

Tetrahedral

Trigonal bipyramidal

Octahedral

Figure 1.2 The shapes of molecules that result from application of VSEPR theory.

Brief illustration 1.2 Molecular shapes

In SF_4 the lone pair adopts an equatorial position and the two axial S–F bonds bend away from it slightly, to give a bent see-saw shaped molecule (Fig. 1.3).

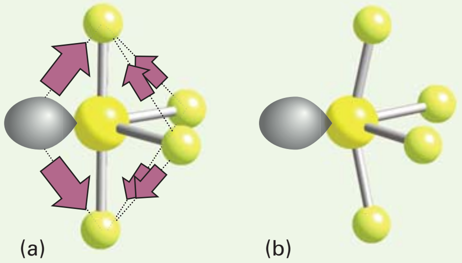


Figure 1.3 (a) In SF_4 the lone pair adopts an equatorial position. (b) The two axial S–F bonds bend away from it slightly, to give a bent see-saw shaped molecule.

Self-test 1.2 Predict the shape of the SO_3^{2-} ion.

Answer: Trigonal pyramid

(c) Polar bonds

Covalent bonds may be **polar**, or correspond to an unequal sharing of the electron pair, with the result that one atom has a partial positive charge (denoted δ+) and the other a partial negative charge (δ–). The ability of an atom to attract electrons to itself when part of a molecule is measured by the **electronegativity**, χ (chi), of the element. The juxtaposition of equal and opposite partial charges constitutes an **electric dipole**. If those charges are $+Q$ and $-Q$ and they are separated by a distance d, the magnitude of the **electric dipole moment**, μ, is

$$\mu = Qd \qquad (1.1)$$

Definition Magnitude of the electric dipole moment

Brief illustration 1.3 Nonpolar molecules with polar bonds

Whether or not a molecule as a whole is polar depends on the arrangement of its bonds, for in highly symmetrical molecules there may be no net dipole. Thus, although the linear CO_2 molecule (which is structurally OCO) has polar CO bonds, their effects cancel and the molecule as a whole is nonpolar.

Self-test 1.3 Is NH_3 polar?

Answer: Yes

1.3 Bulk matter

Bulk matter consists of large numbers of atoms, molecules, or ions. Its physical state may be solid, liquid, or gas:

A **solid** is a form of matter that adopts and maintains a shape that is independent of the container it occupies.

A **liquid** is a form of matter that adopts the shape of the part of the container it occupies (in a gravitational field, the lower part) and is separated from the unoccupied part of the container by a definite surface.

A **gas** is a form of matter that immediately fills any container it occupies.

A liquid and a solid are examples of a **condensed state** of matter. A liquid and a gas are examples of a **fluid** form of matter: they flow in response to forces (such as gravity) that are applied.

(a) Properties of bulk matter

The state of a bulk sample of matter is defined by specifying the values of various properties. Among them are:

The **mass**, m, a measure of the quantity of matter present (unit: 1 kilogram, 1 kg).

Brief illustration 1.4 Volume units

Volume is also expressed as submultiples of $1\ m^3$, such as cubic decimetres ($1\ dm^3 = 10^{-3}\ m^3$) or cubic centimetres ($1\ cm^3 = 10^{-6}\ m^3$). It is also common to encounter the non-SI unit litre ($1\ L = 1\ dm^3$) and its submultiple the millilitre ($1\ mL = 1\ cm^3$). To carry out simple unit conversions, simply replace the fraction of the unit (such as 1 cm) by its definition (in this case, 10^{-2} m). Thus, to convert $100\ cm^3$ to cubic decimetres (litres), use $1\ cm = 10^{-1}\ dm$, in which case $100\ cm^3 = 100\ (10^{-1}\ dm)^3$, which is the same as $0.100\ dm^3$.

Self-test 1.4 Express a volume of $100\ mm^3$ in units of cm^3.

Answer: $0.100\ cm^3$

The **volume**, V, a measure of the quantity of space the sample occupies (unit: 1 cubic metre, $1\ m^3$).

The **amount of substance**, n, a measure of the number of specified entities (atoms, molecules, or formula units) present (unit: 1 mole, 1 mol).

An **extensive property** of bulk matter is a property that depends on the amount of substance present in the sample; an **intensive property** is a property that is independent of the amount of substance. The volume is extensive; the mass density, ρ (rho), with

$$\rho = \frac{m}{V} \qquad \text{Mass density} \qquad (1.2)$$

is intensive.

The amount of substance, n (colloquially, 'the number of moles'), is a measure of the number of specified entities present in the sample. 'Amount of substance' is the official name of the quantity; it is commonly simplified to 'chemical amount' or simply 'amount'. The unit 1 mol is currently defined as the number of carbon atoms in exactly 12 g of carbon-12. (In 2011 the decision was taken to replace this definition, but the change has not yet, in 2014, been implemented.) The number of entities per mole is called **Avogadro's constant**, N_A; the currently accepted value is $6.022\times10^{23}\ mol^{-1}$ (note that N_A is a constant with units, not a pure number).

The **molar mass of a substance**, M (units: formally kilograms per mole but commonly grams per mole, $g\ mol^{-1}$), is the mass per mole of its atoms, its molecules, or its formula units. The amount of substance of specified entities in a sample can readily be calculated from its mass, by noting that

$$n = \frac{m}{M} \qquad \text{Amount of substance} \qquad (1.3)$$

A note on good practice Be careful to distinguish atomic or molecular mass (the mass of a single atom or molecule; units kg) from molar mass (the mass per mole of atoms or molecules; units $kg\ mol^{-1}$). *Relative* molecular masses of atoms and molecules, $M_r = m/m_u$, where m is the mass of the atom or molecule and m_u is the atomic mass constant (see inside front cover), are still widely called 'atomic weights' and 'molecular weights' even though they are dimensionless quantities and not weights (the gravitational force exerted on an object).

A sample of matter may be subjected to a **pressure**, p (unit: 1 pascal, Pa; $1\ Pa = 1\ kg\ m^{-1}\ s^{-2}$), which is defined as the force, F, it is subjected to, divided by the area, A, to which that force is applied. A sample of gas exerts a pressure on the walls of its container because the molecules of gas are in ceaseless, random motion, and exert a force when they strike the walls. The frequency of the collisions is normally so great that the force, and therefore the pressure, is perceived as being steady.

Although 1 pascal is the SI unit of pressure (*The chemist's toolkit* 1.1), it is also common to express pressure in bar (1 bar = 10^5 Pa) or atmospheres (1 atm = 101 325 Pa exactly), both of which correspond to typical atmospheric pressure. Because many physical properties depend on the pressure acting on a sample, it is appropriate to select a certain value of the pressure to report their values. The **standard pressure** for reporting physical quantities is currently defined as $p^{\ominus} = 1$ bar exactly.

To specify the state of a sample fully it is also necessary to give its **temperature**, T. The temperature is formally a property that determines in which direction energy will flow as heat when two samples are placed in contact through thermally conducting walls: energy flows from the sample with the higher temperature to the sample with the lower temperature. The symbol T is used to denote the **thermodynamic temperature**, which is an absolute scale with $T = 0$ as the lowest point. Temperatures above $T = 0$ are then most commonly expressed by using the **Kelvin scale**, in which the gradations of temperature are expressed as multiples of the unit 1 kelvin (1 K). The Kelvin scale is currently defined by setting the triple point of water (the temperature at which ice, liquid water, and water vapour are in mutual equilibrium) at exactly 273.16 K (as for certain other units, a decision has been taken to revise this definition, but it has not yet, in 2014, been implemented). The freezing point of water (the melting point of ice) at 1 atm is then found experimentally to lie 0.01 K below the triple point, so the freezing point of water is 273.15 K. The Kelvin scale is unsuitable for everyday measurements of temperature, and it is common to use the **Celsius scale**, which is defined in terms of the Kelvin scale as

$$\theta/{}^\circ\mathrm{C} = T/\mathrm{K} - 273.15 \qquad (1.4)$$

Definition Celsius scale

Thus, the freezing point of water is 0 °C and its boiling point (at 1 atm) is found to be 100 °C (more precisely 99.974 °C). Note that in this text T invariably denotes the thermodynamic (absolute) temperature and that temperatures on the Celsius scale are denoted θ (theta).

A note on good practice Note that we write $T = 0$, not $T = 0$ K. General statements in science should be expressed without reference to a specific set of units. Moreover, because T (unlike θ) is absolute, the lowest point is 0 regardless of the scale used to express higher temperatures (such as the Kelvin scale). Similarly, we write $m = 0$, not $m = 0$ kg and $l = 0$, not $l = 0$ m.

The chemist's toolkit 1.1 Quantities and units

The result of a measurement is a **physical quantity** that is reported as a numerical multiple of a unit:

$$\text{physical quantity} = \text{numerical value} \times \text{unit}$$

It follows that units may be treated like algebraic quantities and may be multiplied, divided, and cancelled. Thus, the expression (physical quantity)/unit is the numerical value (a dimensionless quantity) of the measurement in the specified units. For instance, the mass m of an object could be reported as $m = 2.5$ kg or $m/\mathrm{kg} = 2.5$. See Table 1.1 in the *Resource section* for a list of units. Although it is good practice to use only SI units, there will be occasions where accepted practice is so deeply rooted that physical quantities are expressed using other, non-SI units. By international convention, all physical quantities are represented by sloping symbols; all units are roman (upright).

Units may be modified by a prefix that denotes a factor of a power of 10. Among the most common SI prefixes are those listed in Table 1.2 in the *Resource section*. Examples of the use of these prefixes are:

$$1\,\mathrm{nm} = 10^{-9}\,\mathrm{m} \qquad 1\,\mathrm{ps} = 10^{-12}\,\mathrm{s} \qquad 1\,\mu\mathrm{mol} = 10^{-6}\,\mathrm{mol}$$

Powers of units apply to the prefix as well as the unit they modify. For example, $1\,\mathrm{cm}^3 = 1\,(\mathrm{cm})^3$, and $(10^{-2}\,\mathrm{m})^3 = 10^{-6}\,\mathrm{m}^3$. Note that $1\,\mathrm{cm}^3$ does not mean $1\,\mathrm{c}(\mathrm{m}^3)$. When carrying out numerical calculations, it is usually safest to write out the numerical value of an observable in scientific notation (as $n.nnn \times 10^n$).

There are seven SI base units, which are listed in Table 1.3 in the *Resource section*. All other physical quantities may be expressed as combinations of these base units (see Table 1.4). *Molar concentration* (more formally, but very rarely, *amount of substance concentration*), for example, which is an amount of substance divided by the volume it occupies, can be expressed using the derived units of mol dm^{-3} as a combination of the base units for amount of substance and length. A number of these derived combinations of units have special names and symbols and we highlight them as they arise.

(b) The perfect gas equation

The properties that define the state of a system are not in general independent of one another. The most important example of a relation between them is provided by the idealized fluid known as a **perfect gas** (also, commonly, an 'ideal gas'):

$$pV = nRT \qquad (1.5)$$

Perfect gas equation

Here R is the **gas constant**, a universal constant (in the sense of being independent of the chemical identity of the gas) with the value 8.3145 J K^{-1} mol^{-1}. Throughout this text, equations applicable only to perfect gases (and other idealized systems) are labelled, as here, with the number in blue.

A note on good practice Although the term 'ideal gas' is almost universally used in place of 'perfect gas', there are reasons for preferring the latter term. In an ideal system the interactions between molecules in a mixture are all the same. In a perfect gas not only are the interactions all the same but they are in fact zero. Few, though, make this useful distinction.

Equation 1.5, the **perfect gas equation**, is a summary of three empirical conclusions, namely Boyle's law ($p \propto 1/V$ at constant temperature and amount), Charles's law ($p \propto T$ at constant volume and amount), and Avogadro's principle ($V \propto n$ at constant temperature and pressure).

Example 1.1 Using the perfect gas equation

Calculate the pressure in kilopascals exerted by 1.25 g of nitrogen gas in a flask of volume 250 cm^3 at 20 °C.

Method To use eqn 1.5, we need to know the amount of molecules (in moles) in the sample, which we can obtain from the mass and the molar mass (by using eqn 1.3) and to convert the temperature to the Kelvin scale (by using eqn 1.4).

Answer The amount of N_2 molecules (of molar mass 28.02 g mol^{-1}) present is

$$n(\text{N}_2) = \frac{m}{M(\text{N}_2)} = \frac{1.25\ \text{g}}{28.02\ \text{g mol}^{-1}} = \frac{1.25}{28.02}\ \text{mol}$$

The temperature of the sample is

$$T/\text{K} = 20 + 273.15,\ \text{so}\ T = (20 + 273.15)\ \text{K}$$

Therefore, after rewriting eqn 1.5 as $p = nRT/V$,

$$p = \frac{\overbrace{(1.25/28.02)\,\text{mol}}^{n} \times \overbrace{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})}^{R} \times \overbrace{(20+273.15)\ \text{K}}^{T}}{\underbrace{(2.50\times10^{-4})\,\text{m}^3}_{V}}$$

$$= \frac{(1.25/28.02)\times(8.3145)\times(20+273.15)}{2.50\times10^{-4}}\ \frac{\text{J}}{\text{m}^3}$$

$$\overset{1\,\text{J m}^{-3}=1\,\text{Pa}}{=}\ 4.35\times10^{5}\ \text{Pa} = 435\ \text{kPa}$$

A note on good practice It is best to postpone a numerical calculation to the last possible stage, and carry it out in a single step. This procedure avoids rounding errors. When we judge it appropriate to show an intermediate result without committing ourselves to a number of significant figures, we write it as *n.nnn*….

Self-test 1.5 Calculate the pressure exerted by 1.22 g of carbon dioxide confined to a flask of volume 500 dm^3 ($5.00\times10^2\ \text{dm}^3$) at 37 °C.

Answer: 143 Pa

All gases obey the perfect gas equation ever more closely as the pressure is reduced towards zero. That is, eqn 1.5 is an example of a **limiting law**, a law that becomes increasingly valid in a particular limit, in this case as the pressure is reduced to zero. In practice, normal atmospheric pressure at sea level (about 1 atm) is already low enough for most gases to behave almost perfectly, and, unless stated otherwise, we assume in this text that the gases we encounter behave perfectly and obey eqn 1.5.

A mixture of perfect gases behaves like a single perfect gas. According to **Dalton's law**, the total pressure of such a mixture is the sum of the pressures to which each gas would give rise if it occupied the container alone:

$$p = p_A + p_B + \ldots \qquad \text{Dalton's law} \qquad (1.6)$$

Each pressure, p_J, can be calculated from the perfect gas equation in the form $p_J = n_J RT/V$.

Checklist of concepts

☐ 1. In the **nuclear model** of an atom, negatively charged electrons occupy atomic orbitals which are arranged in shells around a positively charged nucleus.

☐ 2. The **periodic table** highlights similarities in electronic configurations of atoms, which in turn lead to similarities in their physical and chemical properties.

☐ 3. **Covalent compounds** consist of discrete molecules in which atoms are linked by covalent bonds.

☐ 4. **Ionic compounds** consist of cations and anions in a crystalline array.

☐ 5. **Lewis structures** are useful models of the pattern of bonding in molecules.

☐ 6. The **valence-shell electron pair repulsion theory** (VSEPR theory) is used to predict the three-dimensional shapes of molecules from their Lewis structures.

☐ 7. The electrons in **polar covalent bonds** are shared unequally between the bonded nuclei.

☐ 8. The physical states of bulk matter are solid, liquid, and gas.

☐ 9. The state of a sample of bulk matter is defined by specifying its properties, such as mass, volume, amount, pressure, and temperature.

☐ 10. The **perfect gas equation** is a relation between the pressure, volume, amount, and temperature of an idealized gas.

☐ 11. A **limiting law** is a law that becomes increasingly valid in a particular limit.

Checklist of equations

Property	Equation	Comment	Equation number
Electric dipole moment	$\mu = Qd$		1.1
Mass density	$\rho = m/V$	Intensive property	1.2
Amount of substance	$n = m/M$	Extensive property	1.3
Celsius scale	$\theta/°\mathrm{C} = T/\mathrm{K} - 273.15$	Temperature is an intensive property	1.4
Perfect gas equation	$pV = nRT$		1.5
Dalton's law	$p = p_\mathrm{A} + p_\mathrm{B} + \ldots$		1.6

TOPIC 2

Energy

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➤ Why do you need to know this material?

Energy is the central unifying concept of physical chemistry, and you need to gain insight into how electrons, atoms, and molecules gain, store, and lose energy.

➤ What is the key idea?

Energy, the capacity to do work, is restricted to discrete values in electrons, atoms, and molecules.

➤ What do you need to know already?

You need to review the laws of motion and principles of electrostatics normally covered in introductory physics, and concepts of thermodynamics normally covered in introductory chemistry.

Much of chemistry is concerned with transfers and transformations of energy, and from the outset it is appropriate to define this familiar quantity precisely. We begin here by reviewing **classical mechanics**, which was formulated by Isaac Newton in the seventeenth century, and establishes the vocabulary used to describe the motion and energy of particles. These classical ideas prepare us for **quantum mechanics**, the more fundamental theory formulated in the twentieth century for the study of small particles, such as electrons, atoms, and molecules. We develop the concepts of quantum mechanics throughout the text. Here we begin to see why it is needed as a foundation for understanding atomic and molecular structure.

2.1 Force

Molecules are built from atoms and atoms are built from subatomic particles. To understand their structures we need to know how these bodies move under the influence of the forces they experience.

(a) Momentum

'Translation' is the motion of a particle through space. The **velocity**, v, of a particle is the rate of change of its position $\boldsymbol{r}$:

$$\boldsymbol{v}=\frac{\mathrm{d}\boldsymbol{r}}{\mathrm{d}t} \qquad \textit{Definition} \quad \text{Velocity} \qquad (2.1)$$

For motion confined to a single dimension, we would write $v_x=\mathrm{d}x/\mathrm{d}t$. The velocity and position are vectors, with both direction and magnitude (vectors and their manipulation are treated in detail in *Mathematical background* 4). The magnitude of the velocity is the **speed**, v. The **linear momentum**, $\boldsymbol{p}$, of a particle of mass m is related to its velocity, $\boldsymbol{v}$, by

$$\boldsymbol{p}=m\boldsymbol{v} \qquad \textit{Definition} \quad \text{Linear momentum} \qquad (2.2)$$

Like the velocity vector, the linear momentum vector points in the direction of travel of the particle (Fig. 2.1); its magnitude is denoted p.

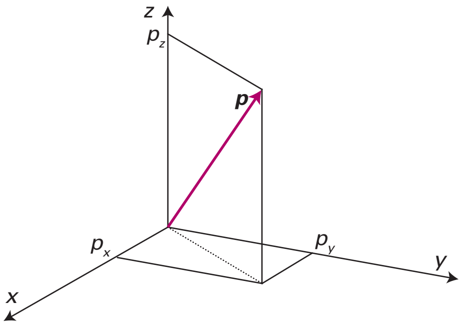

Figure 2.1 The linear momentum ***p*** is denoted by a vector of magnitude *p* and an orientation that corresponds to the direction of motion.

The description of rotation is very similar to that of translation. The rotational motion of a particle about a central point is described by its **angular momentum**, ***J***. The angular momentum is a vector: its magnitude gives the rate at which a particle circulates and its direction indicates the axis of rotation (Fig. 2.2). The magnitude of the angular momentum, *J*, is

$$J = I\omega \qquad \text{Angular momentum} \qquad (2.3)$$

where *ω* is the **angular velocity** of the body, its rate of change of angular position (in radians per second), and *I* is the **moment of inertia**, a measure of its resistance to rotational acceleration. For a point particle of mass *m* moving in a circle of radius *r*, the moment of inertia about the axis of rotation is

$$I = mr^2 \qquad \textit{Point particle} \qquad \text{Moment of inertia} \qquad (2.4)$$

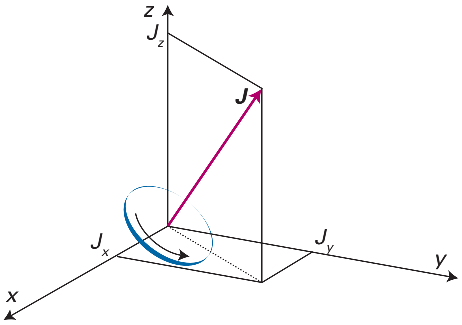

Figure 2.2 The angular momentum ***J*** of a particle is represented by a vector along the axis of rotation and perpendicular to the plane of rotation. The length of the vector denotes the magnitude *J* of the angular momentum. The direction of motion is clockwise to an observer looking in the direction of the vector.

Brief illustration 2.1 The moment of inertia

There are two possible axes of rotation in a $C^{16}O_2$ molecule, each passing through the C atom and perpendicular to the axis of the molecule and to each other. Each O atom is at a distance *R* from the axis of rotation, where *R* is the length of a CO bond, 116 pm. The mass of each ^{16}O atom is $16.00m_u$, where $m_u = 1.660\,54 \times 10^{-27}$ kg is the atomic mass constant. The C atom is stationary (it lies on the axis of rotation) and does not contribute to the moment of inertia. Therefore, the moment of inertia of the molecule around the rotation axis is

$$\begin{aligned} I &= 2m(^{16}\mathrm{O})R^2 \\ &= 2 \times \left(\overbrace{16.00 \times \overbrace{1.660\,54 \times 10^{-27}\,\mathrm{kg}}^{m_\mathrm{u}}}^{m(^{16}\mathrm{O})} \right) \times \left(\overbrace{1.16 \times 10^{-10}\,\mathrm{m}}^{R} \right)^2 \\ &= 7.15 \times 10^{-46}\,\mathrm{kg\,m^2} \end{aligned}$$

Note that the units of moments of inertia are kilograms-metre squared (kg m^2).

Self-test 2.1 The moment of inertia for rotation of a hydrogen molecule, $^1H_2$, about an axis perpendicular to its bond is 4.61×10^{-48} kg m^2. What is the bond length of H_2?

Answer: 74.1 pm

(b) Newton's second law of motion

According to **Newton's second law of motion**, *the rate of change of momentum is equal to the force acting on the particle*:

$$\frac{\mathrm{d}\boldsymbol{p}}{\mathrm{d}t} = \boldsymbol{F} \qquad \text{Newton's second law of motion} \qquad (2.5a)$$

For motion confined to one dimension, we would write $\mathrm{d}p_x/\mathrm{d}t = F_x$. Equation 2.5a may be taken as the definition of force. The SI units of force are newtons (N), with

$$1\,\mathrm{N} = 1\,\mathrm{kg\,m\,s^{-2}}$$

Because $\boldsymbol{p} = m(\mathrm{d}\boldsymbol{r}/\mathrm{d}t)$, it is sometimes more convenient to write eqn 2.5a as

$$m\boldsymbol{a} = \boldsymbol{F} \qquad \boldsymbol{a} = \frac{\mathrm{d}^2\boldsymbol{r}}{\mathrm{d}t^2} \qquad \textit{Alternative form} \qquad \text{Newton's second law of motion} \qquad (2.5b)$$

where ***a*** is the **acceleration** of the particle, its rate of change of velocity. It follows that if we know the force acting everywhere and at all times, then solving eqn 2.5 will give the **trajectory**, the position and momentum of the particle at each instant.

Brief illustration 2.2 Newton's second law of motion

A *harmonic oscillator* consists of a particle that experiences a 'Hooke's law' restoring force, one that is proportional to its displacement from equilibrium. An example is a particle of mass m attached to a spring or an atom attached to another by a chemical bond. For a one-dimensional system, $F_x = -k_f x$, where the constant of proportionality k_f is called the *force constant*. Equation 2.5b becomes

$$m\frac{d^2x}{dt^2} = -k_f x$$

(Techniques of differentiation are reviewed in *Mathematical background* 1). If $x=0$ at $t=0$, a solution (as may be verified by substitution) is

$$x(t) = A\sin 2\pi\nu t \qquad \nu = \frac{1}{2\pi}\left(\frac{k_f}{m}\right)^{1/2}$$

This solution shows that the position of the particle varies *harmonically* (that is, as a sine function) with a frequency ν, and that the frequency is high for light particles (m small) attached to stiff springs (k_f large).

Self-test 2.2 How does the momentum of the oscillator vary with time?

Answer: $p = 2\pi\nu Am\cos(2\pi\nu t)$

To accelerate a rotation it is necessary to apply a **torque**, T, a twisting force. Newton's equation is then

$$\frac{d\boldsymbol{J}}{dt} = \boldsymbol{T} \qquad \textit{Definition} \quad \text{Torque} \tag{2.6}$$

The analogous roles of m and I, of v and ω, and of p and J in the translational and rotational cases respectively should be remembered because they provide a ready way of constructing and recalling equations. These analogies are summarized in Table 2.1.

Table 2.1 Analogies between translation and rotation

Translation		Rotation	
Property	**Significance**	**Property**	**Significance**
Mass, m	Resistance to the effect of a force	Moment of inertia, I	Resistance to the effect of a torque
Speed, v	Rate of change of position	Angular velocity, ω	Rate of change of angle
Magnitude of linear momentum, p	$p = mv$	Magnitude of angular momentum, J	$J = I\omega$
Translational kinetic energy, E_k	$E_k = \frac{1}{2}mv^2 = p^2/2m$	Rotational kinetic energy, E_k	$E_k = \frac{1}{2}I\omega^2 = J^2/2I$
Equation of motion	$d\boldsymbol{p}/dt = \boldsymbol{F}$	Equation of motion	$d\boldsymbol{J}/dt = \boldsymbol{T}$

2.2 Energy: a first look

Before defining the term 'energy', we need to develop another familiar concept, that of 'work', more formally. Then we preview the uses of these concepts in chemistry.

(a) Work

Work, w, is done in order to achieve motion against an opposing force. For an infinitesimal displacement through $d\boldsymbol{s}$ (a vector), the work done is

$$dw = -\boldsymbol{F}\cdot d\boldsymbol{s} \qquad \textit{Definition} \quad \text{Work} \tag{2.7a}$$

where $\boldsymbol{F}\cdot d\boldsymbol{s}$ is the 'scalar product' of the vectors $\boldsymbol{F}$ and $d\boldsymbol{s}$ (see also *Mathematical background* 4):

$$\boldsymbol{F}\cdot d\boldsymbol{s} = F_x dx + F_y dy + F_z dz \qquad \textit{Definition} \quad \text{Scalar product} \tag{2.7b}$$

For motion in one dimension, we write $dw = -F_x dx$. The total work done along a path is the integral of this expression, allowing for the possibility that $\boldsymbol{F}$ changes in direction and magnitude at each point of the path. With force in newtons and distance in metres, the units of work are joules (J), with

$$1\,\text{J} = 1\,\text{N m} = 1\,\text{kg m}^2\,\text{s}^{-2}$$

Brief illustration 2.3 The work of stretching a bond

The work needed to stretch a chemical bond that behaves like a spring through an infinitesimal distance dx is

$$dw = -F_x dx = -(-k_f x)dx = k_f x dx$$

The total work needed to stretch the bond from zero displacement ($x=0$) at its equilibrium length R_e to a length R, corresponding to a displacement $x = R - R_e$, is

$$w = \int_0^{R-R_e} k_f x\,dx = k_f\int_0^{R-R_e} x\,dx \overset{\text{Integral A.1}}{=} \tfrac{1}{2}k_f(R-R_e)^2$$

where we have used Integral A.1 from the *Resource section* (techniques of integration are reviewed in *Mathematical background* 1). We see that the work required increases as the square of the displacement: it takes four times as much work to stretch a bond through 20 pm as it does to stretch the same bond through 10 pm.

Self-test 2.3 The force constant of the H–H bond is about $575\,\text{N m}^{-1}$. How much work is needed to stretch this bond by 10.0 pm?

Answer: 2.88×10^{-20} J

(b) The definition of energy

Energy is the capacity to do work. The SI unit of energy is the same as that of work, namely the joule. The rate of supply of energy is called the **power** (P), and is expressed in watts (W):

$$1\,\text{W} = 1\,\text{J}\,\text{s}^{-1}$$

Calories (cal) and kilocalories (kcal) are still encountered in the chemical literature. The calorie is now defined in terms of the joule, with 1 cal = 4.184 J (exactly). Caution needs to be exercised as there are several different kinds of calorie. The 'thermochemical calorie', cal_{15}, is the energy required to raise the temperature of 1 g of water at 15 °C by 1 °C and the 'dietary Calorie' is 1 kcal.

A particle may possess two kinds of energy, kinetic energy and potential energy. The **kinetic energy**, E_k, of a body is the energy the body possesses as a result of its motion. For a body of mass m travelling at a speed v,

$$E_\text{k} = \frac{1}{2}mv^2 \qquad \textit{Definition} \quad \text{Kinetic energy} \qquad (2.8)$$

It follows from Newton's second law that if a particle of mass m is initially stationary and is subjected to a constant force F for a time τ, then its speed increases from zero to $F\tau/m$ and therefore its kinetic energy increases from zero to

$$E_\text{k} = \frac{F^2\tau^2}{2m} \qquad (2.9)$$

The energy of the particle remains at this value after the force ceases to act. Because the magnitude of the applied force, F, and the time, τ, for which it acts may be varied at will, eqn 2.9 implies that the energy of the particle may be increased to any value.

The **potential energy**, E_p or V, of a body is the energy it possesses as a result of its position. Because (in the absence of losses) the work that a particle can do when it is stationary in a given location is equal to the work that had to be done to bring it there, we can use the one-dimensional version of eqn 2.7 to write $\text{d}V = -F_x\text{d}x$, and therefore

$$F_x = -\frac{\text{d}V}{\text{d}x} \qquad \textit{Definition} \quad \text{Potential energy} \qquad (2.10)$$

No universal expression for the potential energy can be given because it depends on the type and magnitude of the force the body experiences. For a particle of mass m at an altitude h close to the surface of the Earth, the gravitational potential energy is

$$V(h) = V(0) + mgh \qquad \text{Gravitational potential energy} \qquad (2.11)$$

where g is the **acceleration of free fall** (g depends on location, but its 'standard value' is 9.81 m s^{-2}). The zero of potential energy is arbitrary. For a particle close to the surface of the Earth, it is common to set $V(0) = 0$.

The **total energy** of a particle is the sum of its kinetic and potential energies:

$$E = E_\text{k} + E_\text{p}, \text{ or } E = E_\text{k} + V \qquad \textit{Definition} \quad \text{Total energy} \qquad (2.12)$$

We make use of the apparently universal law of nature that *energy is conserved*; that is, energy can neither be created nor destroyed. Although energy can be transferred from one location to another and transformed from one form to another, the total energy is constant. In terms of the linear momentum, the total energy of a particle is

$$E = \frac{p^2}{2m} + V \qquad (2.13)$$

This expression may be used in place of Newton's second law to calculate the trajectory of a particle.

Brief illustration 2.4 The trajectory of a particle

Consider an argon atom free to move in one direction (along the x-axis) in a region where $V = 0$ (so the energy is independent of position). Because $v = \text{d}x/\text{d}t$, it follows from eqns 2.1 and 2.8 that $\text{d}x/\text{d}t = (2E_\text{k}/m)^{1/2}$. As may be verified by substitution, a solution of this differential equation is

$$x(t) = x(0) + \left(\frac{2E_\text{k}}{m}\right)^{1/2} t$$

The linear momentum is

$$p(t) = mv(t) = m\frac{\text{d}x}{\text{d}t} = (2mE_\text{k})^{1/2}$$

and is a constant. Hence, if we know the initial position and momentum, we can predict all later positions and momenta exactly.

Self-test 2.4 Consider an atom of mass m moving along the x direction with an initial position x_1 and initial speed v_1. If the atom moves for a time interval Δt in a region where the potential energy varies as $V(x)$, what is its speed v_2 at position x_2?

Answer: $v_2 = v_1 - \left|\text{d}V(x)/\text{d}x\right|_{x_1} \Delta t/m$

(c) The Coulomb potential energy

One of the most important kinds of potential energy in chemistry is the **Coulomb potential energy** between two electric charges. The Coulomb potential energy is equal to the work that must be done to bring up a charge from infinity to a distance r from a second charge. For a point charge Q_1 at a distance r in a vacuum from another point charge Q_2, their potential energy is

$$V(r)=\frac{Q_1Q_2}{4\pi\varepsilon_0 r} \qquad \textit{Definition} \qquad \text{Coulomb potential energy} \qquad (2.14)$$

Charge is expressed in coulombs (C), often as a multiple of the fundamental charge, e. Thus, the charge of an electron is $-e$ and that of a proton is $+e$; the charge of an ion is ze, with z the **charge number** (positive for cations, negative for anions). The constant ε_0 (epsilon zero) is the **vacuum permittivity**, a fundamental constant with the value 8.854×10^{-12} C^2 J^{-1} m^{-1}. It is conventional (as in eqn 2.14) to set the potential energy equal to zero at infinite separation of charges. Then two opposite charges have a negative potential energy at finite separations whereas two like charges have a positive potential energy.

Brief illustration 2.5 The Coulomb potential energy

The Coulomb potential energy resulting from the electrostatic interaction between a positively charged sodium cation, Na$^+$, and a negatively charged chloride anion, Cl$^-$, at a distance of 0.280 nm, which is the separation between ions in the lattice of a sodium chloride crystal, is

$$V=\frac{\overbrace{(-1.602\times10^{-19}\,\mathrm{C})}^{Q(\mathrm{Cl}^-)}\times\overbrace{(1.602\times10^{-19}\,\mathrm{C})}^{Q(\mathrm{Na}^+)}}{4\pi\times\underbrace{(8.854\times10^{-12}\,\mathrm{C^2J^{-1}m^{-1}})}_{\varepsilon_0}\times\underbrace{(0.280\times10^{-9}\,\mathrm{m})}_{r}}$$
$$=-8.24\times10^{-19}\,\mathrm{J}$$

This value is equivalent to a molar energy of

$$V\times N_A=(-8.24\times10^{-19}\,\mathrm{J})\times(6.022\times10^{23}\ \mathrm{mol^{-1}})$$
$$=-496\ \mathrm{kJ\ mol^{-1}}$$

A note on good practice Write units at *every* stage of a calculation and do not simply attach them to a final numerical value. Also, it is often sensible to express all numerical quantities in scientific notation using exponential format rather than SI prefixes to denote powers of ten.

Self-test 2.5 The centres of neighbouring cations and anions in magnesium oxide crystals are separated by 0.21 nm. Determine the molar Coulomb potential energy resulting from the electrostatic interaction between a Mg^{2+} and a O^{2-} ion in such a crystal.

Answer: −2600 kJ mol^{-1}

In a medium other than a vacuum, the potential energy of interaction between two charges is reduced, and the vacuum permittivity is replaced by the **permittivity**, ε, of the medium. The permittivity is commonly expressed as a multiple of the vacuum permittivity:

$$\varepsilon=\varepsilon_r\varepsilon_0 \qquad \textit{Definition} \qquad \text{Permittivity} \qquad (2.15)$$

with ε_r the dimensionless **relative permittivity** (formerly, the *dielectric constant*). This reduction in potential energy can be substantial: the relative permittivity of water at 25 °C is 80, so the reduction in potential energy for a given pair of charges at a fixed difference (with sufficient space between them for the water molecules to behave as a fluid) is by nearly two orders of magnitude.

Care should be taken to distinguish *potential energy* from *potential*. The potential energy of a charge Q_1 in the presence of another charge Q_2 can be expressed in terms of the **Coulomb potential**, ϕ (phi):

$$V(r)=Q_1\phi \qquad \phi=\frac{Q_2}{4\pi\varepsilon_0 r} \qquad \textit{Definition} \qquad \text{Coulomb potential} \qquad (2.16)$$

The units of potential are joules per coulomb, J C^{-1}, so when ϕ is multiplied by a charge in coulombs, the result is in joules. The combination joules per coulomb occurs widely and is called a volt (V):

$$1\,\mathrm{V}=1\,\mathrm{J\,C^{-1}}$$

If there are several charges Q_2, Q_3, … present in the system, the total potential experienced by the charge q_1 is the sum of the potential generated by each charge:

$$\phi=\phi_2+\phi_3+\ldots \qquad (2.17)$$

Just as the potential energy of a charge Q_1 can be written $V=Q_1\phi$, so the magnitude of the force on Q_1 can be written $F=Q_1\mathcal{E}$, where $\mathcal{E}$ is the magnitude of the **electric field strength** (units: volts per metre, V m^{-1}) arising from Q_2 or from some more general charge distribution. The electric field strength (which, like the force, is actually a vector quantity) is the negative gradient of the electric potential. In one dimension, we write the magnitude of the electric field strength as

$$\mathcal{E}=-\frac{d\phi}{dx} \qquad \text{Electric field strength} \qquad (2.18)$$

The language we have just developed inspires an important alternative energy unit, the **electronvolt** (eV): 1 eV is defined as the kinetic energy acquired when an electron is accelerated from rest through a potential difference of 1 V. The relation between electronvolts and joules is

$$1\,\text{eV} = 1.602 \times 10^{-19}\,\text{J}$$

Many processes in chemistry involve energies of a few electronvolts. For example, to remove an electron from a sodium atom requires about 5 eV.

A particularly important way of supplying energy in chemistry (as in the everyday world) is by passing an electric current through a resistance. An **electric current** (I) is defined as the rate of supply of charge, $I = \mathrm{d}Q/\mathrm{d}t$, and is measured in *amperes* (A):

$$1\,\text{A} = 1\,\text{C s}^{-1}$$

If a charge Q is transferred from a region of potential ϕ_i, where its potential energy is $Q\phi_i$, to where the potential is ϕ_f and its potential energy is $Q\phi_f$, and therefore through a potential difference $\Delta\phi = \phi_f - \phi_i$, the change in potential energy is $Q\Delta\phi$. The rate at which the energy changes is $(\mathrm{d}Q/\mathrm{d}t)\Delta\phi$, or $I\Delta\phi$. The power is therefore

$$P = I\Delta\phi \qquad \text{Electrical power} \qquad (2.19)$$

With current in amperes and the potential difference in volts, the power is in watts. The total energy, E, supplied in an interval Δt is the power (the rate of energy supply) multiplied by the duration of the interval:

$$E = P\Delta t = I\Delta\phi\Delta t \qquad (2.20)$$

The energy is obtained in joules with the current in amperes, the potential difference in volts, and the time in seconds.

(d) Thermodynamics

The systematic discussion of the transfer and transformation of energy in bulk matter is called **thermodynamics**. This subtle subject is treated in detail in the text, but it will be familiar from introductory chemistry that there are two central concepts, the **internal energy**, U (unit: joule, J), and the **entropy**, S (unit: joules per kelvin, J K^{-1}).

The internal energy is the total energy of a system. The **First Law of thermodynamics** states that the internal energy is constant in a system isolated from external influences. The internal energy of a sample of matter increases as its temperature is raised, and we write

$$\Delta U = C\Delta T \qquad \text{Change in internal energy} \qquad (2.21)$$

where ΔU is the change in internal energy when the temperature of the sample is raised by ΔT. The constant C is called the **heat capacity** (units: joules per kelvin, J K^{-1}) of the sample. If the heat capacity is large, a small increase in temperature results in a large increase in internal energy. This remark can be expressed in a physically more significant way by inverting it: if the heat capacity is large, then even a large transfer of energy into the system leads to only a small rise in temperature. The heat capacity is an extensive property, and values for a substance are commonly reported as the **molar heat capacity**, $C_m = C/n$ (units: joules per kelvin per mole, J K^{-1} mol^{-1}) or the **specific heat capacity**, $C_s = C/m$ (units: joules per kelvin per gram, J K^{-1} g^{-1}), both of which are intensive properties.

Thermodynamic properties are often best discussed in terms of infinitesimal changes, in which case we would write eqn 2.21 as $\mathrm{d}U = C\mathrm{d}T$. When this expression is written in the form

$$C = \frac{\mathrm{d}U}{\mathrm{d}T} \qquad \textit{Definition} \quad \text{Heat capacity} \qquad (2.22)$$

we see that the heat capacity can be interpreted as the slope of the plot of the internal energy of a sample against the temperature.

As will also be familiar from introductory chemistry and will be explained in detail later, for systems maintained at constant pressure it is usually more convenient to modify the internal energy by adding to it the quantity pV, and introducing the **enthalpy**, H (unit: joule, J):

$$H = U + pV \qquad \textit{Definition} \quad \text{Enthalpy} \qquad (2.23)$$

The enthalpy, an extensive property, greatly simplifies the discussion of chemical reactions, in part because changes in enthalpy can be identified with the energy transferred as heat from a system maintained at constant pressure (as in common laboratory experiments).

Brief illustration 2.6 The relation between U and H

The internal energy and enthalpy of a perfect gas, for which $pV = nRT$, are related by

$$H = U + nRT$$

Division by n and rearrangement gives

$$H_m - U_m = RT$$

where H_m and U_m are the molar enthalpy and the molar internal energy, respectively. We see that the difference between H_m and U_m increases with temperature.

Self-test 2.6 By how much does the molar enthalpy of oxygen gas differ from its molar internal energy at 298 K?

Answer: 2.48 kJ mol^{-1}

The **entropy**, S, is a measure of the *quality* of the energy of a system. If the energy is distributed over many modes of motion, for example, the rotational, vibrational, and translational motions for the particles which comprise the system, then the entropy is high. If the energy is distributed over only a small number of modes of motion, then the entropy is low. The **Second Law of thermodynamics** states that any spontaneous (that is, natural) change in an isolated system is accompanied by an increase in the entropy of the system. This tendency is commonly expressed by saying that the natural direction of change is accompanied by dispersal of energy from a localized region or to a less organized form.

The entropy of a system and its surroundings is of the greatest importance in chemistry because it enables us to identify the spontaneous direction of a chemical reaction and to identify the composition at which the reaction is at **equilibrium**. In a state of *dynamic* equilibrium, which is the character of all chemical equilibria, the forward and reverse reactions are occurring at the same rate and there is no net tendency to change in either direction. However, to use the entropy to identify this state we need to consider both the system and its surroundings. This task can be simplified if the reaction is taking place at constant temperature and pressure, for then it is possible to identify the state of equilibrium as the state at which the **Gibbs energy**, G (unit: joules, J), of the system has reached a minimum. The Gibbs energy is defined as

$$G = H - TS \qquad \textit{Definition} \quad \text{Gibbs energy} \qquad (2.24)$$

and is of the greatest importance in chemical thermodynamics. The Gibbs energy, which informally is called the 'free energy', is a measure of the energy stored in a system that is free to do useful work, such as driving electrons through a circuit or causing a reaction to be driven in its unnatural (nonspontaneous) direction.

2.3 The relation between molecular and bulk properties

The energy of a molecule, atom, or subatomic particle that is confined to a region of space is **quantized**, or restricted to certain discrete values. These permitted energies are called **energy levels**. The values of the permitted energies depend on the characteristics of the particle (for instance, its mass) and the extent of the region to which it is confined. The quantization of energy is most important—in the sense that the allowed energies are widest apart—for particles of small mass confined to small regions of space. Consequently, quantization is very important for electrons in atoms and molecules, but usually unimportant for macroscopic bodies, for which the separation of translational energy levels of particles in containers of macroscopic dimensions is so small that for all practical purposes their translational motion is unquantized and can be varied virtually continuously.

The energy of a molecule other than its unquantized translational motion arises mostly from three modes of motion: rotation of the molecule as a whole, distortion of the molecule through vibration of its atoms, and the motion of electrons around nuclei. Quantization becomes increasingly important as we change focus from rotational to vibrational and then to electronic motion. The separation of rotational energy levels (in small molecules, about 10^{-21} J or 1 zJ, corresponding to about 0.6 kJ mol^{-1}) is smaller than that of vibrational energy levels (about 10–100 zJ, or 6–60 kJ mol^{-1}), which itself is smaller than that of electronic energy levels (about 10^{-18} J or 1 aJ, where a is another uncommon but useful SI prefix, standing for atto, 10^{-18}, corresponding to about 600 kJ mol^{-1}). Figure 2.3 depicts these typical energy level separations.

(a) The Boltzmann distribution

The continuous thermal agitation that the molecules experience in a sample at $T > 0$ ensures that they are distributed over the available energy levels. One particular molecule may be in a state corresponding to a low energy level at one instant, and then be excited into a high energy state a moment later. Although we cannot keep track of the state of a single molecule, we can speak of the *average* numbers of molecules in each state; even though individual molecules may be changing their states as a result of collisions, the average number in each state is constant (provided the temperature remains the same).

The average number of molecules in a state is called the **population** of the state. Only the lowest energy state is occupied at $T = 0$. Raising the temperature excites some molecules into higher energy states, and more and more states become

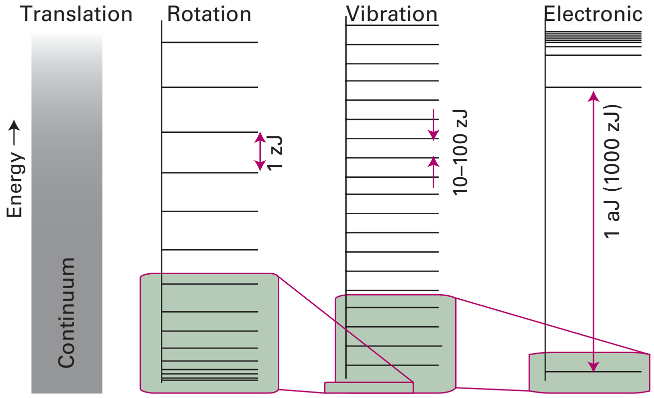

Figure 2.3 The energy level separations typical of four types of system. (1 zJ = 10^{-21} J; in molar terms, 1 zJ is equivalent to about 0.6 kJ mol^{-1}.)

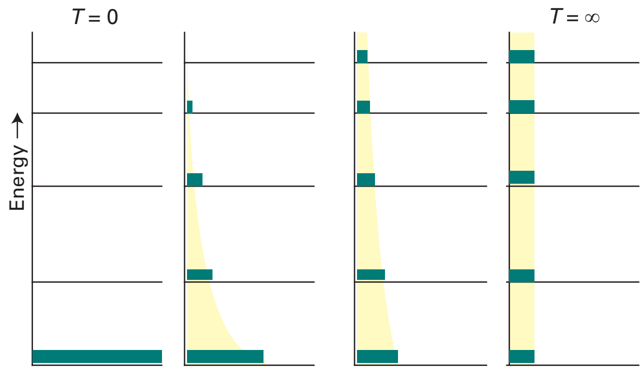

Figure 2.4 The Boltzmann distribution of populations for a system of five energy levels as the temperature is raised from zero to infinity.

accessible as the temperature is raised further (Fig. 2.4). The formula for calculating the relative populations of states of various energies is called the **Boltzmann distribution** and was derived by the Austrian scientist Ludwig Boltzmann towards the end of the nineteenth century. This formula gives the ratio of the numbers of particles in states with energies ε_i and ε_j as

$$\frac{N_i}{N_j}=\mathrm{e}^{-(\varepsilon_i-\varepsilon_j)/kT} \qquad \text{Boltzmann distribution} \qquad (2.25a)$$

where k is **Boltzmann's constant**, a fundamental constant with the value $k=1.381\times10^{-23}$ J K^{-1}. In chemical applications it is common to use not the individual energies but energies per mole of molecules, E_i, with $E_i=N_A\varepsilon_i$, where N_A is Avogadro's constant. When both the numerator and denominator in the exponential are multiplied by N_A, eqn 2.25a becomes

$$\frac{N_i}{N_j}=\mathrm{e}^{-(E_i-E_j)/RT} \qquad \textit{Alternative form} \quad \text{Boltzmann distribution} \qquad (2.25b)$$

where $R=N_Ak$. We see that k is often disguised in 'molar' form as the gas constant. The Boltzmann distribution provides the crucial link for expressing the macroscopic properties of matter in terms of microscopic behaviour.

Brief illustration 2.7 Relative populations

Methylcyclohexane molecules may exist in one of two conformations, with the methyl group in either an equatorial or an axial position. The equatorial form is lower in energy with the axial form being 6.0 kJ mol^{-1} higher in energy. At a temperature of 300 K, this difference in energy implies that the relative populations of molecules in the axial and equatorial states is

$$\frac{N_a}{N_e}=\mathrm{e}^{-(E_a-E_e)/RT}=\mathrm{e}^{-(6.0\times10^3\,\mathrm{J\,mol^{-1}})/(8.3145\ \mathrm{J\ K^{-1}mol^{-1}}\times300\ \mathrm{K})}=0.090$$

where E_a and E_e are molar energies. The number of molecules in an axial conformation is therefore just 9 per cent of those in the equatorial conformation.

Self-test 2.7 Determine the temperature at which the relative proportion of molecules in axial and equatorial conformations in a sample of methylcyclohexane is 0.30 or 30 per cent.

Answer: 600 K

The important features of the Boltzmann distribution to bear in mind are:

- The distribution of populations is an exponential function of energy and temperature.
- At a high temperature more energy levels are occupied than at a low temperature.
- More levels are significantly populated if they are close together in comparison with kT (like rotational and translational states), than if they are far apart (like vibrational and electronic states).

Physical interpretation

Figure 2.5 summarizes the form of the Boltzmann distribution for some typical sets of energy levels. The peculiar shape of the population of rotational levels stems from the fact that eqn 2.25 applies to *individual states*, and for molecular rotation quantum theory shows that the number of rotational states corresponding to a given energy level—broadly speaking, the number of planes of rotation—increases with energy; therefore, although the population of each *state* decreases with energy, the population of the *levels* goes through a maximum.

One of the simplest examples of the relation between microscopic and bulk properties is provided by **kinetic molecular theory**, a model of a perfect gas. In this model, it is assumed that the molecules, imagined as particles of negligible size, are in ceaseless, random motion and do not interact except during

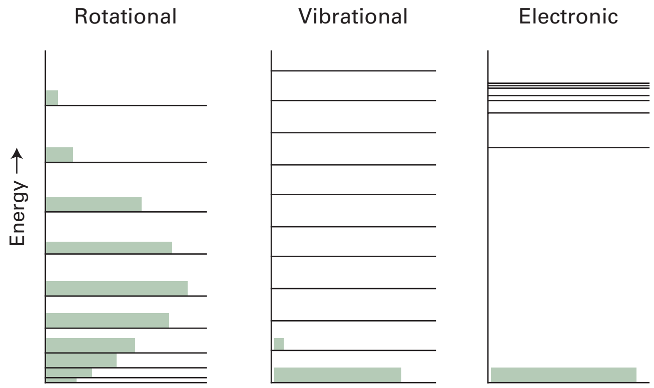

Figure 2.5 The Boltzmann distribution of populations for rotational, vibrational, and electronic energy levels at room temperature.

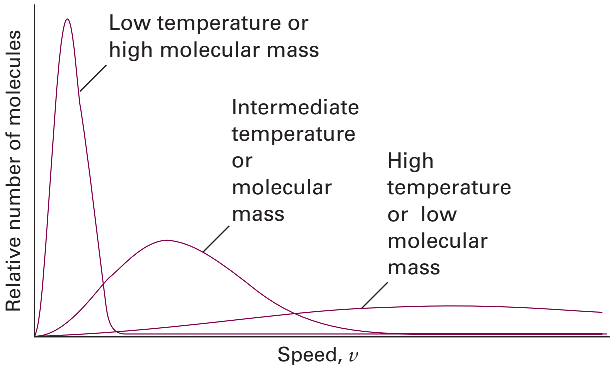

Figure 2.6 The (Maxwell–Boltzmann) distribution of molecular speeds with temperature and molar mass. Note that the most probable speed (corresponding to the peak of the distribution) increases with temperature and with decreasing molar mass, and simultaneously the distribution becomes broader.

their brief collisions. Different speeds correspond to different energies, so the Boltzmann formula can be used to predict the proportions of molecules having a specific speed at a particular temperature. The expression giving the fraction of molecules that have a particular speed is called the **Maxwell–Boltzmann distribution** and has the features summarized in Fig. 2.6. The Maxwell–Boltzmann distribution can be used to show that the average speed, v_{mean}, of the molecules depends on the temperature and their molar mass as

$$v_{\text{mean}} = \left(\frac{8RT}{\pi M}\right)^{1/2} \tag{2.26}$$

Perfect gas Average speed of molecules

Thus, the average speed is high for light molecules at high temperatures. The distribution itself gives more information. For instance, the tail towards high speeds is longer at high temperatures than at low, which indicates that at high temperatures more molecules in a sample have speeds much higher than average.

(b) Equipartition

Although the Boltzmann distribution can be used to calculate the average energy associated with each mode of motion of an atom or molecule in a sample at a given temperature, there is a much simpler shortcut. When the temperature is so high that many energy levels are occupied, we can use the **equipartition theorem**:

> For a sample at thermal equilibrium the average value of each quadratic contribution to the energy is $\frac{1}{2}kT$.

By a ‘quadratic contribution’ we mean a term that is proportional to the square of the momentum (as in the expression for the kinetic energy, $E_{\text{k}}=p^2/2m$) or the displacement from an equilibrium position (as for the potential energy of a harmonic oscillator, $E_{\text{p}}=\frac{1}{2}k_{\text{f}}x^2$). The theorem is strictly valid only at high temperatures or if the separation between energy levels is small because under these conditions many states are populated. The equipartition theorem is most reliable for translational and rotational modes of motion. The separation between vibrational and electronic states is typically greater than for rotation or translation, and so the equipartition theorem is unreliable for these types of motion.

Brief illustration 2.8 Average molecular energies

An atom or molecule may move in three dimensions and its translational kinetic energy is therefore the sum of three quadratic contributions:

$$E_{\text{trans}} = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$

The equipartition theorem predicts that the average energy for each of these quadratic contributions is $\frac{1}{2}kT$. Thus, the average kinetic energy is $E_{\text{trans}}=\frac{3}{2}kT$. The molar translational energy is thus $E_{\text{trans,m}}=\frac{3}{2}kT\times N_{\text{A}}=\frac{3}{2}RT$. At 300 K

$$\begin{aligned} E_{\text{trans,m}} &= \frac{3}{2}\times(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(300\,\text{K}) \\ &= 3700\,\text{J mol}^{-1} = 3.7\,\text{kJ mol}^{-1} \end{aligned}$$

Self-test 2.8 A linear molecule may rotate about two axes in space, each of which counts as a quadratic contribution. Calculate the rotational contribution to the molar energy of a collection of linear molecules at 500 K.

Answer: 4.2 kJ mol^{-1}

Checklist of concepts

☐ 1. **Newton’s second law of motion** states that the rate of change of momentum is equal to the force acting on the particle.
☐ 2. **Work** is done in order to achieve motion against an opposing force.
☐ 3. **Energy** is the capacity to do work.
☐ 4. The **kinetic energy** of a particle is the energy it possesses as a result of its motion.
☐ 5. The **potential energy** of a particle is the energy it possesses as a result of its position.

☐ 6. The total energy of a particle is the sum of its kinetic and potential energies.

☐ 7. The **Coulomb potential energy** between two charges separated by a distance r varies as $1/r$.

☐ 8. The **First Law of thermodynamics** states that the internal energy is constant in a system isolated from external influences.

☐ 9. The **Second Law of thermodynamics** states that any spontaneous change in an isolated system is accompanied by an increase in the entropy of the system.

☐ 10. **Equilibrium** is the state at which the **Gibbs energy** of the system has reached a minimum.

☐ 11. The energy levels of confined particles are quantized.

☐ 12. The **Boltzmann distribution** is a formula for calculating the relative populations of states of various energies.

☐ 13. The **equipartition theorem** states that for a sample at thermal equilibrium the average value of each quadratic contribution to the energy is $\frac{1}{2}kT$.

Checklist of equations

Property	Equation	Comment	Equation number
Velocity	$\boldsymbol{v}=\mathrm{d}\boldsymbol{r}/\mathrm{d}t$	Definition	2.1
Linear momentum	$\boldsymbol{p}=m\boldsymbol{v}$	Definition	2.2
Angular momentum	$J=I\omega,\ I=mr^2$	Point particle	2.3–4
Force	$\boldsymbol{F}=m\boldsymbol{a}=\mathrm{d}\boldsymbol{p}/\mathrm{d}t$	Definition	2.5
Torque	$\boldsymbol{T}=\mathrm{d}\boldsymbol{J}/\mathrm{d}t$	Definition	2.6
Work	$\mathrm{d}w=-\boldsymbol{F}\cdot\mathrm{d}\boldsymbol{s}$	Definition	2.7
Kinetic energy	$E_\mathrm{k}=\frac{1}{2}mv^2$	Definition	2.8
Potential energy	$F_x=-\mathrm{d}V/dx$	One dimension	2.10
Coulomb potential energy	$V(r)=Q_1Q_2/4\pi\varepsilon_0 r$	Vacuum	2.14
Coulomb potential	$\phi=Q_2/4\pi\varepsilon_0 r$	Vacuum	2.16
Electric field strength	$\mathcal{E}=-\mathrm{d}\phi/\mathrm{d}x$	One dimension	2.18
Electrical power	$P=I\Delta\phi$		2.19
Heat capacity	$C=\mathrm{d}U/\mathrm{d}T$	U is the internal energy	2.22
Enthalpy	$H=U+pV$	Definition	2.23
Gibbs energy	$G=H-TS$	Definition	2.24
Boltzmann distribution	$N_i/N_j=\mathrm{e}^{-(\varepsilon_i-\varepsilon_j)/kT}$		2.25a
Average speed of molecules	$v_\mathrm{mean}=(8RT/\pi M)^{1/2}$	Perfect gas	2.26

TOPIC 3

Waves

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Brief illustration 3.1: Resultant waves 20
3.2 The electromagnetic field 20
Brief illustration 3.2: Wavenumbers 20
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Checklist of equations 22

➤ Why do you need to know this material?

Several important investigative techniques in physical chemistry, such as spectroscopy and X-ray diffraction, involve electromagnetic radiation, a wavelike electromagnetic disturbance. We shall also see that the properties of waves are central to the quantum mechanical description of electrons in atoms and molecules. To prepare for those discussions, we need to understand the mathematical description of waves.

➤ What is the key idea?

A wave is a disturbance that propagates through space with a displacement that can be expressed as a harmonic function.

➤ What do you need to know already?

You need to be familiar with the properties of harmonic (sine and cosine) functions.

A **wave** is an oscillatory disturbance that travels through space. Examples of such disturbances include the collective motion of water molecules in ocean waves and of gas particles in sound waves. A **harmonic wave** is a wave with a displacement that can be expressed as a sine or cosine function.

3.1 Harmonic waves

A harmonic wave is characterized by a **wavelength**, λ (lambda), the distance between the neighbouring peaks of the wave, and its **frequency**, ν (nu), the number of times per second at which its displacement at a fixed point returns to its original value (Fig. 3.1). The frequency is measured in hertz, where $1\,\text{Hz} = 1\,\text{s}^{-1}$. The wavelength and frequency are related by

$$\lambda\nu = v \qquad (3.1)$$

Relation between frequency and wavelength

where v is the speed of propagation of the wave.

First, consider the snapshot of a harmonic wave at $t=0$. The displacement $\psi(x,t)$ varies with position x as

$$\psi(x,0) = A\cos\{(2\pi/\lambda)x + \phi\} \qquad (3.2a)$$

Harmonic wave at $t = 0$

where A is the **amplitude** of the wave, the maximum height of the wave, and ϕ is the **phase** of the wave, the shift in the location of the peak from $x=0$ and which may lie between $-\pi$ and π (Fig. 3.2). As time advances, the peaks migrate along the x-axis (the direction of propagation), and at any later instant the displacement is

$$\psi(x,t) = A\cos\{(2\pi/\lambda)x - 2\pi\nu t + \phi\} \qquad (3.2b)$$

Harmonic wave at $t > 0$

A given wave can also be expressed as a sine function with the same argument but with ϕ replaced by $\phi + \frac{1}{2}\pi$.

If two waves, in the same region of space, with the same wavelength, have different phases then the resultant wave, the sum of the two, will have either enhanced or diminished amplitude. If the phases differ by $\pm\pi$ (so the peaks of one wave coincide with the troughs of the other), then the resultant wave, the sum of the two, will have a diminished amplitude.

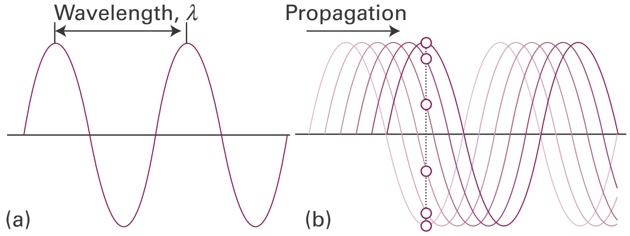


Figure 3.1 (a) The wavelength, λ, of a wave is the peak-to-peak distance. (b) The wave is shown travelling to the right at a speed v. At a given location, the instantaneous amplitude of the wave changes through a complete cycle (the six dots show half a cycle) as it passes a given point. The frequency, ν, is the number of cycles per second that occur at a given point. Wavelength and frequency are related by $\lambda\nu = v$.

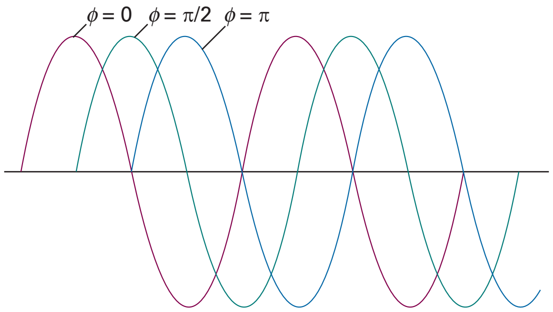


Figure 3.2 The phase ϕ of a wave specifies the relative location of its peaks.

This effect is called **destructive interference**. If the phases of the two waves are the same (coincident peaks), the resultant has an enhanced amplitude. This effect is called **constructive interference**.

Brief illustration 3.1 Resultant waves

To gain insight into cases in which the phase difference is a value other than $\pm\pi$, consider the addition of the waves $f(x)=\cos(2\pi x/\lambda)$ and $g(x)=\cos\{(2\pi x/\lambda)+\phi\}$. Figure 3.3 shows plots of $f(x)$, $g(x)$, and $f(x)+g(x)$ against x/λ for $\phi=\pi/3$. The resultant wave has a higher amplitude than either $f(x)$ or $g(x)$, and has peaks between the peaks of $f(x)$ and $g(x)$.

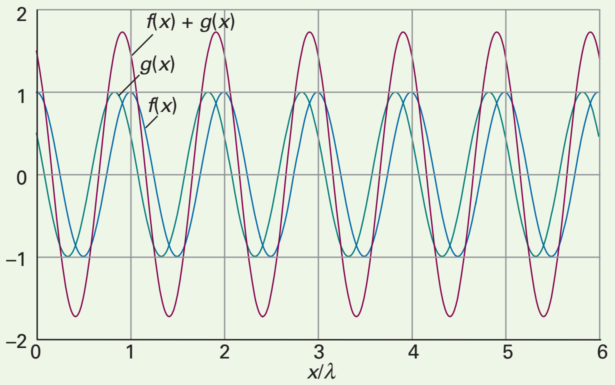


Figure 3.3 Interference between the waves discussed in *Brief illustration* 3.1.

Self-test 3.1 Consider the same waves, but with $\phi=3\pi/4$. Does the resultant wave have diminished or enhanced amplitude?

Answer: Diminished amplitude

3.2 The electromagnetic field

Light is a form of electromagnetic radiation. In classical physics, electromagnetic radiation is understood in terms of the **electromagnetic field**, an oscillating electric and magnetic disturbance that spreads as a harmonic wave through space. An **electric field** acts on charged particles (whether stationary or moving), and a **magnetic field** acts only on moving charged particles.

The wavelength and frequency of an electromagnetic wave in a vacuum are related by

$$\lambda\nu = c \tag{3.3}$$

Electromagnetic wave in a vacuum Relation between frequency and wavelength

where $c=2.997\,924\,58\times10^{8}\,\mathrm{m\,s^{-1}}$ (which we shall normally quote as $2.998\times10^{8}\,\mathrm{m\,s^{-1}}$) is the speed of light in a vacuum. When the wave is passing through a medium (even air), its speed is reduced to c' and although the frequency remains unchanged, its wavelength is reduced accordingly. The reduced speed of light in a medium is normally expressed in terms of the **refractive index**, n_r, of the medium, where

$$n_r = \frac{c}{c'} \tag{3.4}$$

Refractive index

The refractive index depends on the frequency of the light, and for visible light typically increases with frequency. It also depends on the physical state of the medium. For yellow light in water at 25 °C, $n_r=1.3$, so the wavelength is reduced by 30 per cent.

The classification of the electromagnetic field according to its frequency and wavelength is summarized in Fig. 3.4. It is often desirable to express the characteristics of an electromagnetic wave by giving its **wavenumber**, $\tilde{\nu}$ (nu tilde), where

$$\tilde{\nu} = \frac{\nu}{c} = \frac{1}{\lambda} \tag{3.5}$$

Electromagnetic radiation Wavenumber

A wavenumber can be interpreted as the number of complete wavelengths in a given length (of vacuum). Wavenumbers are normally reported in reciprocal centimetres ($\mathrm{cm^{-1}}$), so a wavenumber of $5\,\mathrm{cm^{-1}}$ indicates that there are five complete wavelengths in 1 cm.

Brief illustration 3.2 Wavenumbers

The wavenumber of electromagnetic radiation of wavelength 660 nm is

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{1}{660\times10^{-9}\,\mathrm{m}} = 1.5\times10^{6}\,\mathrm{m^{-1}} = 15\,000\,\mathrm{cm^{-1}}$$

You can avoid errors in converting between units of $\mathrm{m^{-1}}$ and $\mathrm{cm^{-1}}$ by remembering that wavenumber represents the number of wavelengths in a given distance. Thus, a wavenumber expressed as the number of waves per centimetre and hence in units of $\mathrm{cm^{-1}}$ must be 100 times less than the equivalent quantity expressed per metre in units of $\mathrm{m^{-1}}$.

Self-test 3.2 Calculate the wavenumber and frequency of red light, of wavelength 710 nm.

Answer: $\tilde{\nu}=1.41\times10^{6}\,\mathrm{m^{-1}}=1.41\times10^{4}\,\mathrm{cm^{-1}}$, $\nu=422\,\mathrm{THz}$ ($1\,\mathrm{THz}=10^{12}\,\mathrm{s^{-1}}$)

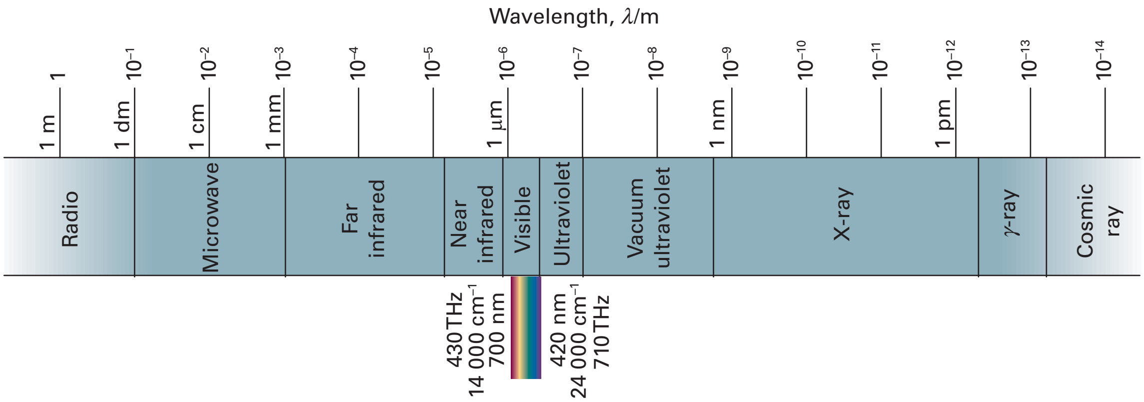


Figure 3.4 The electromagnetic spectrum and its classification into regions (the boundaries are not precise).

The functions that describe the oscillating electric field, $\mathcal{E}(x,t)$, and magnetic field, $\mathcal{B}(x,t)$, travelling along the x-direction with wavelength λ and frequency ν are

$$\mathcal{E}(x,t)=\mathcal{E}_0\cos\{(2\pi/\lambda)x-2\pi\nu t+\phi\} \qquad (3.6a)$$

Electromagnetic radiation Electric field

$$\mathcal{B}(x,t)=\mathcal{B}_0\cos\{(2\pi/\lambda)x-2\pi\nu t+\phi\} \qquad (3.6b)$$

Electromagnetic radiation Magnetic field

where $\mathcal{E}_0$ and $\mathcal{B}_0$ are the amplitudes of the electric and magnetic fields, respectively, and ϕ is the phase of the wave. In this case the amplitude is a vector quantity, because the electric and magnetic fields have a direction as well as an amplitude. The magnetic field is perpendicular to the electric field and both are perpendicular to the propagation direction (Fig. 3.5). According to classical electromagnetic theory, the **intensity** of electromagnetic radiation, a measure of the energy associated with the wave, is proportional to the square of the amplitude of the wave.

Equation 3.6 describes electromagnetic radiation that is **plane polarized**; it is so called because the electric and magnetic fields each oscillate in a single plane. The plane of polarization may be orientated in any direction around the direction of propagation. An alternative mode of polarization is **circular polarization**, in which the electric and magnetic fields rotate around the direction of propagation in either a clockwise or an anticlockwise sense but remain perpendicular to it and to each other (Fig. 3.6).

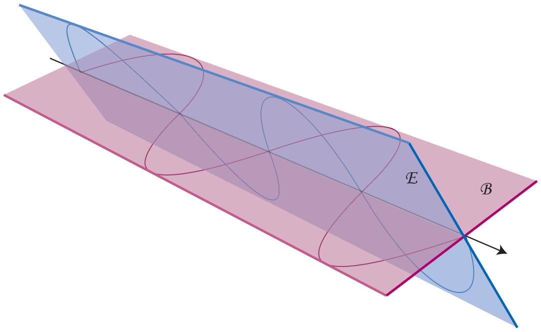


Figure 3.5 In a plane polarized wave, the electric and magnetic fields oscillate in orthogonal planes and are perpendicular to the direction of propagation.

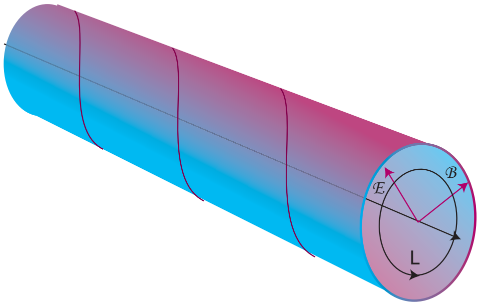


Figure 3.6 In a circularly polarized wave, the electric and magnetic fields rotate around the direction of propagation but remain perpendicular to one another. The illustration also defines 'right-' and 'left-handed' polarizations ('left-handed' polarization is shown as L).

Checklist of concepts

☐ 1. A **wave** is an oscillatory disturbance that travels through space.

☐ 2. A **harmonic wave** is a wave with a displacement that can be expressed as a sine or cosine function.

☐ 3. A harmonic wave is characterized by a **wavelength**, **frequency**, **phase**, and **amplitude**.

☐ 4. **Destructive interference** between two waves of the same wavelength but different phases leads to a resultant wave with diminished amplitude.

☐ 5. **Constructive interference** between two waves of the same wavelength and phase leads to a resultant wave with enhanced amplitude.

☐ 6. The **electromagnetic field** is an oscillating electric and magnetic disturbance that spreads as a harmonic wave through space.

☐ 7. An **electric field** acts on charged particles (whether stationary or moving).

☐ 8. A **magnetic field** acts only on moving charged particles.

☐ 9. In **plane polarized** electromagnetic radiation, the electric and magnetic fields each oscillate in a single plane and are mutually perpendicular.

☐ 10. In **circular polarization**, the electric and magnetic fields rotate around the direction of propagation in either a clockwise or an anticlockwise sense but remain perpendicular to it and each other.

Checklist of equations

Property	Equation	Comment	Equation number
Relation between the frequency and wavelength	$\lambda\nu = v$	For electromagnetic radiation in a vacuum, $v = c$	3.1
Refractive index	$n_r = c/c'$	Definition; $n_r \geq 1$	3.4
Wavenumber	$\tilde{\nu} = \nu/c = 1/\lambda$	Electromagnetic radiation	3.5

Focus 1 on Foundations

Topic 1 Matter

Discussion questions

1.1 Summarize the features of the nuclear model of the atom. Define the terms atomic number, nucleon number, mass number.

1.2 Where in the periodic table are metals, non-metals, transition metals, lanthanoids, and actinoids found?

1.3 Summarize what is meant by a single and a multiple bond.

1.4 Summarize the principal concepts of the VSEPR theory of molecular shape.

1.5 Compare and contrast the properties of (a) the solid, liquid, and gas states of matter, (b) the condensed and gaseous states of matter.

Exercises

1.1(a) Express the typical ground-state electron configuration of an atom of an element in (a) Group 2, (b) Group 7, (c) Group 15 of the periodic table.
1.1(b) Express the typical ground-state electron configuration of an atom of an element in (a) Group 3, (b) Group 5, (c) Group 13 of the periodic table.

1.2(a) Identify the oxidation numbers of the elements in (a) $MgCl_2$, (b) FeO, (c) Hg_2Cl_2.
1.2(b) Identify the oxidation numbers of the elements in (a) CaH_2, (b) CaC_2, (c) LiN_3.

1.3(a) Identify a molecule with a (a) single, (b) double, (c) triple bond between a carbon and a nitrogen atom.
1.3(b) Identify a molecule with (a) one, (b) two, (c) three lone pairs on the central atom.

1.4(a) Draw the Lewis (electron dot) structures of (a) SO_3^{2-}, (b) XeF_4, (c) P_4.
1.4(b) Draw the Lewis (electron dot) structures of (a) O_3, (b) ClF_3^+, (c) N_3^-.

1.5(a) Identify three compounds with an incomplete octet.
1.5(b) Identify four hypervalent compounds.

1.6(a) Use VSEPR theory to predict the structures of (a) PCl_3, (b) PCl_5, (c) XeF_2, (d) XeF_4.
1.6(b) Use VSEPR theory to predict the structures of (a) H_2O_2, (b) FSO_3^-, (c) KrF_2, (d) PCl_4^+.

1.7(a) Identify the polarities (by attaching partial charges $\delta+$ and $\delta-$) of the bonds (a) C–Cl, (b) P–H, (c) N–O.
1.7(b) Identify the polarities (by attaching partial charges $\delta+$ and $\delta-$) of the bonds (a) C–H, (b) P–S, (c) N–Cl.

1.8(a) State whether you expect the following molecules to be polar or nonpolar: (a) CO_2, (b) SO_2, (c) N_2O, (d) SF_4.
1.8(b) State whether you expect the following molecules to be polar or nonpolar: (a) O_3, (b) XeF_2, (c) NO_2, (d) C_6H_{14}.

1.9(a) Arrange the molecules in Exercise 1.8(a) by increasing dipole moment.
1.9(b) Arrange the molecules in Exercise 1.8(b) by increasing dipole moment.

1.10(a) Classify the following properties as extensive or intensive: (a) mass, (b) mass density, (c) temperature, (d) number density.
1.10(b) Classify the following properties as extensive or intensive: (a) pressure, (b) specific heat capacity, (c) weight, (d) molality.

1.11(a) Calculate (a) the amount of C_2H_5OH (in moles) and (b) the number of molecules present in 25.0 g of ethanol.
1.11(b) Calculate (a) the amount of $C_6H_{22}O_{11}$ (in moles) and (b) the number of molecules present in 5.0 g of glucose.

1.12(a) Calculate (a) the mass, (b) the weight on the surface of the Earth (where $g = 9.81\,\mathrm{m\,s^{-2}}$) of 10.0 mol $H_2O(l)$.
1.12(b) Calculate (a) the mass, (b) the weight on the surface of Mars (where $g = 3.72\,\mathrm{m\,s^{-2}}$) of 10.0 mol $C_6H_6(l)$.

1.13(a) Calculate the pressure exerted by a person of mass 65 kg standing (on the surface of the Earth) on shoes with soles of area 150 $\mathrm{cm^2}$.
1.13(b) Calculate the pressure exerted by a person of mass 60 kg standing (on the surface of the Earth) on shoes with stiletto heels of area 2 $\mathrm{cm^2}$ (assume that the weight is entirely on the heels).

1.14(a) Express the pressure calculated in Exercise 1.13(a) in atmospheres.
1.14(b) Express the pressure calculated in Exercise 1.13(b) in atmospheres.

1.15(a) Express a pressure of 1.45 atm in (a) pascal, (b) bar.
1.15(b) Express a pressure of 222 atm in (a) pascal, (b) bar.

1.16(a) Convert blood temperature, 37.0 °C, to the Kelvin scale.
1.16(b) Convert the boiling point of oxygen, 90.18 K, to the Celsius scale.

1.17(a) Equation 1.4 is a relation between the Kelvin and Celsius scales. Devise the corresponding equation relating the Fahrenheit and Celsius scales and use it to express the boiling point of ethanol (78.5 °C) in degrees Fahrenheit.
1.17(b) The Rankine scale is a version of the thermodynamic temperature scale in which the degrees (°R) are the same size as degrees Fahrenheit. Derive an expression relating the Rankine and Kelvin scales and express the freezing point of water in degrees Rankine.

1.18(a) A sample of hydrogen gas was found to have a pressure of 110 kPa when the temperature was 20.0 °C. What can its pressure be expected to be when the temperature is 7.0 °C?
1.18(b) A sample of 325 mg of neon occupies 2.00 $\mathrm{dm^3}$ at 20.0 °C. Use the perfect gas law to calculate the pressure of the gas.

1.19(a) At 500 °C and 93.2 kPa, the mass density of sulfur vapour is 3.710 $\mathrm{kg\,m^{-3}}$. What is the molecular formula of sulfur under these conditions?
1.19(b) At 100 °C and 1.60 kPa, the mass density of phosphorus vapour is 0.6388 $\mathrm{kg\,m^{-3}}$. What is the molecular formula of phosphorus under these conditions?

1.20(a) Calculate the pressure exerted by 22 g of ethane behaving as a perfect gas when confined to 1000 $\mathrm{cm^3}$ at 25.0 °C.
1.20(b) Calculate the pressure exerted by 7.05 g of oxygen behaving as a perfect gas when confined to 100 $\mathrm{cm^3}$ at 100.0 °C.

1.21(a) A vessel of volume 10.0 $\mathrm{dm^3}$ contains 2.0 mol H_2 and 1.0 mol N_2 at 5.0 °C. Calculate the partial pressure of each component and their total pressure.
1.21(b) A vessel of volume 100 $\mathrm{cm^3}$ contains 0.25 mol O_2 and 0.034 mol CO_2 at 10.0 °C. Calculate the partial pressure of each component and their total pressure.

Topic 2 Energy

Discussion questions

2.1 What is energy?

2.2 Distinguish between kinetic and potential energy.

2.3 State the Second Law of thermodynamics. Can the entropy of the system that is not isolated from its surroundings decrease during a spontaneous process?

2.4 What is meant by quantization of energy? In what circumstances are the effects of quantization most important for microscopic systems?

2.5 What are the assumptions of the kinetic molecular theory?

2.6 What are the main features of the Maxwell distribution of speeds?

Exercises

2.1(a) A particle of mass 1.0 g is released near the surface of the Earth, where the acceleration of free fall is $g = 8.91\ \text{m s}^{-2}$. What will be its speed and kinetic energy after (a) 1.0 s, (b) 3.0 s. Ignore air resistance?

2.1(b) The same particle in Exercise 2.1(a) is released near the surface of Mars, where the acceleration of free fall is $g = 3.72\ \text{m s}^{-2}$. What will be its speed and kinetic energy after (a) 1.0 s, (b) 3.0 s? Ignore air resistance.

2.2(a) An ion of charge ze moving through water is subject to an electric field of strength $\mathcal{E}$ which exerts a force $ze\mathcal{E}$, but it also experiences a frictional drag proportional to its speed s and equal to $6\pi\eta Rs$, where R is its radius and η (eta) is the viscosity of the medium. What will be its terminal velocity?

2.2(b) A particle descending through a viscous medium experiences a frictional drag proportional to its speed s and equal to $6\pi\eta Rs$, where R is its radius and η (eta) is the viscosity of the medium. If the acceleration of free fall is denoted g, what will be the terminal velocity of a sphere of radius R and mass density ρ (rho)?

2.3(a) Confirm that the general solution of the harmonic oscillator equation of motion ($m\text{d}^2x/\text{d}t^2 = -k_\text{f}x$) is $x(t) = A \sin \omega t + B \cos \omega t$ with $\omega = (k_\text{f}/m)^{1/2}$.

2.3(b) Consider a harmonic oscillator with $B = 0$ (in the notation of Exercise 2.3a); relate the total energy at any instant to its maximum displacement amplitude.

2.4(a) In an early ('semiclassical') picture of a hydrogen atom, an electron travels in a circular path of radius 53 pm at $2188\ \text{km s}^{-1}$. What is the magnitude of the average acceleration that the electron undergoes during one-quarter of a revolution?

2.4(b) Given the acceleration calculated in Exercise 2.4(a), what is the magnitude of the average force that the electron experiences in its orbit?

2.5(a) Use the information in Exercise 2.4(a) to calculate the magnitude of the angular momentum of an electron in the semiclassical picture of the hydrogen atom. Go on to express your result as a multiple of $h/2\pi$, where h is Planck's constant (see inside front cover).

2.5(b) In a continuation of the semiclassical picture (Exercise 2.5(a)), the electron is excited into an orbit of radius $4a_0$ but continues to travel at $2188\ \text{km s}^{-1}$. Calculate the magnitude of the angular momentum of the electron and express your result as a multiple of $h/2\pi$, where h is Planck's constant (see inside front cover).

2.6(a) The force constant of a C–H bond is about $450\ \text{N m}^{-1}$. How much work is needed to stretch such bond by (a) 10 pm, (b) 20 pm?

2.6(b) The force constant of the H–H bond is about $510\ \text{N m}^{-1}$. How much work is needed to stretch such bond by 20 pm?

2.7(a) An electron is accelerated in an electron microscope from rest through a potential difference $\Delta\phi = 100\ \text{kV}$ and acquires an energy of $e\Delta\phi$. What is its final speed? What is its energy in electronvolts (eV)?

2.7(b) A $C_6H_4^{2+}$ ion is accelerated in a mass spectrometer from rest through a potential difference $\Delta\phi = 20\ \text{kV}$ and acquires an energy of $e\Delta\phi$. What is its final speed? What is its energy in electronvolts (eV)?

2.8(a) Calculate the work that must be done in order to remove a Na^+ ion from 200 pm away from a Cl^- ion to infinity (in a vacuum). What work would be needed if the separation took place in water?

2.8(b) Calculate the work that must be done in order to remove an Mg^{2+} ion from 250 pm away from an O^{2-} ion to infinity (in a vacuum). What work would be needed if the separation took place in water?

2.9(a) Calculate the electric potential due to the nuclei at a point in a LiH molecule located at 200 pm from the Li nucleus and 150 pm from the H nucleus.

2.9(b) Plot the electric potential due to the nuclei at a point in a Na^+Cl^- ion pair located on a line halfway between the nuclei (the internuclear separation is 283 pm) as the point approaches from infinity and ends at the midpoint between the nuclei.

2.10(a) An electric heater is immersed in a flask containing 200 g of water, and a current of 2.23 A from a 15.0 V supply is passed for 12.0 minutes. How much energy is supplied to the water? Estimate the rise in temperature (for water, $C_\text{m} = 75.3\ \text{J K}^{-1}\ \text{mol}^{-1}$).

2.10(b) An electric heater is immersed in a flask containing 150 g of ethanol, and a current of 1.12 A from a 12.5 V supply is passed for 172 s. How much energy is supplied to the ethanol? Estimate the rise in temperature (for ethanol, $C_\text{m} = 111.5\ \text{J K}^{-1}\ \text{mol}^{-1}$).

2.11(a) The heat capacity of a sample of iron was $3.67\ \text{J K}^{-1}$. By how much would its temperature rise if 100 J of energy was transferred to it as heat?

2.11(b) The heat capacity of a sample of water was $5.77\ \text{J K}^{-1}$. By how much would its temperature rise if 50.0 kJ of energy was transferred to it as heat?

2.12(a) The molar heat capacity of lead is $26.44\ \text{J K}^{-1}\ \text{mol}^{-1}$. How much energy must be supplied (by heating) to 100 g of lead to increase its temperature by 10.0 °C?

2.12(b) The molar heat capacity of water is $75.2\ \text{J K}^{-1}\ \text{mol}^{-1}$. How much energy must be supplied by heating to 10.0 g of water to increase its temperature by 10.0 °C?

2.13(a) The molar heat capacity of ethanol is $111.46\ \text{J K}^{-1}\ \text{mol}^{-1}$. What is its specific heat capacity?

2.13(b) The molar heat capacity of sodium is $28.24\ \text{J K}^{-1}\ \text{mol}^{-1}$. What is its specific heat capacity?

2.14(a) The specific heat capacity of water is $4.18\ \text{J K}^{-1}\ \text{g}^{-1}$. What is its molar heat capacity?

2.14(b) The specific heat capacity of copper is $0.384\ \text{J K}^{-1}\ \text{g}^{-1}$. What is its molar heat capacity?

2.15(a) By how much does the molar enthalpy of hydrogen gas differ from its molar internal energy at 1000 °C? Assume perfect gas behaviour.
2.15(b) The mass density of water is 0.997 g cm^{-3}. By how much does the molar enthalpy of water differ from its molar internal energy at 298 K?

2.16(a) Which do you expect to have the greater entropy at 298 K and 1 bar, liquid water or water vapour?
2.16(b) Which do you expect to have the greater entropy at 0 °C and 1 atm, liquid water or ice?

2.17(a) Which do you expect to have the greater entropy, 100 g of iron at 300 K or 3000 K?
2.17(b) Which do you expect to have the greater entropy, 100 g of water at 0 °C or 100 °C?

2.18(a) Give three examples of a system that is in dynamic equilibrium. What might happen when the equilibrium is disturbed?
2.18(b) Give three examples of a system that is in static equilibrium. What might happen when the equilibrium is disturbed?

2.19(a) Suppose two states differ in energy by 1.0 eV (electronvolts, see inside the front cover); what is the ratio of their populations at (a) 300 K, (b) 3000 K?
2.19(b) Suppose two states differ in energy by 2.0 eV (electronvolts, see inside the front cover); what is the ratio of their populations at (a) 200 K, (b) 2000 K?

2.20(a) Suppose two states differ in energy by 1.0 eV; what can be said about their populations when $T = 0$?
2.20(b) Suppose two states differ in energy by 1.0 eV; what can be said about their populations when the temperature is infinite?

2.21(a) A typical vibrational excitation energy of a molecule corresponds to a wavenumber of 2500 cm^{-1} (convert to an energy separation by multiplying by hc; see Topic 3). Would you expect to find molecules in excited vibrational states at room temperature (20 °C)?
2.21(b) A typical rotational excitation energy of a molecule corresponds to a frequency of about 10 GHz (convert to an energy separation by multiplying by h; see Topic 3). Would you expect to find gas-phase molecules in excited rotational states at room temperature (20 °C)?

2.22(a) Suggest a reason why most molecules survive for long periods at room temperature.
2.22(b) Suggest a reason why the rates of chemical reactions typically increase with increasing temperature.

2.23(a) Calculate the relative mean speeds of N_2 molecules in air at 0 °C and 40 °C.
2.23(b) Calculate the relative mean speeds of CO_2 molecules in air at 20 °C and 30 °C.

2.24(a) Calculate the relative mean speeds of N_2 and CO_2 molecules in air.
2.24(b) Calculate the relative mean speeds of Hg_2 and H_2 molecules in a gaseous mixture.

2.25(a) Use the equipartition theorem to calculate the contribution of translational motion to the internal energy of 5.0 g of argon at 25 °C.
2.25(b) Use the equipartition theorem to calculate the contribution of translational motion to the internal energy of 10.0 g of helium at 30 °C.

2.26(a) Use the equipartition theorem to calculate the contribution to the total internal energy of a sample of 10.0 g of (a) carbon dioxide, (b) methane at 20 °C; take into account translation and rotation but not vibration.
2.26(b) Use the equipartition theorem to calculate the contribution to the total internal energy of a sample of 10.0 g of lead at 20 °C, taking into account the vibrations of the atoms.

2.27(a) Use the equipartition theorem to compute the molar heat capacity of argon.
2.27(b) Use the equipartition theorem to compute the molar heat capacity of helium.

2.28(a) Use the equipartition theorem to estimate the heat capacity of (a) carbon dioxide, (b) methane.
2.28(b) Use the equipartition theorem to estimate the heat capacity of (a) water vapour, (b) lead.

Topic 3 Waves

Discussion questions

3.1 How many types of wave motion can you identify?

3.2 What is the wave nature of the sound of a sudden 'bang'?

Exercises

3.1(a) What is the speed of light in water if the refractive index of the latter is 1.33?
3.1(b) What is the speed of light in benzene if the refractive index of the latter is 1.52?

3.2(a) The wavenumber of a typical vibrational transition of a hydrocarbon is 2500 cm^{-1}. Calculate the corresponding wavelength and frequency.
3.2(b) The wavenumber of a typical vibrational transition of an O–H bond is 3600 cm^{-1}. Calculate the corresponding wavelength and frequency.

Integrated activities

F1.1 In Topic 78 we show that for a perfect gas the fraction of molecules that have a speed in the range v to $v + \mathrm{d}v$ is $f(v)\mathrm{d}v$, where

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 \mathrm{e}^{-Mv^2/2RT}$$

is the Maxwell–Boltzmann distribution with T the temperature and M the molar mass. Use this expression and mathematical software, a spreadsheet, or the *Living graphs* (labelled $^{\text{LG}}$) on the website of this book for the following exercises:

(a) $^{\text{LG}}$ Refer to the graph in Fig. 2.6. Plot different distributions by keeping the molar mass constant at 100 g mol^{-1} and varying the temperature of the sample between 200 K and 2000 K.

(b) $^{\text{LG}}$ Consider a sample of gas consisting of a substance with molar mass 100 g mol^{-1}. Evaluate numerically the fraction of molecules with speeds in the range 100 m s^{-1} to 200 m s^{-1} at 300 K and 1000 K.

F1.2 Based on your observations from Problem F1.1, provide a molecular interpretation of temperature.

Mathematical background 1 Differentiation and integration

Two of the most important mathematical techniques in the physical sciences are differentiation and integration. They occur throughout the subject, and it is essential to be aware of the procedures involved.

MB1.1 Differentiation: definitions

Differentiation is concerned with the slopes of functions, such as the rate of change of a variable with time. The formal definition of the **derivative**, $\mathrm{d}f/\mathrm{d}x$, of a function $f(x)$ is

$$\frac{\mathrm{d}f}{\mathrm{d}x}=\lim_{\delta x\to 0}\frac{f(x+\delta x)-f(x)}{\delta x}\qquad \textit{Definition}\qquad \text{First derivative}\tag{MB1.1}$$

As shown in Fig. MB1.1, the derivative can be interpreted as the slope of the tangent to the graph of $f(x)$. A positive first derivative indicates that the function slopes upwards (as x increases), and a negative first derivative indicates the opposite. It is sometimes convenient to denote the first derivative as $f'(x)$. The **second derivative**, $\mathrm{d}^2f/\mathrm{d}x^2$, of a function is the derivative of the first derivative (here denoted f'):

$$\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}=\lim_{\delta x\to 0}\frac{f'(x+\delta x)-f'(x)}{\delta x}\qquad \textit{Definition}\qquad \text{Second derivative}\tag{MB1.2}$$

It is sometimes convenient to denote the second derivative f''. As shown in Fig. MB1.1, the second derivative of a function can be interpreted as an indication of the sharpness of the curvature[1] of the function. A positive second derivative indicates that the function is ∪ shaped, and a negative second derivative indicates that it is ∩ shaped.

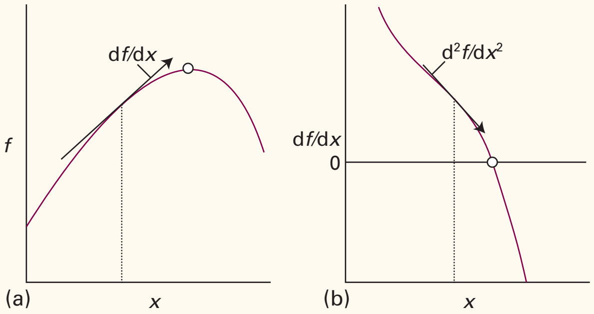


Figure MB1.1 (a) The first derivative of a function is equal to the slope of the tangent to the graph of the function at that point. The small circle indicates the extremum (in this case, maximum) of the function, where the slope is zero. (b) The second derivative of the same function is the slope of the tangent to a graph of the first derivative of the function. It can be interpreted as an indication of the sharpness of curvature of the function at that point.

The derivatives of some common functions are as follows:

$$\frac{\mathrm{d}}{\mathrm{d}x}x^n=nx^{n-1}\tag{MB1.3a}$$

$$\frac{\mathrm{d}}{\mathrm{d}x}\mathrm{e}^{ax}=a\mathrm{e}^{ax}\tag{MB1.3b}$$

$$\frac{\mathrm{d}}{\mathrm{d}x}\sin ax=a\cos ax\qquad \frac{\mathrm{d}}{\mathrm{d}x}\cos ax=-a\sin ax\tag{MB1.3c}$$

$$\frac{\mathrm{d}}{\mathrm{d}x}\ln ax=\frac{1}{x}\tag{MB1.3d}$$

When a function depends on more than one variable, we need the concept of a **partial derivative**, $\partial f/\partial x$. Note the change from d to ∂: partial derivatives are dealt with at length in *Mathematical background* 8; all we need know at this stage is that they signify that all variables other than the stated variable are regarded as constant when evaluating the derivative.

Brief illustration MB1.1 Partial derivatives

Suppose we are told that f is a function of two variables, and specifically $f=4x^2y^3$. Then, to evaluate the partial derivative of f with respect to x, we regard y as a constant (just like the 4), and obtain

$$\frac{\partial f}{\partial x}=\frac{\partial}{\partial x}(4x^2y^3)=4y^3\frac{\partial}{\partial x}x^2=8xy^3$$

Similarly, to evaluate the partial derivative of f with respect to y, we regard x as a constant (again, like the 4), and obtain

$$\frac{\partial f}{\partial y}=\frac{\partial}{\partial y}(4x^2y^3)=4x^2\frac{\partial}{\partial y}y^3=12x^2y^2$$

MB1.2 Differentiation: manipulations

It follows from the definition of the derivative that a variety of combinations of functions can be differentiated by using the following rules:

$$\frac{\mathrm{d}}{\mathrm{d}x}(u+v)=\frac{\mathrm{d}u}{\mathrm{d}x}+\frac{\mathrm{d}v}{\mathrm{d}x}\tag{MB1.4a}$$

---

[1] We are using the term 'curvature' informally. The precise technical definition of the curvature of a function f is $(\mathrm{d}^2f/\mathrm{d}x^2)/\{1+(\mathrm{d}f/\mathrm{d}x)^2\}^{3/2}$.

$$\frac{d}{dx}uv = u\frac{dv}{dx} + v\frac{du}{dx} \qquad \text{(MB1.4b)}$$

$$\frac{d}{dx}\frac{u}{v} = \frac{1}{v}\frac{du}{dx} - \frac{u}{v^2}\frac{dv}{dx} \qquad \text{(MB1.4c)}$$

Brief illustration MB1.2 Derivatives

To differentiate the function $f = \sin^2 ax/x^2$ use eqn MB1.4 to write

$$\begin{aligned}\frac{d}{dx}\frac{\sin^2 ax}{x^2} &= \frac{d}{dx}\left(\frac{\sin ax}{x}\right)\left(\frac{\sin ax}{x}\right) = 2\left(\frac{\sin ax}{x}\right)\frac{d}{dx}\left(\frac{\sin ax}{x}\right)\\ &= 2\left(\frac{\sin ax}{x}\right)\left\{\frac{1}{x}\frac{d}{dx}\sin ax + \sin ax\frac{d}{dx}\frac{1}{x}\right\}\\ &= 2\left\{\frac{a}{x^2}\sin ax\cos ax - \frac{\sin^2 ax}{x^3}\right\}\end{aligned}$$

The function and this first derivative are plotted in Fig. MB1.2.

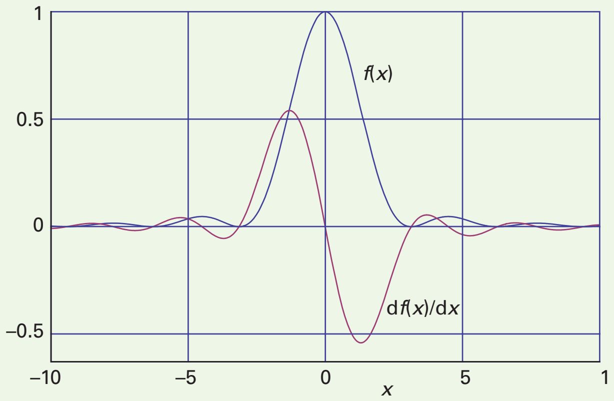


Figure MB1.2 The function considered in *Brief illustration* MB1.2 and its first derivative.

MB1.3 Series expansions

One application of differentiation is to the development of power series for functions. The **Taylor series** for a function $f(x)$ in the vicinity of $x = a$ is

$$\begin{aligned}f(x) &= f(a) + \left(\frac{df}{dx}\right)_a (x-a) + \frac{1}{2!}\left(\frac{d^2 f}{dx^2}\right)_a (x-a)^2 + \cdots\\ &= \sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{d^n f}{dx^n}\right)_a (x-a)^n\end{aligned} \qquad \text{(MB1.5)}$$

Taylor series

where the notation $(\ldots)_a$ means that the derivative is evaluated at $x = a$ and $n!$ denotes a **factorial** given by

$$n! = n(n-1)(n-2)\cdots 1, \quad 0! = 1 \qquad \text{(MB1.6)}$$

Factorial

The **Maclaurin series** for a function is a special case of the Taylor series in which $a = 0$.

Brief illustration MB1.3 Series expansion

To evaluate the expansion of $\cos x$ around $x = 0$ we note that

$$\left(\frac{d}{dx}\cos x\right)_0 = (-\sin x)_0 = 0 \quad \left(\frac{d^2}{dx^2}\cos x\right)_0 = (-\cos x)_0 = -1$$

and in general

$$\left(\frac{d^n}{dx^n}\cos x\right)_0 = \begin{cases} 0 & \text{for } n \text{ odd}\\ (-1)^{n/2} & \text{for } n \text{ even}\end{cases}$$

Therefore,

$$\cos x = \sum_{n\ \text{even}}^{\infty}\frac{(-1)^{n/2}}{n!}x^n = 1 - \frac{1}{2}x^2 + \frac{1}{24}x^4 - \cdots$$

The following Taylor series (specifically, Maclaurin series) are used at various stages in the text:

$$(1+x)^{-1} = 1 - x + x^2 - \cdots = \sum_{n=0}^{\infty}(-1)^n x^n \qquad \text{(MB1.7a)}$$

$$e^x = 1 + x + \frac{1}{2}x^2 + \cdots = \sum_{n=0}^{\infty}\frac{x^n}{n!} \qquad \text{(MB1.7b)}$$

$$\ln(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 - \cdots = \sum_{n=1}^{\infty}(-1)^{n+1}\frac{x^n}{n} \qquad \text{(MB1.7c)}$$

Taylor series are used to simplify calculations, for when $x \ll 1$ it is possible, to a good approximation, to terminate the series after one or two terms. Thus, provided $x \ll 1$ we can write

$$(1+x)^{-1} \approx 1 - x \qquad \text{(MB1.8a)}$$

$$e^x \approx 1 + x \qquad \text{(MB1.8b)}$$

$$\ln(1+x) \approx x \qquad \text{(MB1.8c)}$$

A series is said to **converge** if the sum approaches a finite, definite value as n approaches infinity. If the sum does not approach a finite, definite value, then the series is said to **diverge**. Thus, the series in eqn MB1.7a converges for $x < 1$ and diverges for $x \geq 1$.There are a variety of tests for convergence, which are explained in mathematics texts.

MB1.4 Integration: definitions

Integration (which formally is the inverse of differentiation) is concerned with the areas under curves. The **integral** of a function $f(x)$, which is denoted $\int f\,\mathrm{d}x$ (the symbol $\int$ is an elongated S denoting a sum), between the two values $x=a$ and $x=b$ is defined by imagining the x axis as divided into strips of width δx and evaluating the following sum:

$$\int_a^b f(x)\mathrm{d}x = \lim_{\delta x\to 0}\sum_i f(x_i)\delta x$$

Definition Integration (MB1.9)

As can be appreciated from Fig. MB1.3, the integral is the area under the curve between the limits a and b. The function to be integrated is called the **integrand**. It is an astonishing mathematical fact that the integral of a function is the inverse of the differential of that function in the sense that if we differentiate f and then integrate the resulting function, then we obtain the original function f (to within a constant). The function in eqn MB1.9 with the limits specified is called a **definite integral**. If it is written without the limits specified, then we have an **indefinite integral**. If the result of carrying out an indefinite integration is $g(x)+C$, where C is a constant, the following notation is used to evaluate the corresponding definite integral:

$$\begin{aligned} I &= \int_a^b f(x)\mathrm{d}x = \{g(x)+C\}\big|_a^b = \{g(b)+C\}-\{g(a)+C\} \\ &= g(b)-g(a) \end{aligned}$$

Definite integral (MB1.10)

Note that the constant of integration disappears. The definite and indefinite integrals encountered in this text are listed in the *Resource section*.

MB1.5 Integration: manipulations

When an indefinite integral is not in the form of one of those listed in the *Resource section* it is sometimes possible to transform it into one of the forms by using integration techniques such as:

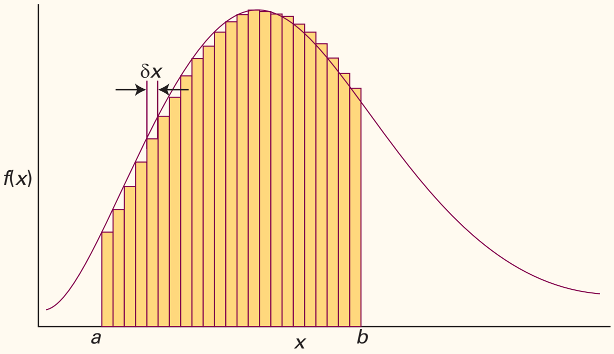


Figure MB1.3 A definite integral is evaluated by forming the product of the value of the function at each point and the increment δx, with $\delta x \to 0$, and then summing the products $f(x)\delta x$ for all values of x between the limits a and b. It follows that the value of the integral is the area under the curve between the two limits.

> *Substitution*. Introduce a variable u related to the independent variable x (for example, an algebraic relation such as $u=x^2-1$ or a trigonometric relation such as $u=\sin x$). Express the differential $\mathrm{d}x$ in terms of $\mathrm{d}u$ (for these substitutions, $\mathrm{d}u = 2x\,\mathrm{d}x$ and $\mathrm{d}u = \cos x\,\mathrm{d}x$, respectively). Then transform the original integral written in terms of x into an integral in terms of u upon which, in some cases, a standard form such as one of those listed in the *Resource section* can be used.

Brief illustration MB1.4 Integration by substitution

To evaluate the indefinite integral $\int\cos^2 x \sin x\,\mathrm{d}x$ we make the substitution $u=\cos x$. It follows that $\mathrm{d}u/\mathrm{d}x=-\sin x$, and therefore that $\sin x\,\mathrm{d}x = -\mathrm{d}u$. The integral is therefore

$$\int \cos^2 x \sin x\,\mathrm{d}x = -\int u^2\mathrm{d}u = -\frac{1}{3}u^3 + C = -\frac{1}{3}\cos^3 x + C$$

To evaluate the corresponding definite integral, we have to convert the limits on x into limits on u. Thus, if the limits are $x=0$ and $x=\pi$, the limits become $u=\cos 0=1$ and $u=\cos\pi=-1$:

$$\int_0^{\pi}\cos^2 x\sin x\,\mathrm{d}x = -\int_1^{-1}u^2\mathrm{d}u = \left\{-\frac{1}{3}u^3+C\right\}\Bigg|_1^{-1} = \frac{2}{3}$$

Integration by parts. For two functions $f(x)$ and $g(x)$,

$$\int f\frac{\mathrm{d}g}{\mathrm{d}x}\mathrm{d}x = fg - \int g\frac{\mathrm{d}f}{\mathrm{d}x}\mathrm{d}x$$

Integration by parts (MB1.11a)

which may be abbreviated as

$$\int f\mathrm{d}g = fg - \int g\mathrm{d}f \tag{MB1.11b}$$

Brief illustration MB1.5 Integration by parts

Integrals over $x\mathrm{e}^{-ax}$ and their analogues occur commonly in the discussion of atomic structure and spectra. They may be integrated by parts, as in the following:

$$\begin{aligned} \int_0^{\infty}\overbrace{x}^{f}\,\overbrace{\mathrm{e}^{-ax}}^{\mathrm{d}g/\mathrm{d}x}\,\mathrm{d}x &= \overbrace{x}^{f}\,\frac{\overbrace{\mathrm{e}^{-ax}}^{g}}{-a}\Bigg|_0^{\infty} - \int_0^{\infty}\frac{\overbrace{\mathrm{e}^{-ax}}^{g}}{-a}\;\overbrace{1}^{\mathrm{d}f/\mathrm{d}x}\;\mathrm{d}x \\ &= -\frac{x\mathrm{e}^{-ax}}{a}\Bigg|_0^{\infty} + \frac{1}{a}\int_0^{\infty}\mathrm{e}^{-ax}\mathrm{d}x = 0 - \frac{\mathrm{e}^{-ax}}{a^2}\Bigg|_0^{\infty} \\ &= \frac{1}{a^2} \end{aligned}$$

MB1.6 Multiple integrals

A function may depend on more than one variable, in which case we may need to integrate over both the variables:

$$I=\int_a^b\int_c^d f(x,y)\mathrm{d}x\mathrm{d}y \qquad \text{(MB1.12)}$$

We (but not everyone) adopt the convention that a and b are the limits of the variable x and c and d are the limits for y (as depicted by the colours in this instance). This procedure is simple if the function is a product of functions of each variable and of the form $f(x,y)=X(x)Y(y)$. In this case, the double integral is just a product of each integral:

$$I=\int_a^b\int_c^d X(x)Y(y)\mathrm{d}x\mathrm{d}y=\int_a^b X(x)\mathrm{d}x\int_c^d Y(y)\mathrm{d}y \qquad \text{(MB1.13)}$$

Brief illustration MB1.6 A double integral

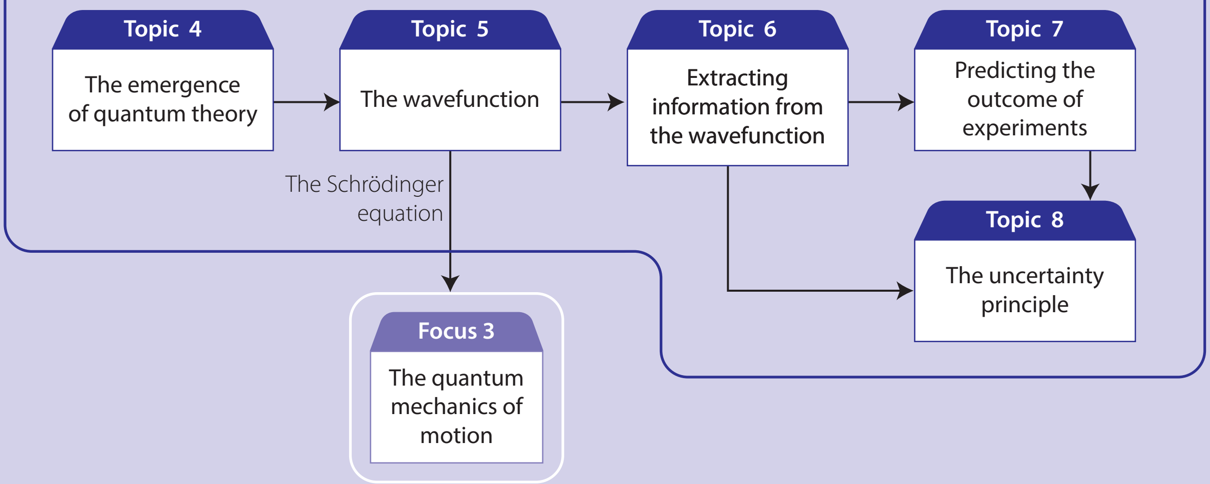
Double integrals of the form

$$I=\int_0^{L_1}\int_0^{L_2}\sin^2(\pi x/L_1)\sin^2(\pi y/L_2)\mathrm{d}x\mathrm{d}y$$

occur in the discussion of the translational motion of a particle in two dimensions, where L_1 and L_2 are the maximum extents of travel along the x- and y-axes, respectively. To evaluate I we use MB1.13 and Integral T.2 in the *Resource section* to write

$$\begin{aligned}I&=\int_0^{L_1}\sin^2(\pi x/L_1)\mathrm{d}x\int_0^{L_2}\sin^2(\pi y/L_2)\mathrm{d}y\\&=\left\{\frac{1}{2}x-\frac{\sin(2\pi x/L_1)}{4\pi/L_1}+C\right\}\Bigg|_0^{L_1}\left\{\frac{1}{2}y-\frac{\sin(2\pi y/L_2)}{4\pi/L_2}+C\right\}\Bigg|_0^{L_2}\\&=\frac{1}{4}L_1L_2\end{aligned}$$

FOCUS 2 ON The principles of quantum mechanics



Two cherished concepts in classical physics are the distinction between particles and waves and the continuous variation of the energy of bodies. However, experiments conducted towards the end of the nineteenth century and early in the twentieth century on light, electrons, atoms, and molecules could be explained only if the distinction between waves and particles were discarded and energy assumed to be confined to discrete values (**Topic 4**). These shortcomings required a new theory to provide the essential foundation for understanding the properties of atoms and molecules. As this theory, which is called 'quantum mechanics', was developed, it was found that it could be expressed in terms of a small set of basic rules or 'postulates', which are collected at the end of **Topic 7**.

First, we need to know that all the information that can be known about a system is carried by its wavefunction (**Topic 5**). Then we need to know how to extract that information. For example, the 'Born interpretation' (**Topic 5**) shows us how to use the wavefunction to calculate the probability of finding a particle in a region of space. The extraction of other kinds of dynamical information is less straightforward and depends on being able to construct a mathematical device, an 'operator', that when applied to the wavefunction produces the value of the observable. We see how to set up and use these operators in **Topic 6**. Of course, we need to know how to find the wavefunction in the first place: that is done by setting up a very special version of an operator called the 'hamiltonian' and then solving the resulting Schrödinger equation (this equation is also introduced in **Topic 6**).

Unlike in classical mechanics, where precise trajectories can be calculated, in quantum mechanics it is sometimes possible to calculate only average values of observables (**Topic 7**). In some cases the difference is even more pronounced, because it might be the case that if one observable is known precisely, then the value of another observable might be wholly indeterminate. This is the domain of the famous 'uncertainty principle' (**Topic 8**), which represents one of the most remarkable departures of quantum mechanics from classical mechanics, and has implications throughout chemistry.

These fundamental principles of quantum mechanics are used throughout the text. For example, solving the Schrödinger equation is a central feature of the discussion of the three basic types of motion of particles, their translation, rotation and vibration (see *The quantum mechanics of motion*).

What is the impact of this material?

Concepts of quantum theory lie at the heart of what may prove one day to be a revolution in the way in which certain calculations are carried out in a new generation of computers. 'Quantum computing' is potentially capable of solving in seconds problems that conventional computing might be unable to solve in the lifetime of the universe (*Impact* 2.1).

To read more about the impact of this material, scan the QR code or go to http://bcs.whfreeman.com/webpub/chemistry/qmc2e/impact/qchem_impact2.html.

TOPIC 4

The emergence of quantum theory

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➤ Why do you need to know this material?

You should know how experimental results motivated the development of quantum theory, which underlies all descriptions of the structure of atoms and molecules and pervades the whole of spectroscopy and chemistry in general.

➤ What is the key idea?

Experimental evidence accumulated near the end of the nineteenth and beginning of the twentieth centuries led to the conclusions that energy cannot be continuously varied and that the classical concepts of a 'particle' and a 'wave' blend together when applied to light, atoms, and molecules.

➤ What do you need to know already?

You should be familiar with the basic principles of classical mechanics, which are reviewed in *Foundations*, Topic 2.

As science developed during the late nineteenth century it was thought that the internal structure of atoms and the newly discovered electron could be expressed using **classical mechanics**, the laws of motion concerning mass, force, speed, and acceleration introduced in the seventeenth century by Isaac Newton. However, towards the end of the century and early in the twentieth century, experimental evidence accumulated showing that classical mechanics failed when it was applied to particles as small as electrons. In this Topic, we describe several crucial experiments that showed that classical mechanics fails when applied to transfers of very small energies and to objects of very small mass. The observations led to the formulation of an entirely new and currently hugely successful theory called **quantum mechanics**, which is developed in Topics 5–30.

4.1 The quantization of energy

According to classical mechanics, the energy of a body can be continuously varied: a pendulum, for instance, can possess any energy by starting it to swing from any angle. In particular, it was thought that the oscillators responsible for the emission and absorption of electromagnetic radiation by a hot body could also take on any energy. However, that turned out not to be the case: the characteristics of the radiation could be explained only if it was assumed that their energy is confined to discrete values. In due course, it was established that this 'quantization' of energy was a universal phenomenon.

(a) Black-body radiation

It is common experience that a heated metal bar glows red when heated. At high temperatures, an appreciable proportion is in the visible region of the electromagnetic spectrum and, as the temperature is increased, more short-wavelength blue light is generated. The red-hot iron bar begins to glow 'white hot' when heated further.

The formal experimental investigation of this type of observation makes use of an empty container with a pinhole to allow radiation to escape and be analysed (Fig. 4.1). When the container is heated, radiation is absorbed and re-emitted inside it so many times as it is reflected around that it comes to thermal equilibrium with the walls before leaking out of the pinhole. This system is a good approximation to a **black body**, an object capable of emitting and absorbing all wavelengths of radiation uniformly.

Figure 4.2 shows how the energy output of the black-body radiation varies with wavelength at different temperatures. The energy output is expressed as its **spectral density of states** $\rho(\lambda,T)$, the energy density of the electromagnetic radiation emitted at wavelengths between λ and $\lambda+d\lambda$ at the temperature T. The energy density is the energy in the specified range divided by the volume enclosed by the black body. The observation that the maximum of ρ moves to shorter wavelengths as the temperature is raised is summarized by **Wien's displacement law**:

$$\lambda_{\max}T=\text{constant} \qquad \text{Wien's displacement law} \qquad (4.1)$$

The empirical value of the constant is 2.9 mm K.

Brief illustration 4.1 Wien's displacement law

The peak in the Sun's emitted energy occurs at about 480 nm. The temperature of its surface can be estimated by regarding the Sun as a black-body emitter and using eqn 4.1:

$$T=\frac{\text{constant}}{\lambda_{\max}}=\frac{2.9\times10^{-3}\,\text{m K}}{480\times10^{-9}\,\text{m}}=6000\,\text{K}$$

Self-test 4.1 A metal object is heated to 500 °C. What is the wavelength of maximum emission?

Answer: 3.8 μm

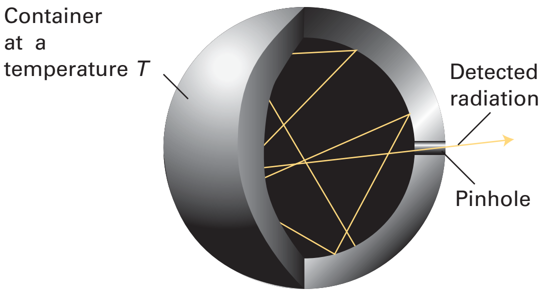

Figure 4.1 An experimental representation of a black body is a pinhole in an otherwise closed container. The radiation is reflected many times within the container and comes to thermal equilibrium with the walls. Radiation leaking out through the pinhole is characteristic of the radiation within the container.

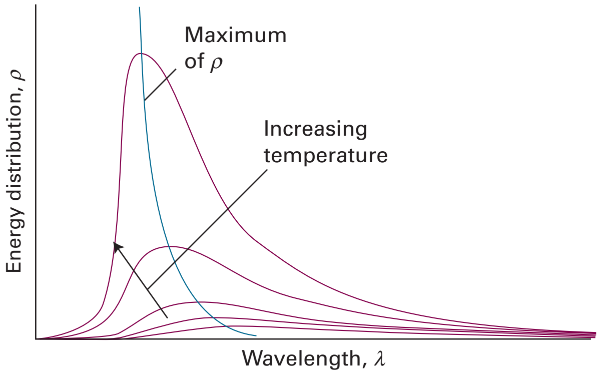

Figure 4.2 The energy distribution in a black-body cavity at several temperatures. Note how the spectral density of states increases in the region of shorter wavelength as the temperature is raised, and how the peak shifts to shorter wavelengths.

One of the most challenging problems at the end of the nineteenth century was to explain the behaviour observed in Fig. 4.2. Lord Rayleigh, using his expertise in classical physics, derived an expression for ρ by imagining the electromagnetic field as a collection of oscillators of all possible frequencies and using the classical equipartition theorem (Topic 2) for the average energy of each oscillator. He regarded the presence of radiation of frequency ν (and wavelength $\lambda=c/\nu$) as signifying that the electromagnetic oscillator of that frequency had been excited (Fig. 4.3). With minor help from James Jeans, he arrived at the **Rayleigh–Jeans law**:

$$\rho(\lambda,T)=\frac{8\pi kT}{\lambda^4} \qquad \text{Rayleigh–Jeans law} \qquad (4.2)$$

where k is Boltzmann's constant ($k=1.381\times10^{-23}\,\text{J K}^{-1}$).

Although the Rayleigh–Jeans law is quite successful at long wavelengths (low frequencies), it fails badly at short wavelengths (high frequencies), predicting that as λ decreases, ρ increases without bound (Fig. 4.4). Therefore, oscillators of very short wavelength (corresponding to ultraviolet radiation, X-rays, and even γ-rays) are strongly excited even at room temperature. According to this absurd result, which is called the **ultraviolet catastrophe**, even cool objects should radiate in the visible and ultraviolet regions.

In 1900, the German physicist Max Planck found that he could account for the form of ρ by proposing that the energy

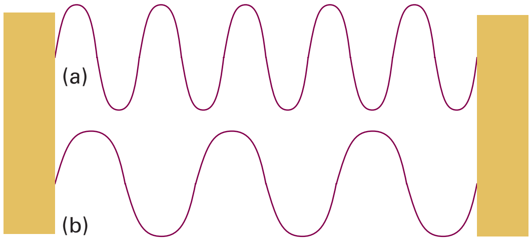

Figure 4.3 The electromagnetic vacuum can be regarded as able to support oscillations of the electromagnetic field. When a high-frequency, short-wavelength oscillator (a) is excited, radiation of that frequency is present. The presence of low-frequency, long-wavelength radiation (b) signifies that an oscillator of the corresponding frequency has been excited.

of each electromagnetic oscillator is limited to discrete values. That suggestion contradicts the viewpoint of classical physics, in which all possible energies are allowed. The limitation of energies to discrete values is called the **quantization of energy**. In particular, Planck found that he could account for the observed distribution of energies if he supposed that the permitted energies of an electromagnetic oscillator of frequency ν are integer multiples of $h\nu$:

$$E=nh\nu \qquad n=0,\ 1,\ 2,\ \ldots$$

where h is a fundamental constant now known as **Planck's constant**. On the basis of this supposition, Planck was able to derive the **Planck distribution**:

$$\rho(\lambda,T)=\frac{8\pi hc}{\lambda^5(\mathrm{e}^{hc/\lambda kT}-1)} \qquad \text{Planck distribution} \tag{4.3}$$

This expression fits the experimental curve very well at all wavelengths if h, which is an undetermined parameter in the theory, has the value 6.626×10^{-34} J s (Fig. 4.5). It is easy to understand why Planck's approach avoided the ultraviolet catastrophe. According to his hypothesis, oscillators are excited only if they can acquire an energy of at least $h\nu$. This energy is too large for the walls of the black body to supply in the case of the very high frequency oscillators, so they remain unexcited.

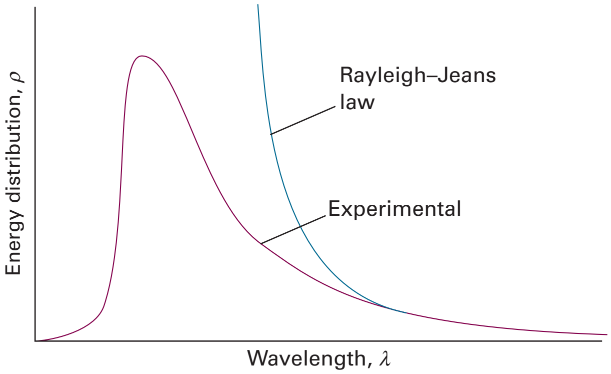

Figure 4.4 The Rayleigh–Jeans law (eqn 4.2) predicts an infinite spectral density of states at short wavelengths. This approach to infinity is called the *ultraviolet catastrophe*.

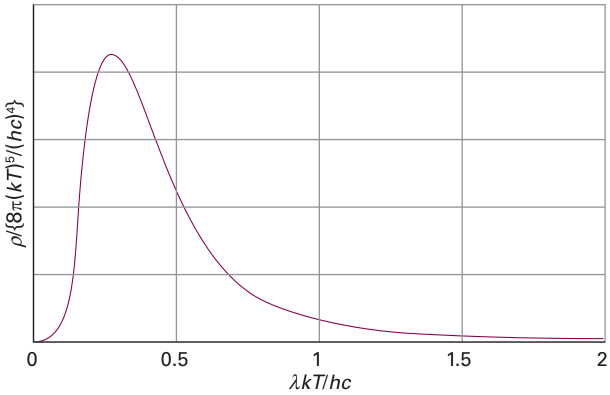

Figure 4.5 The Planck distribution (eqn 4.3) accounts very well for the experimentally determined distribution of black-body radiation. Planck's quantization hypothesis essentially quenches the contributions of high-frequency, short-wavelength oscillators. The distribution coincides with the Rayleigh–Jeans distribution at long wavelengths.

The Planck distribution reduces to the Rayleigh–Jeans law in the limit of long wavelengths, where the classical expression is successful at explaining the observed energy distribution of the black-body radiator (Fig. 4.4). For long wavelengths, $hc/\lambda kT \ll 1$, and the denominator in eqn 4.3 can be replaced by:

$$\lambda^5(\mathrm{e}^{hc/\lambda kT}-1)=\lambda^5\left\{\left(1+\frac{hc}{\lambda kT}+\cdots\right)-1\right\}\approx\frac{\lambda^4 hc}{kT}$$

where we have used the expansion $\mathrm{e}^x=1+x+\ldots$. The Planck distribution therefore reduces to

$$\rho(\lambda,T)\approx\frac{8\pi hc}{(\lambda^4 hc/kT)}=\frac{8\pi kT}{\lambda^4}$$

which is the Rayleigh–Jeans law (eqn 4.2). However, at short wavelengths, the Planck distribution avoids the ultraviolet catastrophe of classical physics because $\mathrm{e}^{hc/\lambda kT}\to\infty$ faster than $\lambda^5\to0$, and therefore $\rho\to0$ as $\lambda\to0$. In addition, the Planck distribution can be used to derive Wien's displacement law and to show that the constant in eqn 4.1 is equal to $hc/5k$ (see Problem 4.2).

Example 4.1 Using the Planck distribution

Compare the energy output of a black-body radiator (such as an incandescent lamp) at two different wavelengths by calculating the ratio of the energy output at 450 nm (blue light) to that at 700 nm (red light) at 298 K.

Method Use eqn 4.3. At a temperature T, the ratio of the spectral density of states at a wavelength λ_1 to that at λ_2 is given by

$$\frac{\rho(\lambda_1,T)}{\rho(\lambda_2,T)}=\left(\frac{\lambda_2}{\lambda_1}\right)^5\times\frac{(e^{hc/\lambda_2 kT}-1)}{(e^{hc/\lambda_1 kT}-1)}$$

Insert the data and evaluate this ratio.

Answer With $\lambda_1=450$ nm and $\lambda_2=700$ nm,

$$\frac{hc}{\lambda_1 kT}=\frac{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{8}\,\mathrm{m\,s^{-1}})}{(450\times10^{-9}\,\mathrm{m})\times(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}=107.2\ldots$$

$$\frac{hc}{\lambda_2 kT}=\frac{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{8}\,\mathrm{m\,s^{-1}})}{(700\times10^{-9}\,\mathrm{m})\times(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}=68.9\ldots$$

and therefore

$$\frac{\rho(450\,\mathrm{nm},298\,\mathrm{K})}{\rho(700\,\mathrm{nm},298\,\mathrm{K})}=\left(\frac{700\times10^{-9}\,\mathrm{m}}{450\times10^{-9}\,\mathrm{m}}\right)^5\times\frac{(e^{68.9\ldots}-1)}{(e^{107.2\ldots}-1)}$$
$$=9.11\times(2.30\times10^{-17})=2.10\times10^{-16}$$

At room temperature, the proportion of short-wavelength radiation is insignificant.

Self-test 4.2 Repeat the calculation for a temperature of 13.6 MK, which is close to the temperature at the core of the Sun.

Answer: 5.85

(b) Spectroscopy

Compelling additional evidence that energy is quantized comes from **spectroscopy**, the detection and analysis of the electromagnetic radiation absorbed, emitted, or scattered by a substance. Two typical atomic emission and molecular absorption spectra are shown in Figs 4.6 and 4.7. The obvious feature of both is that radiation is emitted or absorbed at a series of discrete wavelengths (or frequencies).

The observation of discrete spectral lines rather than the continuum of emission characteristic of a black body suggests that some of the oscillators responsible for the emission or absorption of radiation are not present in isolated atoms and molecules. This conclusion is consistent with the existence of **photons**, which are particles of electromagnetic radiation. As will be developed later in this Topic, a photon of radiation of frequency ν possesses an energy $h\nu$. Therefore, the observation of a photon of frequency ν in the radiation emitted by an atom indicates that the atom has lost an energy of $h\nu$. This conclusion is summarized by the **Bohr frequency condition**

$$\Delta E=h\nu \qquad \text{Bohr frequency condition} \qquad (4.4)$$

where ΔE is the change in energy of the atom. The observation of discrete values of ν then implies that the change in energy of the atom can take place only in discrete steps (Fig. 4.8). That in turn implies that the atom can possess only discrete energies.

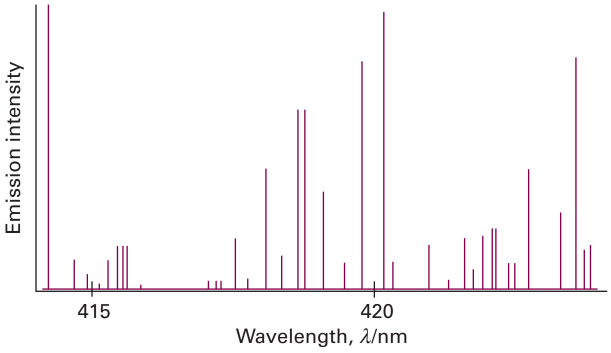

Figure 4.6 A region of the spectrum of radiation emitted by excited iron atoms consists of radiation at a series of discrete wavelengths (or frequencies).

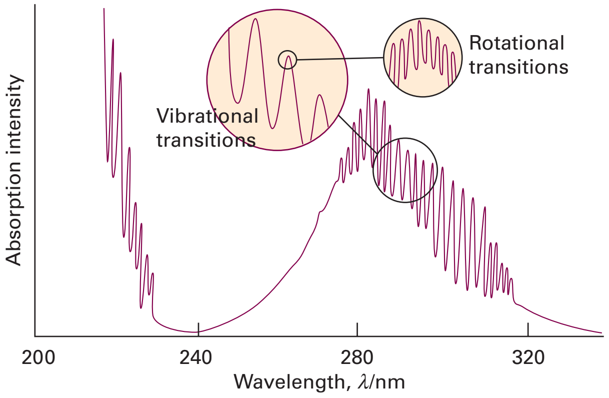

Figure 4.7 When a molecule changes its state, it does so by absorbing radiation at definite frequencies. This spectrum is part of that due to the electronic, vibrational, and rotational excitation of sulfur dioxide (SO_2) molecules. This observation suggests that molecules can possess only discrete energies, not an arbitrary energy.

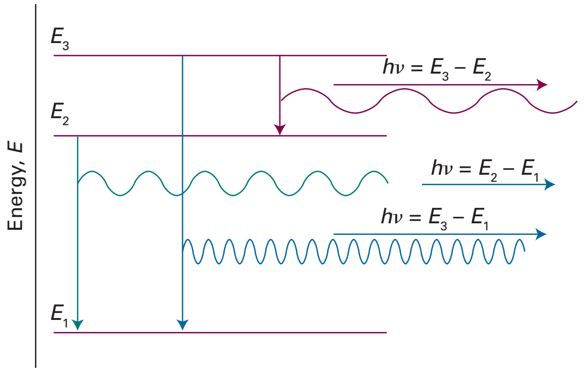

Figure 4.8 Spectroscopic transitions, such as those shown above, can be accounted for if we assume that a molecule emits electromagnetic radiation as it changes between discrete energy levels. Note that high-frequency radiation is emitted when the energy change is large.

In other words, its energy is quantized and it can exist in only certain **energy levels**. Similar remarks and implications apply to the absorption of radiation and to molecules.

Brief illustration 4.2 The Bohr frequency condition

Atomic sodium produces a yellow glow (as in some street lamps) resulting from the emission of radiation of 590 nm. The spectroscopic transition responsible for the emission involves electronic energy levels that have a separation given by eqn 4.4:

$$\begin{aligned}\Delta E = h\nu = \frac{hc}{\lambda} &= \frac{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{8}\,\mathrm{m\,s^{-1}})}{590\times10^{-9}\,\mathrm{m}}\\ &= 3.37\times10^{-19}\,\mathrm{J}\end{aligned}$$

This energy difference can be expressed in a variety of ways. For instance, multiplication by Avogadro's constant results in an energy separation per mole of atoms of 203 kJ mol^{-1}, comparable to the energy of a weak chemical bond. A very useful conventional unit is the electronvolt (eV), with 1 eV corresponding to the kinetic energy gained by an electron when it is accelerated through a potential difference of 1 V: $1\,\mathrm{eV} = 1.602\times10^{-19}$ J. Therefore the calculated value of ΔE corresponds to 2.10 eV. The ionization energies of atoms are typically several electronvolts.

Self-test 4.3 Neon lamps emit red radiation of wavelength 736 nm. What is the energy separation of the levels in joules, kilojoules per mole, and electronvolts responsible for the emission?

Answer: $2.70\times10^{-9}\,\mathrm{J}, 163\,\mathrm{kJ\,mol^{-1}}, 1.69\,\mathrm{eV}$

The quantized energy levels responsible for spectral lines may involve rotational, vibrational, and electronic motion; they are considered in detail in Topics 41–45. In general, electronic energy levels are the most widely spaced, followed by vibrational and then rotational levels. Therefore, by the Bohr frequency condition, electronic transitions occur at the highest frequencies (shortest wavelengths; ultraviolet and visible radiation), vibrational transitions at lower frequencies (longer wavelengths; infrared radiation), and rotational transitions at even lower frequencies (longest wavelengths; microwave radiation).

4.2 Wave–particle duality

As we have seen, the possession of arbitrary amounts of energy assumed by classical mechanics had to be discarded. There was more revolution to come. Classical mechanics makes a clear distinction between a 'particle' and a 'wave': electromagnetic radiation is treated as a wave and an electron, or any object with mass, is treated as a particle. However, this fundamental distinction between these two concepts had to be discarded when more experimental information about the behaviour of electromagnetic radiation and electrons was accumulated at the beginning of the twentieth century.

(a) The photoelectric effect

The **photoelectric effect** is the ejection of electrons from metals when they are exposed to visible or ultraviolet radiation. The experimental characteristics of the effect are:

1. No electrons are ejected, regardless of the intensity of the radiation, unless the frequency of the radiation exceeds a threshold value characteristic of the metal.
2. The kinetic energy of the ejected electrons increases linearly with the frequency of the incident radiation but is independent of the intensity of the radiation.
3. Even at low light intensities, electrons are ejected if the frequency is above the threshold.

Figure 4.9 illustrates the first and second characteristics.

In 1905 Albert Einstein devised an explanation of the photoelectric effect when he suggested that it depends on the ejection of an electron when it is involved in a collision with a sufficiently energetic particle-like projectile. Einstein supposed that the projectile is a photon of energy $h\nu$, where ν is the frequency of the radiation. It then follows from the conservation of energy that the kinetic energy of the ejected electron, E_k, should be given by

$$E_\mathrm{k} = h\nu - \Phi \qquad \text{Photoelectric effect} \qquad (4.5)$$

In this expression, Φ (uppercase phi) is a characteristic of the metal called its **work function**, the minimum energy required

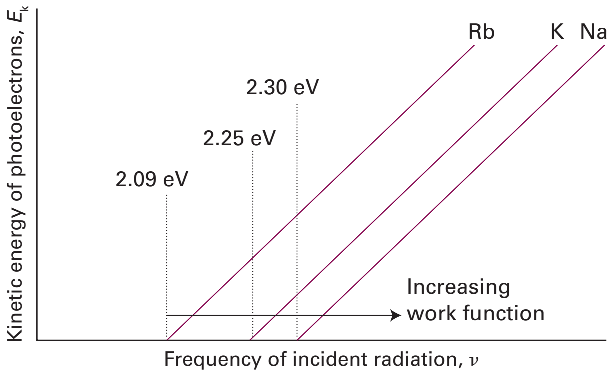

Figure 4.9 In the photoelectric effect, it is found that no electrons are ejected when the incident radiation has a frequency below a value characteristic of the metal, and that, above that value, the kinetic energy of the photoelectrons varies linearly with the frequency of the incident radiation.

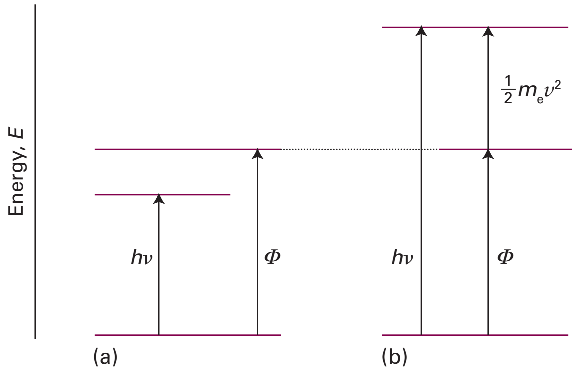

Figure 4.10 The photoelectric effect can be explained if it is supposed that the incident radiation is composed of photons that have energy proportional to the frequency of the radiation. (a) The energy of the photon is insufficient to drive an electron out of the metal. (b) The energy of the photon is more than enough to eject an electron, and the excess energy is carried away as the kinetic energy of the photoelectron.

to remove an electron from the metal (Fig. 4.10). The work function is the analogue of the ionization energy of an individual atom or molecule. Equation 4.5 accounts for the three observations given above:

Physical interpretation

- Photoejection cannot occur if $h\nu < \Phi$ because the photon brings insufficient energy; this accounts for observation (1).
- The kinetic energy of the ejected electron increases linearly with frequency but does not depend on the intensity of the radiation, in agreement with observation (2).
- When a photon collides with an electron, it gives up all its energy, so we should expect electrons to appear as soon as the collisions begin, provided the photons have sufficient energy; this conclusion agrees with observation (3).

The revolutionary idea stimulated by this interpretation of the photoelectric effect is the view that a beam of electromagnetic radiation is a collection of particles, photons, each with energy $h\nu$.

A practical application of the photoelectric effect is the photomultiplier tube, a vacuum tube that is a very sensitive detector of ultraviolet and visible radiation. The electrons photoejected by incident light strike an electrode in the vacuum tube, resulting in the emission of additional electrons. The current produced by this cascade of electrons can be amplified by a factor of 10^8, yielding a sensitive and efficient way to detect photons in a wide variety of applications including spectroscopy, medical imaging, and particle physics.

Example 4.2 Calculating the maximum wavelength capable of photoejection

A photon of radiation of wavelength 305 nm ejects an electron from a metal with a kinetic energy of 1.77 eV. Calculate the maximum wavelength of radiation capable of ejecting an electron from the metal.

Method Use eqn 4.5 rearranged into $\Phi = h\nu - E_k$ with $\nu = c/\lambda$ to calculate the work function of the metal from the data. The threshold for photoejection, the frequency able to remove the electron but not give it any excess energy, then corresponds to radiation of frequency $\nu_{min} = \Phi/h$. Use this value of the frequency to calculate the maximum wavelength capable of photoejection.

Answer From the expression for the work function $\Phi = h\nu - E_k$ the minimum frequency for photoejection is

$$\nu_{min} = \frac{\Phi}{h} = \frac{h\nu - E_k}{h} \overset{\nu=c/\lambda}{\overbrace{=}} \frac{c}{\lambda} - \frac{E_k}{h}$$

The maximum wavelength is therefore

$$\lambda_{max} = \frac{c}{\nu_{min}} = \frac{c}{c/\lambda - E_k/h} = \frac{1}{1/\lambda - E_k/hc}$$

Now we substitute the data. The kinetic energy of the electron is

$$E_k = 1.77\ \text{eV} \times (1.602 \times 10^{-19}\ \text{J eV}^{-1}) = 2.83\ldots \times 10^{-19}\ \text{J}$$

$$\frac{E_k}{hc} = \frac{2.83\ldots \times 10^{-19}\ \text{J}}{(6.626 \times 10^{-34}\ \text{J s}) \times (2.998 \times 10^8\ \text{m s}^{-1})} = 1.42\ldots \times 10^6\ \text{m}^{-1}$$

Therefore, with

$$1/\lambda = 1/305\ \text{nm} = 3.27\ldots \times 10^6\ \text{m}^{-1},$$

$$\lambda_{max} = \frac{1}{(3.27\ldots \times 10^6\ \text{m}^{-1}) - (1.42\ldots \times 10^6\ \text{m}^{-1})} = 5.40 \times 10^{-7}\ \text{m}$$

or 540 nm.

Note on good practice To avoid rounding and other numerical errors, it is best to carry out algebraic calculations first, and to substitute numerical values into a single, final formula. Moreover, an analytical result may be used for other data without having to repeat the entire calculation.

Self-test 4.4 When ultraviolet radiation of wavelength 165 nm strikes a certain metal surface, electrons are ejected with a speed of 1.24 Mm s^{-1}. Calculate the speed of electrons ejected by radiation of wavelength 265 nm.

Answer: 735 km s^{-1}

Example 4.3 Calculating the number of photons

Calculate the number of photons emitted by a monochromatic (single-frequency) 100 W sodium vapour lamp in 1.0 s. Take the wavelength as 589 nm and assume 100 per cent efficiency.

Method Each photon has an energy $E = h\nu = hc/\lambda$, so the total energy of the photons emitted by the sodium lamp is $E_{\text{tot}} = Nhc/\lambda$, where N is the number of photons. The total energy is also the product of the power (P, in watts) and the time interval for which the lamp is turned on: $E_{\text{tot}} = P\Delta t$. It follows that $E_{\text{tot}} = Nhc/\lambda = P\Delta t$ and therefore

$$N = \frac{\lambda P \Delta t}{hc}$$

Answer Substitution of the data into the expression for N gives

$$N = \frac{(589 \times 10^{-9}\,\text{m}) \times (100\,\text{W}) \times (1.0\,\text{s})}{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{8}\,\text{m s}^{-1})} = 3.0 \times 10^{20}$$

This number corresponds to 0.50 mmol photons. To produce 1 mol photons therefore requires 2000 times as long, or 2.0×10^{3} s (corresponding to 33 min).

Self-test 4.5 How many photons does a monochromatic infrared source of power 1 mW and wavelength 1000 nm emit in 0.1 s?

Answer: 5×10^{14}

Another laboratory application of eqn 4.5 is that it provides a technique for the determination of Planck's constant, for the slopes of the lines in Fig. 4.9 are all equal to h (see Problem 4.4).

(b) Diffraction

We have seen that what classically is regarded as a wave is also a stream of particles. Could the opposite be true: could what is classically regarded as a particle actually be a wave? Indeed, experiments carried out in 1925 required consideration of the possibility that electrons, and matter in general, possess wave-like properties. The crucial experiment was performed by the American physicists Clinton Davisson and Lester Germer, who observed the diffraction of electrons by a crystal (Fig. 4.11). Diffraction is the interference caused by an object in the path of waves (Topic 3). At almost the same time, George Thomson, working in Scotland, showed that a beam of electrons was diffracted when passed through a thin gold foil.

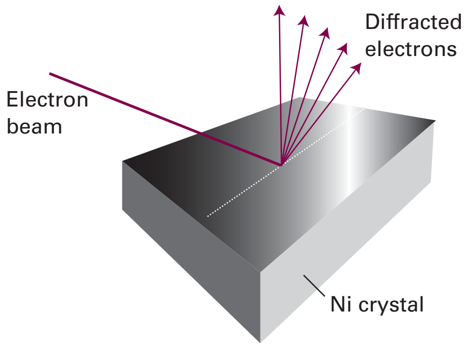

Figure 4.11 The Davisson–Germer experiment. The scattering of an electron beam from a nickel crystal shows a variation of intensity characteristic of a diffraction experiment in which waves interfere constructively and destructively in different directions.

Some progress towards accommodating the wavelike properties of matter had already been made by the French physicist Louis de Broglie when, in 1924, he suggested that *any* particle, not only photons, travelling with a linear momentum p should have (in some sense) a wavelength given by the **de Broglie relation**:

$$\lambda = \frac{h}{p} \qquad \text{de Broglie relation} \tag{4.6}$$

That is, a particle with a high linear momentum has a short wavelength (Fig. 4.12). The joint particle and wave character of matter (and of radiation), summarized by the de Broglie relation, is called **wave–particle duality.** Duality strikes at the heart of classical physics, where particles and waves are treated as entirely distinct entities.

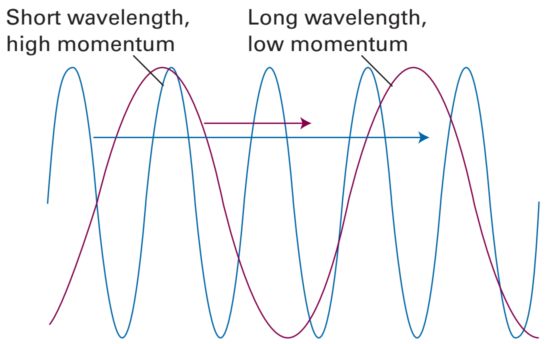

Figure 4.12 An illustration of the de Broglie relation between momentum and wavelength. The wave is associated with a particle. A particle with high momentum corresponds to a wave with a short wavelength, and vice versa.

Example 4.4 Estimating the de Broglie wavelength

Estimate the wavelength of electrons that have been accelerated from rest through a potential difference of 40 kV.

Method To use the de Broglie relation, we need to know the linear momentum, *p*, of the electrons. To calculate the linear momentum, we note that the energy acquired by an electron accelerated through a potential difference $\Delta\phi$ is $e\Delta\phi$, where *e* is the magnitude of its charge. At the end of the period of acceleration, all the acquired energy is in the form of kinetic energy, $E_k = \frac{1}{2}m_e v^2 = p^2/2m_e$, so we can determine *p* by setting $p^2/2m_e$ equal to $e\Delta\phi$.

Answer The expression $p^2/2m_e = e\Delta\phi$ implies that $p = (2m_e e\Delta\phi)^{1/2}$; then, from the de Broglie relation $\lambda = h/p$,

$$\lambda = \frac{h}{(2m_e e\Delta\phi)^{1/2}}$$

Substitution of the data and the fundamental constants (from inside the front cover) gives

$$\begin{aligned}\lambda &= \frac{6.626\times10^{-34}\,\mathrm{J\,s}}{\{2\times(9.109\times10^{-31}\,\mathrm{kg})\times(1.602\times10^{-19}\,\mathrm{C})\times(4.0\times10^{4}\,\mathrm{V}\}^{1/2}}\\ &= 6.1\times10^{-12}\,\mathrm{m}\end{aligned}$$

or 6.1 pm. We have used $1\,\mathrm{V\,C} = 1\,\mathrm{J}$ and $1\,\mathrm{J} = 1\,\mathrm{kg\,m^2\,s^{-2}}$. The wavelength of 6.1 pm is shorter than typical bond lengths in molecules (about 100 pm). Electrons accelerated in this way are used in the technique of electron diffraction for the determination of molecular structure (Topic 37).

Self-test 4.6 Calculate (a) the wavelength of a neutron with a translational kinetic energy equal to *kT* at 300 K, (b) a tennis ball of mass 57 g travelling at 80 km h^{-1}.

Answer: (a) 178 pm, (b) 5.2×10^{-34} m

For microscopic particles, such as electrons and neutrons, their de Broglie wavelengths make them ideally suited for use in diffraction experiments; for example, neutron diffraction is a well-established technique for investigating the structures and dynamics of condensed phases (Topic 37) and electron diffraction is the basis for special techniques in microscopy. On the other hand, macroscopic bodies have such high momenta, even when they are moving slowly (because their mass is so great), that their wavelengths are undetectably small, and the wavelike properties cannot be observed (see Self-test 4.6(b)).

4.3 Retrospect and summary

The concepts of wave–particle duality and quantization have brought us to the heart of modern physics. We have seen that, when examined on an atomic scale, the classical concepts of particle and wave melt together, particles taking on the characteristics of waves, and waves the characteristics of particles. We have also seen that the energies of electromagnetic radiation and of matter cannot be varied continuously as assumed in classical physics, and that for microscopic objects the discreteness of energy is highly significant.

Such total failure of classical physics implied that its basic concepts were false. A new mechanics had to be devised to take its place. Topic 5 begins our exploration of this new mechanics, which became known as 'quantum mechanics' and now pervades the whole of science.

Checklist of concepts

- ☐ 1. A **black body** is an object capable of emitting and absorbing all wavelengths of radiation uniformly.
- ☐ 2. The spectral distribution of the energy output of a black-body emitter is explained by assuming that the energies of the oscillators giving rise to electromagnetic radiation are quantized.
- ☐ 3. **Spectroscopy**, the detection and analysis of the electromagnetic radiation absorbed, emitted, or scattered by a substance, provides evidence for quantization of energy in particles.
- ☐ 4. The **photoelectric effect** is the ejection of electrons from metals when they are exposed to ultraviolet radiation.
- ☐ 5. A beam of electromagnetic radiation can be treated both as a collection of propagating waves and as a collection of particles called **photons**, each with energy *hν*.
- ☐ 6. Diffraction experiments reveal that electrons, and matter in general, possess wave-like properties.
- ☐ 7. **Wave–particle duality** is the joint particle and wave character of matter and radiation.

Checklist of equations

Property	Equation	Comment	Equation number
Wien's displacement law	$\lambda_{\max}T=\text{constant}$	constant $=hc/5k$	4.1
Planck distribution	$\rho(\lambda,T)=8\pi hc/\{\lambda^5(\mathrm{e}^{hc/\lambda kT}-1)\}$		4.3
Bohr frequency condition	$\Delta E=h\nu$		4.4
Photoelectric effect	$\frac{1}{2}m_\mathrm{e}v^2=h\nu-\Phi$	Φ is the work function	4.5
de Broglie relation	$\lambda=h/p$		4.6

TOPIC 5

The wavefunction

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➤ Why do you need to know this material?

Quantum theory provides the essential foundation for understanding the properties of electrons in atoms and molecules. Consequently, it underlies the explanation of the physical and chemical properties described throughout the text.

➤ What is the key idea?

All the dynamical properties of a system are contained in the wavefunction.

➤ What do you need to know already?

You need to be aware of the shortcomings of classical physics that drove the development of quantum theory (Topic 4).

There are two approaches to the formal introduction of quantum mechanics. One is to see the theory gradually emerging from the work of Planck, Einstein, Heisenberg, Schrödinger, and Dirac, in which experiment and intuition together determined the form of the theory. The other approach is to stand at a point in time at which the theory has already been well-developed and look at its underlying structure. We adopt the latter approach here and see how quantum mechanics can be expressed in terms of and developed from a small set of underlying principles or postulates. It should never be forgotten, however, that these postulates have been developed on the basis of experimental evidence of the type described in Topic 4: they are clever statements that, when unwrapped, account for observations.

In this Topic we establish the postulates that relate to selecting and interpreting the wavefunction; in Topic 6 we describe how to extract the information that it contains.

5.1 Postulate I: the wavefunction

Quantum mechanics acknowledges the wave–particle duality of matter (Topic 4) by supposing that, rather than travelling along a definite path, a particle is distributed through space like a wave. The mathematical representation of this wave is called a **wavefunction**, ψ (psi). A principal tenet of quantum mechanics is that the wavefunction contains information about all the properties of the system that are open to experimental determination.

This discussion is summarized by the first postulate of quantum mechanics.

> **Postulate I.** The state of the system is described as fully as possible by the wavefunction $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, t)$, where $\boldsymbol{r}_1$, $\boldsymbol{r}_2$, … are the locations of the particles and t is the time.

The wavefunction $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, t)$ is called the 'time-dependent wavefunction'; if the wavefunction does not depend on time it is written $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots)$ and called the 'time-independent wavefunction'. In most of these introductory Topics we shall be concerned with systems that consist of a single particle and do not vary with time, so the wavefunction is denoted $\psi(\boldsymbol{r})$, where $\boldsymbol{r}$ is the location of the particle. In the simplest applications, the system is one-dimensional, so the wavefunction is simply a function of x, and we write it $\psi(x)$. For simplicity, we often denote the wavefunction as the plain letter ψ.

Brief illustration 5.1 The wavefunction

The time-independent wavefunction of an electron in a hydrogen atom depends on its position, $\boldsymbol{r}$, relative to the nucleus, and is therefore denoted $\psi(\boldsymbol{r})$. In its lowest energy state, the wavefunction depends only on its distance, r, from the nucleus (not on the orientation of $\boldsymbol{r}$), and is proportional to e^{-r/a_0}, where $a_0 = 53$ pm.

Self-test 5.1 Consider a time-dependent wavefunction describing the state of the electrons in a helium atom. Identify the variables upon which the electronic wavefunction depends.

Answer: t, $\boldsymbol{r}_1$, and $\boldsymbol{r}_2$ (the positions of electrons 1 and 2 relative to nucleus)

Don't be alarmed at the thought of having to manipulate complicated wavefunctions: they can be as simple as sin x or e^{-x}. Wavefunctions might be complex in the technical sense of depending on $i = (-1)^{1/2}$ (see *The chemist's toolkit* 5.1), but even then are often simple in the colloquial sense, as in e^{ikx}.

The chemist's toolkit 5.1 Complex numbers

Complex numbers have the general form $z = x + iy$ where $i = (-1)^{1/2}$. The real numbers x and y are, respectively, the real and imaginary parts of z, denoted Re(z) and Im(z). When $y = 0$, z is the real number x; when $x = 0$, z is the pure imaginary number iy. The **complex conjugate** of z, denoted z^*, is formed by replacing i by –i: $z^* = x - iy$.

The product of z and z^*, denoted $|z|^2$, is called **the square modulus** of z. It is always a real number:

$$|z|^2 = (x+iy)(x-iy) = x^2 - ixy + ixy + y^2 = x^2 + y^2$$

because $i^2 = -1$. The **absolute value** or **modulus** of z is denoted $|z|$ and is given by

$$|z| = (z^* z)^{1/2} = (x^2 + y^2)^{1/2}$$

A useful relation involving complex numbers is **Euler's formula**:

$$e^{ix} = \cos x + i \sin x$$

A more compete discussion of complex numbers is given in *Mathematical background* 3.

5.2 Postulate II: the Born interpretation

The interpretation of the wavefunction is based on a suggestion made by Max Born in 1926. He made use of an analogy with the wave theory of light, in which the square of the amplitude of an electromagnetic wave in a region is interpreted as its intensity and therefore (in quantum terms) as a measure of the probability of finding a photon present in the region.

(a) Probabilities and probability densities

The **Born interpretation** of the wavefunction focuses on the square of the wavefunction if ψ is real or the square modulus, $|\psi|^2 = \psi^*\psi$, if ψ is complex, where ψ^* is the complex conjugate of the wavefunction.

> **Postulate II′** For a system described by the wavefunction $\psi(\boldsymbol{r})$, the probability of finding the particle in the volume element $d\tau$ at $\boldsymbol{r}$ is proportional to $|\psi(\boldsymbol{r})|^2 d\tau$.

Thus, because $|\psi|^2$ must be multiplied by a volume to obtain the probability (just like mass density must be multiplied by the volume of a body to get the body's mass), it is called a **probability density** (Fig. 5.1). In line with this usage, the wavefunction ψ itself is called the **probability amplitude**. The prime on this postulate number will be discarded when it is generalized to more than one particle at the end of this section.

The wavefunction might be negative in some regions or even complex. However, the Born interpretation does away with any worry about the significance of such values because $|\psi|^2$ is real and never negative. There is no *direct* significance in the negative (or complex) value of a wavefunction: only the square modulus, a positive quantity, is directly physically significant, and both negative and positive regions of a wavefunction may correspond to a high probability of finding a particle in a region (Fig. 5.2). However, later we shall see that the presence of positive and negative regions of a wavefunction is of great *indirect* significance, because, like waves in general, it gives rise to the possibility of constructive and destructive interference between different wavefunctions.

When we come to deal with atoms and molecules we need to be aware of the interpretation of the wavefunction for a system

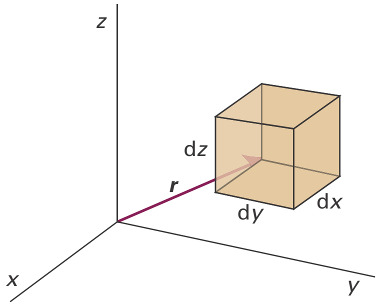

Figure 5.1 The Born interpretation of the wavefunction in three-dimensional space implies that the probability of finding the particle in the volume element $d\tau = dxdydz$ at some location $\boldsymbol{r}$ is proportional to the product of $d\tau$ and the value of $|\psi|^2$ at that location.

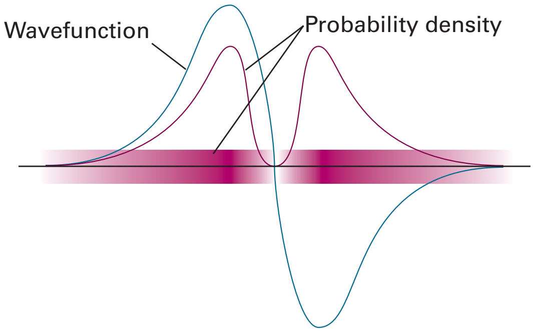

Figure 5.2 The sign of a wavefunction has no direct physical significance: the positive and negative regions of this wavefunction both correspond to the same probability distribution (as given by the square modulus of ψ and depicted by the density of the shading).

with more than one particle, such as the two-electron helium atom and the 16-electron O_2 molecule. In this case, $\psi(r_1, r_2, \ldots)$ is used to calculate the *overall* probability of finding each particle in its own specific volume element. The generalization of Postulate II′ is then:

> **Postulate II.** For a system described by the wavefunction $\psi(r_1, r_2, \ldots)$, the probability of finding particle 1 in the volume element $d\tau_1$ at r_1, particle 2 in the volume element $d\tau_2$ at r_2, etc. is proportional to $|\psi|^2 d\tau_1 d\tau_2 \ldots$.

Example 5.1 Interpreting a wavefunction

The wavefunction of an electron in the lowest energy state of a hydrogen atom is proportional to e^{-r/a_0}, with a_0 a constant and r the distance of the electron from the nucleus. Calculate the relative probabilities of finding the electron inside a region of volume 1.0 pm^3, which is small even on the scale of the atom, located at (a) the nucleus and at (b) a distance a_0 from the nucleus.

Method The region of interest is so small on the scale of the atom that we can ignore the variation of ψ within it and write the probability, P, as proportional to the probability density (ψ^2; note that ψ is real so $|\psi|^2 = \psi^2$) evaluated at the point of interest multiplied by the volume of interest, δV. That is, $P \propto \psi^2 \delta V$, with $\psi^2 \propto e^{-2r/a_0}$.

Answer In each case $\delta V = 1.0\ pm^3$. (a) At the nucleus, $r = 0$, so

$$P \propto e^0 \times (1.0\ pm^3) = (1.0) \times (1.0\ pm^3)$$

(b) At a distance $r = a_0$ in an arbitrary direction,

$$P \propto e^{-2} \times (1.0\ pm^3) = (0.14) \times (1.0\ pm^3)$$

Therefore, the ratio of probabilities is 1.0/0.14 = 7.1. Note that it is more probable (by a factor of about 7) that the electron will be found at the nucleus than in a volume element of the same size located at a distance a_0 from the nucleus. The negatively charged electron is attracted to the positively charged nucleus, and is likely to be found close to it.

Self-test 5.2 The wavefunction for the electron in its lowest energy state in the ion He^+ is proportional to e^{-2r/a_0}. Repeat the calculation for this ion. Any comment?

Answer: 55; more compact wavefunction

(b) Normalization

Postulate II′ refers to a *proportionality* between probability and $|\psi|^2 d\tau$. To determine the actual value of the probability we write $\psi' = N\psi$, where N is a (real) constant selected so that $|\psi'|^2 d\tau$ is *equal* to the probability that the particle is in the volume element $d\tau$. To determine this constant, we note that the total probability of finding the particle anywhere in space must be 1 (it must be somewhere). If the system is one-dimensional, the total probability of finding the particle is the sum (integral) of all the infinitesimal contributions $|\psi'|^2 d\tau$, and we can write

$$\int_{-\infty}^{\infty} (\psi')^* \psi' \, dx = 1 \qquad (5.1)$$

A wavefunction that satisfies condition (5.1) is said to be **normalized** (strictly, normalized to 1). In terms of the original wavefunction this equation becomes

$$N^2 \int_{-\infty}^{\infty} \psi^* \psi \, dx = 1$$

It follows that the **normalization constant** N is given by

$$N = \frac{1}{\left(\int_{-\infty}^{\infty} \psi^* \psi \, dx \right)^{1/2}} \qquad \textit{Definition} \quad \text{Normalization constant} \qquad (5.2)$$

Almost all wavefunctions go to zero at sufficiently great distances so there is rarely any difficulty with the evaluation of the integral in eqn 5.2. Wavefunctions for which the integral exists (in the sense of having a finite value) are said to be 'square-integrable'.

From now on, unless we state otherwise, we always use wavefunctions that have been normalized to 1. That is, from now on we assume that ψ already includes a factor which ensures that (in one dimension)

$$\int_{-\infty}^{\infty} \psi^* \psi \, dx = 1 \qquad \textit{One dimension} \quad \text{Normalization condition} \qquad (5.3a)$$

In three dimensions, the wavefunction is normalized if

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi^* \psi \, dx\,dy\,dz = 1 \qquad \textit{Three dimensions} \quad \text{Normalization condition} \qquad (5.3b)$$

In general, the normalization condition may be written

$$\int \psi^{*}\psi \, \mathrm{d}\tau = 1 \qquad \textit{General case} \qquad \text{Normalization condition} \qquad (5.4)$$

where $\mathrm{d}\tau$ stands for the volume element in the appropriate number of dimensions and the limits of integrations are not written explicitly. In all such integrals, the integration is over all the space accessible to the particle.

Example 5.2 Normalizing a wavefunction

Carbon nanotubes are thin hollow cylinders of carbon atoms that are excellent electrical conductors and can be used as wires in nanodevices (nanowires are discussed in the online *Impact* 2.1). The tubes have diameters between 1 and 2 nm and lengths of several micrometres. A long carbon nanotube can be modelled as a one-dimensional structure. According to a simple model introduced in Topic 9, the lowest-energy electrons of the nanotube are described by the wavefunction $\sin(\pi x/L)$, where L is the length of the nanotube. Find the normalized wavefunction.

Method We need to carry out the integration specified in eqn 5.3a where the limits of integration are 0 and L. The wavefunction is real, so $\psi^{*} = \psi$. Use Integral T.2 listed in the *Resource section*.

Answer We write the wavefunction as $\psi = N\sin(\pi x/L)$, where N is the normalization factor. It follows that

$$\int \psi^{*}\psi \, \mathrm{d}\tau = N^{2}\overbrace{\int_{0}^{L} \sin^{2}\frac{\pi x}{L}\,\mathrm{d}x}^{(L/2)} = \frac{1}{2}N^{2}L = 1$$

and

$$N = \left(\frac{2}{L}\right)^{1/2}$$

The normalized wavefunction is then

$$\psi = \left(\frac{2}{L}\right)^{1/2} \sin\frac{\pi x}{L}$$

Note that because L is a length, the dimensions of ψ are $1/\text{length}^{1/2}$ and therefore those of ψ^{2} are 1/length, as is appropriate for a probability density.

Self-test 5.3 The wavefunction for the next-higher energy level for the electrons in the same tube is $\sin(2\pi x/L)$. Normalize this wavefunction.

Answer: $N = (2/L)^{1/2}$

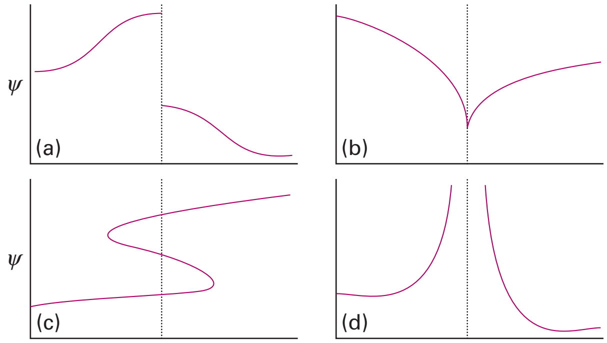

Figure 5.3 The wavefunction must satisfy stringent conditions for it to be acceptable. (a) Unacceptable because it is not continuous; (b) unacceptable because its slope is discontinuous; (c) unacceptable because it is not single-valued; (d) unacceptable because it is infinite over a finite region.

(c) Constraints on the wavefunction

The Born interpretation puts severe restrictions on the acceptability of wavefunctions:

- ψ must not be infinite over a finite region
- ψ must be single-valued
- ψ must be continuous
- The slope of ψ (that is, $\mathrm{d}\psi/\mathrm{d}x$) must be continuous.

These restrictions are summarized in Fig. 5.3. If ψ were infinite over a finite region, it would not be square-integrable and the Born interpretation would fail. Note the emphasis on a finite region: an infinitely sharp spike is acceptable provided it has zero width.

The constraint that the wavefunction must be single-valued (that is, have a single value at each point of space) is also a consequence of the Born interpretation because it would be absurd to have more than one probability that a particle is at the same point.

The remaining two constraints, the continuity of the wavefunction and its first derivative, ensure that it can be calculated from the second-order differential equation, the Schrödinger equation, which we introduce shortly. That equation depends on second derivatives of ψ (that is, $\mathrm{d}^{2}\psi/\mathrm{d}x^{2}$), which exist only if ψ and $\mathrm{d}\psi/\mathrm{d}x$ are continuous.

Once we have obtained the normalized wavefunction, we can then proceed to determine the probability of finding the system in a given *finite* region of space by summing (that is, integrating) the probability density over the region of space of interest. For example, for a one-dimensional real wavefunction, the probability of finding the particle between x_1 and x_2 is given by

$$P = \int_{x_1}^{x_2} \psi(x)^{2}\,\mathrm{d}x \qquad \textit{One-dimensional finite region} \qquad \text{Probability} \qquad (5.5)$$

Brief illustration 5.2 A probability calculation

According to the simple model explored in Example 5.2, the lowest-energy electrons of a carbon nanotube can described by the normalized wavefunction $(2/L)^{1/2}\sin(\pi x/L)$, where L is the length of the nanotube. The probability of finding the electron between $x=L/4$ and $x=L/2$ is given by eqn 5.5:

$$P=\int_{L/4}^{L/2}\left(\frac{2}{L}\right)\sin^2(\pi x/L)\,\mathrm{d}x$$

The integral is evaluated by using Integral T.2 listed in the *Resource section*.

$$P=\left(\frac{2}{L}\right)\left(\frac{x}{2}-\frac{\sin(2\pi x/L)}{4\pi/L}\right)\Bigg|_{L/4}^{L/2}=\left(\frac{2}{L}\right)\left(\frac{L}{4}-\frac{L}{8}-0+\frac{L}{4\pi}\right)=0.409$$

Self-test 5.4 The next-higher energy wavefunction of the electron in the nanotube is described by the normalized wavefunction $(2/L)^{1/2}\sin(2\pi x/L)$. What is the probability of finding the electron between $x=L/4$ and $x=L/2$?

Answer: 0.25

Checklist of concepts

☐ 1. The **wavefunction** contains information about all the properties of the system that are open to experimental determination.

☐ 2. The **Born interpretation** gives the probability of finding the particles in a region of space.

☐ 3. Wavefunctions must be single-valued, continuous, not infinite over a finite region of space, and have continuous slopes.

Checklist of equations

Property	Equation	Comment	Equation number
Normalization constant	$N=1/\left(\int_{-\infty}^{\infty}\psi^*\psi\,\mathrm{d}x\right)^{1/2}$	One dimension	5.2
Normalization condition	$\int\psi^*\psi\,\mathrm{d}\tau=1$	General case	5.4
Probability of being present in a finite region	$P=\int_{x_1}^{x_2}\psi(x)^2\,\mathrm{d}x$	One dimension, real wavefunction	5.5

TOPIC 6

Extracting information from the wavefunction

Contents

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➤ Why do you need to know this material?

The wavefunction is the central feature in quantum mechanics so you need to know how to extract dynamical information from it. The procedures described here allow you to predict the results of measurements of observables.

➤ What is the key idea?

The wavefunction is obtained by solving the Schrödinger equation, and the dynamical information it contains is extracted by determining the eigenvalues of Hermitian operators.

➤ What do you need to know already?

You need to know that the state of a system is fully described by a wavefunction (Topic 5). You need to be familiar with elementary manipulation of complex functions and integration by parts.

Topic 5 introduces the concept of the wavefunction in quantum mechanics and describes how to use the Born interpretation to determine information about the location of particles. In this Topic, we begin to see how to deduce the form of the wavefunction as well as how to extract information from it. In the process, we introduce two more postulates.

6.1 Postulate III: quantum mechanical operators

In 1926, the Austrian physicist Erwin Schrödinger proposed a special second-order differential equation for finding the wavefunction of any system. (For an introduction to differential equations, see *Mathematical background* 2.) The **time-independent Schrödinger equation** for a particle of mass m moving in one dimension with energy E is

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+V\psi=E\psi \qquad (6.1)$$

One dimension, time-independent Schrödinger equation

where V is the potential energy of the particle and $\hbar=h/2\pi$ (which is read h-cross or h-bar) is a convenient modification of Planck's constant. Extensions of the Schrödinger equation to more than one dimension and its time-dependent form are shown in Table 6.1. We could regard eqn 6.1 itself as a postulate, but it turns out to be far more fruitful to interpret it in a special way and to regard it as a consequence of deeper, more general postulates.

Equation 6.1 and its multi-dimensional counterparts in Table 6.1 may all be written in the succinct form

$$\hat{H}\psi=E\psi \qquad (6.2a)$$

Table 6.1 The Schrödinger equation

Expression	Equation	Comment
Time-independent Schrödinger equation	$\hat{H}\psi = E\psi$	General case
	$-\dfrac{\hbar^2}{2m}\dfrac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x)\psi(x) = E\psi(x)$	One dimension
	$-\dfrac{\hbar^2}{2m}\left(\dfrac{\partial^2\psi}{\partial x^2} + \dfrac{\partial^2\psi}{\partial y^2}\right) + V(x,y)\psi(x,y) = E\psi(x,y)$	Two dimensions
	$-\dfrac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$	Three dimensions
Laplacian operator	$\nabla^2 = \dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}$	Cartesian coordinates
	$\nabla^2 = \dfrac{1}{r}\dfrac{\partial^2}{\partial r^2}r + \dfrac{1}{r^2}\Lambda^2$ $= \dfrac{\partial^2}{\partial r^2} + \dfrac{2}{r}\dfrac{\partial}{\partial r} + \dfrac{1}{r^2}\Lambda^2$ $= \dfrac{1}{r^2}\dfrac{\partial}{\partial r}r^2\dfrac{\partial}{\partial r} + \dfrac{1}{r^2}\Lambda^2$	Alternative forms in spherical polar coordinates
Legendrian operator	$\Lambda^2 = \dfrac{1}{\sin^2\theta}\dfrac{\partial^2}{\partial\phi^2} + \dfrac{1}{\sin\theta}\dfrac{\partial}{\partial\theta}\sin\theta\dfrac{\partial}{\partial\theta}$	
Time-dependent Schrödinger equation	$\hat{H}\Psi = i\hbar\dfrac{\partial\Psi}{\partial t}$	

where in one dimension

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)\times \qquad \textit{One dimension} \tag{6.2b}$$

Hamiltonian operator

For reasons that will shortly become clear, we have noted that the potential energy of the particle depends on its position, x, and have included the multiplication sign explicitly. The quantity $\hat{H}$ is an **operator**, something that carries out a mathematical operation on the function ψ. In this case, the operation is to take the second derivative of ψ and (after multiplication by $-\hbar^2/2m$) to add the result to the outcome of multiplying ψ by the value of V at the position x. The operator $\hat{H}$, as well as all other operators encountered in quantum mechanics, is **linear**, in the sense that

- $\hat{H}(\psi_1 + \psi_2) = \hat{H}\psi_1 + \hat{H}\psi_2$
- $\hat{H}c\psi_1 = c\hat{H}\psi_1$

for any functions ψ_1 and ψ_2 and any constant c.

The operator $\hat{H}$ plays a special role in quantum mechanics, and is called the **hamiltonian operator** after the nineteenth century mathematician William Hamilton, who developed a form of classical mechanics that, it subsequently turned out, is well suited to the formulation of quantum mechanics. We can infer from the form of eqn 6.2a that the hamiltonian operator is the operator corresponding to the total energy of the system, the sum of the kinetic and potential energies. It then follows that the first term in eqn 6.2b (the term proportional to the second derivative) must be the operator for the kinetic energy.

Equation 6.2a is highly suggestive of a more general formulation. First, it suggests that there might be other **observables,** or measurable properties, of a system that can be represented by other operators, and that the structure

$$[\text{energy operator (hamiltonian)}]\psi = [\text{value of energy}]\times\psi$$

is a special case of the more general form

$$[\text{operator for the observable } \Omega]\psi = [\text{value of the observable } \Omega] \times \psi$$

From now on, we represent the operator corresponding to the observable Ω (uppercase omega) by $\hat{\Omega}$ and the value of the observable Ω by ω (lowercase omega), and write the last equation as

$$\hat{\Omega}\psi = \omega\psi \tag{6.3}$$

Our immediate problem is to discover how to formulate the operator corresponding to an observable. Once again, eqn 6.2 gives us a clue. In classical mechanics, the total energy of a particle in one dimension can be expressed in terms of the linear momentum p as

$$E = \frac{p^2}{2m} + V(x)$$

Comparison of this expression with eqn 6.2b strongly suggests that the operator for position, x, is just multiplication by position ($x\times$), because then the potential energy $V(x)$ is represented by the multiplicative operation $V(x)\times$. Further comparison with eqn 6.2b suggests that the operator for kinetic energy, $p^2/2m$, can be identified with $-(\hbar^2/2m)\mathrm{d}^2/\mathrm{d}x^2$.

Now we bring these points together by formulating a postulate that summarizes them:

> **Postulate III.** For each observable property Ω of a system there is a corresponding operator $\hat{\Omega}$ built from the following position and linear momentum operators:
>
> $$\hat{x} = x\times \tag{6.4a}$$
>
> *Definition* Position operator
>
> $$\hat{p}_x = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x} \tag{6.4b}$$
>
> *Definition* Linear momentum operator

The multiplication sign for multiplicative operators is not normally written, and from now on we shall omit it. However, it must always be remembered that x is the operation that multiplies any function on its right. When we are discussing one-dimensional systems, we discard the index x on p; for three-dimensional systems, we use subscripts x, y, and z to denote the components of the vector $\boldsymbol{p}$ along each direction, with the corresponding operators defined analogously.

With Postulate III established, we can immediately write down the operator for the kinetic energy, E_k, of a particle in one dimension. Because

$$E_\mathrm{k} = \frac{p^2}{2m}$$

it follows that the kinetic energy operator is

$$\hat{E}_\mathrm{k} = \frac{\hat{p}^2}{2m}$$

and therefore because

$$\frac{\hat{p}^2}{2m} = \frac{1}{2m}\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right)\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right) = \frac{1}{2m}\left(\frac{\hbar}{\mathrm{i}}\right)^2\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)\left(\frac{\mathrm{d}}{\mathrm{d}x}\right) = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$$

we can conclude that

$$\hat{E}_\mathrm{k} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} \tag{6.5}$$

Kinetic energy operator

Brief illustration 6.1 The kinetic energy operator in two dimensions

The kinetic energy of a particle moving in two dimensions, such as a particle moving on a plane, is $E_\mathrm{k} = p_x^2/2m + p_y^2/2m$. Therefore the kinetic energy operator is $\hat{E}_\mathrm{k} = \hat{p}_x^2/2m + \hat{p}_y^2/2m$ or

$$\hat{E}_\mathrm{k} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$$

Self-test 6.1 Construct (a) the operator for kinetic energy of a particle moving in three dimensions (such as an electron in an atom) and (b) the operator for the potential energy for a harmonic oscillator, $V = \frac{1}{2}k_\mathrm{f}x^2$.

Answer: (a) $\hat{E}_\mathrm{k} = -(\hbar^2/2m)(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2)$, (b) $\frac{1}{2}k_\mathrm{f}x^2\times$

In mathematics, the second derivative of a function is a measure of its curvature (*Mathematical background* 1). A large second derivative indicates a sharply curved function (Fig. 6.1). It follows that a sharply curved wavefunction is associated with a high kinetic energy, and one with a low curvature is associated with a low kinetic energy. This interpretation is consistent with the de Broglie relation (eqn 4.6, $\lambda = h/p$), which predicts a short wavelength (a sharply curved wavefunction) when

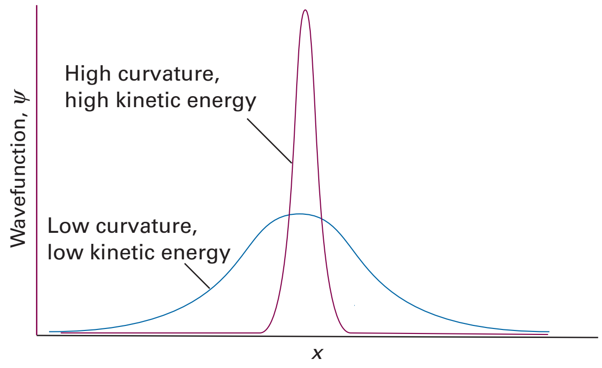

Figure 6.1 Even if the wavefunction does not have the form of a periodic wave, it is still possible to infer from it the average kinetic energy of a particle by noting its average curvature. This figure shows two wavefunctions: the sharply curved function corresponds to a higher kinetic energy than the less sharply curved function.

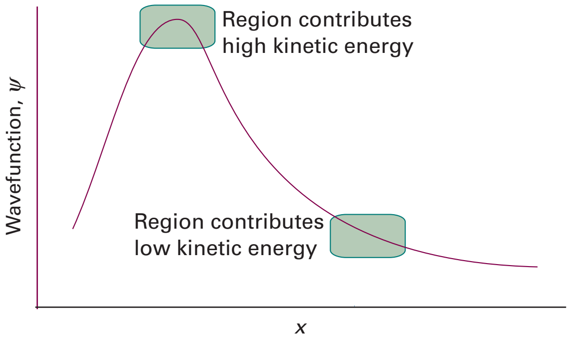

Figure 6.2 The observed kinetic energy of a particle is an average of contributions from the entire space covered by the wavefunction. Sharply curved regions contribute a high kinetic energy to the average; slightly curved regions contribute only a small kinetic energy.

the linear momentum (and hence the kinetic energy) is high. However, it extends the interpretation to wavefunctions that do not spread through space and resemble those shown in Fig. 6.1. The curvature of a wavefunction in general varies from place to place. Wherever a wavefunction is sharply curved, its contribution to the total kinetic energy is large (Fig. 6.2). Wherever the wavefunction is not sharply curved, its contribution to the overall kinetic energy is low.

A list of the operators more commonly encountered in quantum mechanics is collected in the *Resource section* at the end of the text.

6.2 Postulate IV: eigenvalues and eigenfunctions

At this point in the presentation of the postulates of quantum mechanics, we know

- how to construct operators for observables,
- that wavefunctions are solutions of the Schrödinger equation,
- that the observable Ω of interest has the value ω in the expression $\hat{\Omega}\psi=\omega\psi$, where $\hat{\Omega}$ is the corresponding operator.

We need to develop this last point.

First, we note that eqn 6.3, $\hat{\Omega}\psi=\omega\psi$, has the form

$$(\text{Operator})\underbrace{(\text{function})}_{\text{eigenfunction}}=\underbrace{(\text{numerical factor})}_{\text{eigenvalue}}\times\underbrace{(\text{same function})}_{\text{eigenfunction}}$$

Definition Eigenvalue equation (6.6)

An equation of this form is called an **eigenvalue equation;** the numerical factor is called the **eigenvalue** of the operator and the function that occurs on both sides of the equation is called the **eigenfunction** of the operator. Each eigenfunction corresponds to a specific eigenvalue. In terms of this new language, by referring to eqn 6.2a ($\hat{H}\psi=E\psi$) it follows that another way of saying 'solve the Schrödinger equation' is to say 'find the eigenvalues and the corresponding eigenfunctions of the hamiltonian operator for the system'. The wavefunctions are the eigenfunctions of the hamiltonian operator, and the corresponding eigenvalues are the allowed energies. Eigenfunctions and eigenvalues of operators play a crucial role in quantum mechanics and we encounter them throughout the text.

Example 6.1 Identifying an eigenfunction

Show that $\mathrm{e}^{\mathrm{i}kx}$ is an eigenfunction of the linear momentum operator, and find the corresponding eigenvalue. Then show that the bell-shaped 'Gaussian function' e^{-ax^2} is not an eigenfunction of this operator.

Method We need to operate on the function with the operator and check whether the result is a constant factor times the original function. In each case we identify the operator with the linear momentum operator $\hat{p}=(\hbar/\mathrm{i})\mathrm{d}/\mathrm{d}x$.

Answer For $\psi=\mathrm{e}^{\mathrm{i}kx}$,

$$\hat{p}\psi=\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\mathrm{e}^{\mathrm{i}kx}=\frac{\hbar}{\mathrm{i}}\mathrm{i}k\mathrm{e}^{\mathrm{i}kx}=k\hbar\psi$$

Therefore $\mathrm{e}^{\mathrm{i}kx}$ is indeed an eigenfunction of $\hat{p}$, and its eigenvalue is $k\hbar$. For $\psi=\mathrm{e}^{-ax^2}$,

$$\hat{p}\psi=\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\mathrm{e}^{-ax^2}=\frac{\hbar}{\mathrm{i}}(-2ax)\mathrm{e}^{-ax^2}=2\mathrm{i}a\hbar x\times\psi$$

We have used $-2/\mathrm{i}=2\mathrm{i}$. This is not an eigenvalue equation even though the same function ψ occurs on the right, because ψ is now multiplied by a function of x ($2\mathrm{i}a\hbar x$), not a numerical factor. Alternatively, if the right-hand side is written $2\mathrm{i}a\hbar\,(x\mathrm{e}^{-ax^2})$, we see that it is a constant ($2\mathrm{i}a\hbar$) times a *different* function.

Self-test 6.2 Is the function cos ax an eigenfunction of (a) the linear momentum operator, (b) the kinetic energy operator? If yes, identify the eigenvalue.

Answer: (a) No, (b) yes; ($\hbar^2a^2/2m$)

There are far-reaching consequences that result from the interpretation of eqn 6.3 (and the Schrödinger equation, eqn 6.2) as an eigenvalue equation. First, we need to note that the allowed value of an observable Ω (such as the energy E) is the eigenvalue in an eigenvalue equation. Therefore, once we have found all the permitted eigenvalues of an operator, we shall know the permitted values of that observable. Each eigenfunction corresponds to a particular eigenvalue (specifically, each wavefunction corresponds to a particular energy), and we have already seen that there are severe restrictions on the acceptability of wavefunctions. We can anticipate, therefore, that because only certain wavefunctions are acceptable, only certain eigenvalues are allowed. In other words, in general, *an observable is quantized*. We summarize the discussion so far in the language introduced in this section with the following postulate:

> **Postulate IV.** If the system is described by a wavefunction ψ that is an eigenfunction of $\hat{\Omega}$ such that $\hat{\Omega}\psi = \omega\psi$, then the outcome of a measurement of Ω will be the eigenvalue ω.

Brief illustration 6.2 The wavefunction as an eigenfunction

We saw in Example 6.1 that e^{ikx} is an eigenfunction of the linear momentum operator with eigenvalue $+k\hbar$. Therefore,

(a) if the wavefunction of an electron accelerated in a linear accelerator to a certain energy is e^{ikx}, then we know from Postulate IV that if we were to measure its linear momentum, we would find the value $p = +k\hbar$;

(b) if the wavefunction is e^{-ikx}, then, because the eigenvalue is now $-k\hbar$ (note the change in sign), a measurement of the linear momentum would give the value $p = -k\hbar$.

The magnitude of the linear momentum of the electron is the same in each case ($k\hbar$), but the signs are different: in (a) the electron is travelling to the right (positive x) but in (b) the linear accelerator is pointed in the opposite direction and the electron is travelling to the left (negative x).

Self-test 6.3 As a result of its acceleration in a linear accelerator, the wavefunction of a proton became cos kx. What is the kinetic energy of the proton?

Answer: $E_k = k^2\hbar^2/2m_p$

Because the value of an observable is a real quantity (real, that is, in the mathematical sense of not involving the imaginary number i), Postulate IV implies that the eigenvalues of any operator that corresponds to an observable must themselves be real. The reality of eigenvalues is guaranteed if the operator has the special property of 'hermiticity' (named for the nineteenth century French mathematician Charles Hermite). A **Hermitian operator** is one for which the following equality is true:

$$\int f^* \hat{\Omega} g\,\mathrm{d}x = \left\{ \int g^* \hat{\Omega} f\,\mathrm{d}x \right\}^* \qquad \textit{Definition} \quad \text{Hermiticity} \qquad (6.7)$$

where f and g are any two wavefunctions. It is easy to confirm that the position operator ($x\times$) is Hermitian because we are free to change the order of the factors in the integrand:

$$\int_{-\infty}^{\infty} f^* xg\,\mathrm{d}x \overset{\text{change order}}{\overset{\frown}{=}} \int_{-\infty}^{\infty} gxf^*\,\mathrm{d}x$$

$$\overset{\text{use } g^{**}=g \text{ and } x^*=x}{\overset{\frown}{=}} \int_{-\infty}^{\infty} g^{**}x^*f^*\,\mathrm{d}x = \left\{ \int_{-\infty}^{\infty} g^* xf\,\mathrm{d}x \right\}^*$$

The demonstration that the linear momentum operator is Hermitian is more involved because we cannot just alter the order of functions we differentiate; but it is Hermitian, as we show in the following *Justification*.

Justification 6.1 The hermiticity of the linear momentum operator

Our task is to show that

$$\int_{-\infty}^{\infty} f^* \hat{p} g\,\mathrm{d}x = \left\{ \int_{-\infty}^{\infty} g^* \hat{p} f\,\mathrm{d}x \right\}^*$$

with $\hat{p}$ given in eqn 6.4b. To do so, we use 'integration by parts', the relation

$$\int u \frac{\mathrm{d}v}{\mathrm{d}x}\mathrm{d}x = uv - \int v \frac{\mathrm{d}u}{\mathrm{d}x}\mathrm{d}x$$

with $u = f^*$ and $v = g$. In the present case we write

$$\int_{-\infty}^{\infty} f^* \hat{p} g\,\mathrm{d}x = \frac{\hbar}{\mathrm{i}} \int_{-\infty}^{\infty} f^* \frac{\mathrm{d}g}{\mathrm{d}x}\mathrm{d}x = \frac{\hbar}{\mathrm{i}} f^* g \Big|_{-\infty}^{\infty} - \frac{\hbar}{\mathrm{i}} \int_{-\infty}^{\infty} g \frac{\mathrm{d}f^*}{\mathrm{d}x}\mathrm{d}x$$

The first term on the right is zero, because all wavefunctions are zero at infinity in either direction (or, in special cases, the function f (and g) is not zero but is equal at $+\infty$ and $-\infty$), so we are left with

$$\int_{-\infty}^{\infty} f^* \hat{p} g\,\mathrm{d}x = -\frac{\hbar}{\mathrm{i}} \int_{-\infty}^{\infty} g \frac{\mathrm{d}f^*}{\mathrm{d}x}\mathrm{d}x \overset{\text{use } \mathrm{i}^* = -\mathrm{i}}{\overset{\frown}{=}} \left\{ \frac{\hbar}{\mathrm{i}} \int_{-\infty}^{\infty} g^* \frac{\mathrm{d}f}{\mathrm{d}x}\mathrm{d}x \right\}^*$$

$$= \left\{ \int_{-\infty}^{\infty} g^* \hat{p} f\,\mathrm{d}x \right\}^*$$

as we set out to prove.

A general property of operators is that the product of a Hermitian operator with itself is also a Hermitian operator (see Problem 6.4). Therefore, $\hat{p}^2 = \hat{p} \times \hat{p}$ is a Hermitian operator and it follows that the kinetic energy operator ($\hat{E}_k = \hat{p}^2/2m$) is too.

Equation 6.7 might seem to be far removed from being equivalent to the statement that the eigenvalues of Hermitian operators are real, but in fact the proof is quite straightforward, as the following *Justification* shows.

Justification 6.2 The reality of eigenvalues of Hermitian operators

For a wavefunction ψ that is normalized to 1 and is an eigenfunction of a Hermitian operator with eigenvalue ω, we can write

$$\int \psi^{*}\hat{\Omega}\psi\,\mathrm{d}\tau \overset{\hat{\Omega}\psi=\omega\psi}{=} \int \psi^{*}\omega\psi\,\mathrm{d}\tau = \omega \overbrace{\int \psi^{*}\psi\,\mathrm{d}\tau}^{1} = \omega$$

However, by taking the complex conjugate we can write

$$\omega^{*} = \left\{\int \psi^{*}\hat{\Omega}\,\psi\,\mathrm{d}\tau\right\}^{*} \overset{\text{eqn 6.7 with } f=g=\psi}{=} \int \psi^{*}\hat{\Omega}\psi\,\mathrm{d}\tau =$$

The conclusion that $\omega^{*}=\omega$ confirms that ω is real.

If the wavefunction is an eigenfunction of the operator corresponding to the observable of interest, then Postulate IV tells us that the result of a measurement is simply that eigenvalue. But suppose the wavefunction is not an eigenfunction of the operator: how do we proceed? One further postulate, which is presented Topic 7, provides the answer.

Checklist of concepts

☐ **1.** The wavefunction is a solution of the Schrödinger equation.

☐ **2.** For each observable property Ω of a system there is a corresponding operator $\hat{\Omega}$ built from the position and linear momentum operators.

☐ **3.** If the system is described by a wavefunction ψ that is an **eigenfunction** of $\hat{\Omega}$ such that $\hat{\Omega}\psi=\omega\psi$, then the outcome of a measurement of Ω will be the **eigenvalue** ω.

☐ **4.** The eigenvalues of **Hermitian operators** are real.

Checklist of equations

Property	Equation	Comment	Equation number
Schrödinger equation	$-\dfrac{\hbar^2}{2m}\dfrac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+V\psi=E\psi$	One dimension, time-independent	6.1
Hamiltonian operator	$\hat{H}=-\dfrac{\hbar^2}{2m}\dfrac{\mathrm{d}^2}{\mathrm{d}x^2}+V(x)\times$	One dimension	6.2b
Position operator	$\hat{x}=x\times$	One dimension	6.4a
Linear momentum operator	$\hat{p}_x=\dfrac{\hbar}{\mathrm{i}}\dfrac{\mathrm{d}}{\mathrm{d}x}$	One dimension	6.4b
Eigenvalue equation	$\hat{\Omega}\psi=\omega\psi$		6.6
Hermiticity	$\int f^{*}\hat{\Omega}g\,\mathrm{d}x=\left\{\int g^{*}\hat{\Omega}f\,\mathrm{d}x\right\}^{*}$		6.7

TOPIC 7

Predicting the outcome of experiments

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➤ Why do you need to know this material?

You need to know how to extract dynamical information from the wavefunction, even when the wavefunction describing the system is not an eigenfunction of the operator corresponding to the observable.

➤ What is the key idea?

The procedures described here allow you to predict an average result from measurements, provided that you are given the operator corresponding to the observable and the wavefunction describing the state of the system.

➤ What do you need to know already?

You need to know how to form operators corresponding to observables (Topic 6) and be able to recognize if a wavefunction is an eigenfunction of an operator.

Topic 6 (Postulate IV) tells us that if the wavefunction is an eigenfunction of the operator corresponding to an observable, then it is easy to identify the value of that observable: we just pick out the corresponding eigenvalue. Suppose, though, that the wavefunction is not an eigenfunction of the operator corresponding to the property of interest: what can we then say? For instance, suppose the wavefunction is $\cos kx$. This wavefunction is an eigenfunction of the kinetic energy operator (with eigenvalue $k^2\hbar^2/2m$) so we know that a measurement of the kinetic energy will certainly give that value. However, $\cos kx$ is not an eigenfunction of the linear momentum operator (because $\mathrm{d}\cos kx/\mathrm{d}x = -k\sin kx$), and so in this case we cannot use Postulate IV to predict the outcome of a measurement of the linear momentum. In this Topic we develop techniques for using quantum theory to predict the outcome of observations—even when the wavefunction of a particle is not an eigenfunction of the operator associated with the observable.

7.1 Wavefunctions as linear combinations

The clue we need in order to make progress in the case of the wavefunction $\cos kx$ is to note that we can use Euler's formula (see *The chemist's toolkit* 5.1) to write

$$\cos kx = \frac{1}{2}\mathrm{e}^{\mathrm{i}kx} + \frac{1}{2}\mathrm{e}^{-\mathrm{i}kx}$$

Each exponential function is an eigenfunction of the linear momentum operator (see *Brief illustration* 6.2) with eigenvalues $+k\hbar$ and $-k\hbar$, respectively. We say that the actual wavefunction is a **linear combination** of two contributing wavefunctions, namely $\mathrm{e}^{\mathrm{i}kx}$ and $\mathrm{e}^{-\mathrm{i}kx}$. In general, a linear combination of two functions f and g is $c_1 f + c_2 g$, where c_1 and c_2 are numerical coefficients, so a linear combination is a more general term than 'sum', for which $c_1=c_2=1$. Another way to express the fact that the wavefunction is a linear combination of individual wavefunctions is to say that the state is a **superposition** of individual states.

At this point we recognize that the wavefunction cos kx can be written symbolically as

$$\psi = \underset{\text{Particle with linear momentum }+k\hbar}{\psi_{\rightarrow}} + \underset{\text{Particle with linear momentum }-k\hbar}{\psi_{\leftarrow}}$$

The interpretation of this composite wavefunction is that if the momentum of the particle is repeatedly measured in a long series of observations, then its *magnitude* will found to be $k\hbar$ in all the measurements (because that is the value for each of the eigenfunctions). However, because the two eigenfunctions occur equally in the wavefunction (the same numerical coefficient occurs in the linear combination), half the measurements will show that the particle is moving to the right ($p=+k\hbar$) and half the measurements will show that it is moving to the left ($p=-k\hbar$). According to quantum mechanics, we cannot predict in which direction the particle will in fact be found to be travelling; all we can say is that, in a long series of observations, if the particle is described by this wavefunction, then there are equal probabilities of finding the particle travelling to the right and to the left. Furthermore, since half the measurements yield $p=+k\hbar$ and half yield $p=-k\hbar$, we expect the average value of a large number of measurements to be zero.

This discussion motivates the following generalization to the case when the system is known to be a linear combination of many different eigenfunctions of the operator corresponding to the observable of interest and is written as

$$\psi = c_1\psi_1 + c_2\psi_2 + \cdots = \sum_k c_k\psi_k \tag{7.1}$$

where the c_k are numerical (and possibly complex) coefficients and the ψ_k correspond to different eigenfunctions of the operator, with $\hat{\Omega}\,\psi_k=\omega_k\psi_k$. Then:

> **Postulate V.** When the value of an observable Ω is measured for a system that is described by a linear combination of eigenfunctions of $\hat{\Omega}$, with coefficients c_k, each measurement gives one of the eigenvalues ω_k of $\hat{\Omega}$ with a probability proportional to $|c_k|^2$.

If the system is described by a wavefunction that is normalized, then the probability of obtaining the eigenvalue ω_k is equal to $|c_k|^2$.

Brief illustration 7.1 The measurement of an observable

A linear accelerator does not accelerate particles to a precisely defined linear momentum, so the wavefunction of the particles is a linear combination of functions corresponding to the range of momenta present in the beam. Suppose that three momenta (three values of k) are present in a beam of electrons, centred at k_1, and that the normalized wavefunction is given by

$$\psi=(1/20)^{1/2}\,\mathrm{e}^{\mathrm{i}(k_1-\Delta k)x}+(9/10)^{1/2}\,\mathrm{e}^{\mathrm{i}k_1x}+(1/20)^{1/2}\,\mathrm{e}^{\mathrm{i}(k_1+\Delta k)x}$$

where Δk is small. Because $\mathrm{e}^{\mathrm{i}kx}$ is an eigenfunction of the linear momentum operator with an eigenvalue $+k\hbar$, the wavefunction of the 'blurred' electron beam is a linear combination of three eigenfunctions. According to Postulate V, a single measurement of the linear momentum will yield one of three results $+(k_1-\Delta k)\hbar$, $+k_1\hbar$, or $+(k_1+\Delta k)\hbar$ with probabilities 1/20, 9/10, and 1/20, respectively.

Self-test 7.1 What would be the result of measuring the kinetic energy of the electrons of this *Brief illustration*?

Answer: individual measurements: $(k_1-\Delta k)^2\hbar^2/2m_\mathrm{e}$, $k_1^2\hbar^2/2m_\mathrm{e}$, and $(k_1+\Delta k)^2\hbar^2/2m_\mathrm{e}$; probabilities 1/20, 9/10, and 1/20, respectively

7.2 Mean values as expectation values

Because in general a series of measurements of a property gives a number of different outcomes, it is often important to know the average value of these outcomes. The mean (that is, average) value from measurement of the observable Ω is equal to the **expectation value** of the operator $\hat{\Omega}$, denoted $\langle\Omega\rangle$ and defined as

$$\langle\Omega\rangle=\frac{\int\psi^*\hat{\Omega}\psi\,\mathrm{d}\tau}{\int\psi^*\psi\,\mathrm{d}\tau} \qquad \textit{Definition} \quad \text{Expectation value} \tag{7.2a}$$

This definition applies whether or not ψ is written as a linear combination of eigenfunctions. For a normalized wavefunction, the denominator in eqn 7.2a is 1 and this expression simplifies to

$$\langle\Omega\rangle=\int\psi^*\hat{\Omega}\psi\,\mathrm{d}\tau \tag{7.2b}$$

If ψ happens to be an eigenfunction of $\hat{\Omega}$, then by Postulate IV, every measurement of the observable will yield a single eigenvalue, ω, and therefore the average value is also ω. In this case, the expectation value of $\hat{\Omega}$ is simply

$$\langle\Omega\rangle=\int\psi^*\hat{\Omega}\psi\,\mathrm{d}\tau\overset{\hat{\Omega}\psi=\omega\psi}{=}\int\psi^*\omega\psi\,\mathrm{d}\tau=\omega\overbrace{\int\psi^*\psi\,\mathrm{d}\tau}^{1}=\omega$$

If ψ is not an eigenfunction of the observable of interest, each measurement of the property gives a different outcome. To investigate the relationship between the outcome of a measurement and the expectation value, we need to develop another feature of eigenfunctions.

Example 7.1 Calculating an expectation value

Calculate the average value of the position of an electron in the carbon nanotube described in Example 5.2.

Method The average value of the position is the expectation value of the operator corresponding to position, which is multiplication by x. To evaluate $\langle x\rangle$, we need to know the normalized wavefunction (from Example 5.2) and then evaluate the integral in eqn 7.2b. Use Integral T.11 listed in the *Resource section*.

Answer The average value is given by the expectation value

$$\langle x\rangle=\int\psi^*\hat{x}\psi\,\mathrm{d}x \quad \text{with } \psi=\left(\frac{2}{L}\right)^{1/2}\sin\frac{\pi x}{L} \quad \text{and } \hat{x}=x\times$$

which evaluates to

$$x=\frac{2}{L}\overbrace{\int_0^L x\sin^2\frac{\pi x}{L}\,\mathrm{d}x}^{L^2/4}=\frac{1}{2}L$$

This result means that if a very large number of measurements of the position of the electron are made, then their mean value will be exactly one-half the length of the nanotube. However, each different observation will give a different and unpredictable individual result because the wavefunction is not an eigenfunction of the operator corresponding to x.

Self-test 7.2 Evaluate the root mean square position, $\langle x^2\rangle^{1/2}$, of the electron using the Integral T.12 listed in the *Resource section*.

Answer: $L\{1/3-1/(2\pi^2)\}^{1/2}$

7.3 The orthogonality of eigenfunctions

A very special feature of Hermitian operators is, as we show in the *Justification* below, that *eigenfunctions corresponding to different eigenvalues of the same Hermitian operator are orthogonal.* To say that two different functions ψ_i and ψ_j are **orthogonal** means that the integral (over all space) of their product is zero:

$$\int\psi_i^*\psi_j\,\mathrm{d}\tau=0 \qquad \textit{Definition} \quad \text{Orthogonality} \tag{7.3a}$$

For example, the hamiltonian operator is Hermitian (it corresponds to an observable, the energy). Therefore, if ψ_i corresponds to one energy and ψ_j corresponds to a different energy, then we know at once that the two functions are orthogonal and that the integral of their product is zero. Being able to set integrals to zero in this way greatly simplifies the calculations that we shall do in the following Topics and also provides a foundation for the justification of Postulate V, as we shall see.

Functions that are both orthogonal and normalized are said to be **othornormal:**

$$\int\psi_i^*\psi_j\,\mathrm{d}\tau=\delta_{ij} \qquad \textit{Definition} \quad \text{Orthonormality} \tag{7.3b}$$

where δ_{ij}, which is called the **Kronecker delta**, is 1 when $i=j$ and 0 when $i\neq j$.

Justification 7.1 The orthogonality of eigenfunctions

Suppose we have two eigenfunctions of $\hat{\Omega}$, with unequal eigenvalues:

$$\hat{\Omega}\psi_i=\omega_i\psi_i \quad \text{and} \quad \hat{\Omega}\psi_j=\omega_j\psi_j$$

with ω_i not equal to ω_j. Multiply the first of these eigenvalue equations on both sides by ψ_j^* and the second by ψ_i^* and integrate over all space:

$$\int\psi_j^*\hat{\Omega}\psi_i\,\mathrm{d}\tau=\omega_i\int\psi_j^*\psi_i\,\mathrm{d}\tau$$
$$\int\psi_i^*\hat{\Omega}\psi_j\,\mathrm{d}\tau=\omega_j\int\psi_i^*\psi_j\,\mathrm{d}\tau$$

Now take the complex conjugate of the first of these two expressions (noting that, by the hermiticity of $\hat{\Omega}$, the eigenvalues are real):

$$\left\{\int\psi_j^*\hat{\Omega}\psi_i\,\mathrm{d}\tau\right\}^*=\omega_i\int\psi_j\psi_i^*\,\mathrm{d}\tau=\omega_i\int\psi_i^*\psi_j\,\mathrm{d}\tau$$

However, by hermiticity, the first term on the left is

$$\left\{\int\psi_j^*\hat{\Omega}\psi_i\,\mathrm{d}\tau\right\}^*=\int\psi_i^*\hat{\Omega}\psi_j\,\mathrm{d}\tau=\omega_j\int\psi_i^*\psi_j\,\mathrm{d}\tau$$

Subtraction of this line from the preceding line then gives

$$0=(\omega_i-\omega_j)\int\psi_i^*\psi_j\,\mathrm{d}\tau$$

But we know that the two eigenvalues are not equal, so the integral must be zero, as we set out to prove.

Example 7.2 Verifying orthogonality

Two possible wavefunctions for an electron confined to a one-dimensional quantum dot (a collection of atoms with dimensions in the range of nanometres and of great interest in nanotechnology) are of the form sin x and sin $2x$. These two wavefunctions are eigenfunctions of the kinetic energy operator, which is Hermitian, and correspond to the eigenvalues $\hbar^2/2m_e$ and $2\hbar^2/m_e$, respectively. Verify that the two wavefunctions are mutually orthogonal.

Method To verify the orthogonality of two functions, we integrate their product, $\sin 2x \sin x$, over all space, which we may take to span from $x=0$ to $x=2\pi$, because both functions repeat themselves outside that range. Hence proving that the integral of their product is zero within that range implies that the integral over the whole of space is also zero (Fig. 7.1). Use Integral T.5 listed in the *Resource section*.

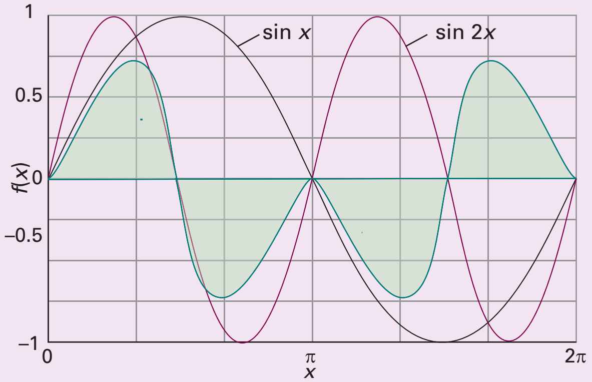

Figure 7.1 The integral of the function $f(x)=\sin 2x \sin x$ is equal to the area (tinted) below the blue curve, and is zero, as can be inferred by symmetry. The function, and the value of the integral, repeats itself for all replications of the section between 0 and 2π, so the integral from −∞ to +∞ is zero.

Answer It follows that, for $a=2$ and $b=1$, and given the fact that $\sin 0=0$, $\sin 2\pi=0$, and $\sin 6\pi=0$,

$$\int_0^{2\pi} \sin 2x \sin x \, dx = \overbrace{\left.\frac{\sin x}{2}\right|_0^{2\pi}}^{0} - \overbrace{\left.\frac{\sin 3x}{6}\right|_0^{2\pi}}^{0} = 0$$

and the two functions are mutually orthogonal.

Self-test 7.3 When the electron is excited to higher energies, its wavefunction may become $\sin 3x$. Confirm that the functions $\sin x$ and $\sin 3x$ are mutually orthogonal.

Answer: $\int_0^{2\pi} \sin 3x \sin x \, dx = 0$

7.4 The expectation value of a linear combination of eigenfunctions

Now consider the case that the wavefunction is a linear combination of eigenfunctions. For simplicity, we suppose the (normalized) wavefunction is the sum of two eigenfunctions (the general case can easily be developed). Then, from eqn 7.2b,

$$\begin{aligned}\langle \Omega \rangle &= \int (c_1\psi_1 + c_2\psi_2)^* \hat{\Omega}(c_1\psi_1 + c_2\psi_2)\,d\tau \\ &= \int (c_1\psi_1 + c_2\psi_2)^* (c_1\hat{\Omega}\psi_1 + c_2\hat{\Omega}\psi_2)\,d\tau \\ &= \int (c_1\psi_1 + c_2\psi_2)^* (c_1\omega_1\psi_1 + c_2\omega_2\psi_2)\,d\tau \\ &= c_1^*c_1\omega_1 \overbrace{\int \psi_1^*\psi_1\,d\tau}^{1} + c_2^*c_2\omega_2 \overbrace{\int \psi_2^*\psi_2\,d\tau}^{1} \\ &\quad + c_1^*c_2\omega_2 \overbrace{\int \psi_1^*\psi_2\,d\tau}^{0} + c_2^*c_1\omega_1 \overbrace{\int \psi_2^*\psi_1\,d\tau}^{0}\end{aligned}$$

The first two integrals on the right are both equal to 1 because the eigenfunctions are individually normalized. Because ψ_1 and ψ_2 correspond to different eigenvalues of a Hermitian operator, they are orthogonal, so the third and fourth integrals on the right are zero. We can conclude that

$$\langle \Omega \rangle = |c_1|^2\omega_1 + |c_2|^2\omega_2$$

In the general case

$$\psi = \sum_k c_k\psi_k$$

where ψ_k is an eigenfunction of $\hat{\Omega}$ with eigenvalue ω_k, the expectation value is given by

$$\langle \Omega \rangle = \sum_k |c_k|^2\omega_k \qquad \textit{Linear combination} \quad \text{Expectation value} \qquad (7.4)$$

Equation 7.4 shows that the expectation value is a weighted average of the eigenvalues of $\hat{\Omega}$, with the weighting equal to the square modulus of the expansion coefficients c_k. This is the basis of Postulate V, for it strongly suggests that the measurement of the property Ω gives a series of values ω_k, with occurrences that are determined by the values of $|c_k|^2$.

Brief illustration 7.2 The expectation value for a superposition of states

For the system described in *Brief illustration* 7.1, the mean value of the linear momentum, from eqn 7.4, is

$$\langle p \rangle = \frac{1}{20}(k_1 - \Delta k)\hbar + \frac{9}{10}k_1\hbar + \frac{1}{20}(k_1 + \Delta k)\hbar = k_1\hbar$$

Self-test 7.4 What is the mean value of the kinetic energy of the system of this *Brief illustration*?

Answer: $\langle E_k \rangle = (\hbar^2/2m_e)\{k_1^2 + (\Delta k)^2/10\}$

Checklist of concepts

- ☐ 1. A state that is a **superposition** of individual states is described by a wavefunction that is a linear combination of the corresponding individual wavefunctions.
- ☐ 2. When the value of an observable Ω is measured for a system that is described by a (normalized) linear combination of eigenfunctions of $\hat{\Omega}$, with coefficients c_k, each measurement gives one of the eigenvalues ω_k of $\hat{\Omega}$ with a probability equal to $|c_k|^2$.
- ☐ 3. The **expectation value** of the operator $\hat{\Omega}$, denoted $\langle\Omega\rangle$, is equal to the mean value of a series of measurements.
- ☐ 4. Eigenfunctions corresponding to different eigenvalues of the same Hermitian operator are **orthogonal**.
- ☐ 5. The **five postulates of quantum mechanics** are collected in a summarized form here for convenience:
    - I. (Topic 5) The state of the system is described as fully as possible by the wavefunction $\psi(r_1,r_2,\ldots,t)$.
    - II. (Topic 5) For a system described by a normalized wavefunction, the probability of finding particle 1 in the volume element $d\tau_1$ at r_1, particle 2 in the volume element $d\tau_2$ at r_2, etc. is equal to $|\psi|^2 d\tau_1 d\tau_2\ldots$
    - III. (Topic 6) For each observable property Ω of a system there is a corresponding Hermitian operator $\hat{\Omega}$ built from $\hat{x}=x\times$ and $\hat{p}_x=(\hbar/\mathrm{i})\mathrm{d}/\mathrm{d}x$.
    - IV. (Topic 6) If the system is described by a wavefunction ψ that is an eigenfunction of $\hat{\Omega}$ with eigenvalue ω, then the outcome of a measurement of the observable property Ω will be ω.
    - V. (Topic 7) If the system is described by a normalized wavefunction ψ that is a linear combination of eigenfunctions of $\hat{\Omega}$, then the outcome of the determination of the observable Ω will be one of the eigenvalues ω_k of $\hat{\Omega}$ with probability $|c_k|^2$. The mean value of the measurements is equal to the expectation value $\langle\Omega\rangle$.

Checklist of equations

Property	Equation	Comment	Equation number
Linear combination	$\psi=\sum_k c_k\psi_k$	Represents a superposition of states	7.1
Expectation value	$\langle\Omega\rangle=\int\psi^*\hat{\Omega}\psi\,\mathrm{d}\tau$	Normalized wavefunction	7.2
Orthogonality	$\int\psi_i^*\psi_j\,\mathrm{d}\tau=0$		7.3a
Orthonormality	$\int\psi_i^*\psi_j\,\mathrm{d}\tau=\delta_{ij}$	$\delta_{ij}=\begin{cases}1, & i=j\\ 0, & i\neq j\end{cases}$	7.3b
Expectation value for superposition of states	$\langle\Omega\rangle=\sum_k \lvert c_k\rvert^2\omega_k$	Normalized wavefunction	7.4

TOPIC 8

The uncertainty principle

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➤ Why do you need to know this material?

You need to know how the wave properties of small particles, such as electrons, affect the quantitative treatment of their positions and momenta. Only then will you be ready to consider the electronic structure of atoms, molecules, and materials.

➤ What is the key idea?

The uncertainty principle states that it is not possible to specify the values of two observables simultaneously with arbitrarily high precision if the observables correspond to non-commuting operators.

➤ What do you need to know already?

You should know how to construct operators corresponding to observables (Topic 6) and how to extract information from the wavefunction using the properties of operators (Topics 6 and 7).

In this Topic, we explore limitations imposed by quantum mechanics on the ability to specify the values of two observables simultaneously and with high precision.

8.1 Complementarity

Some of the profound differences between quantum mechanics and classical mechanics can be appreciated by considering a particle travelling in one dimension towards positive x with linear momentum $+k\hbar$. According to classical mechanics, we can specify the trajectory of the particle, its location and momentum, at all times. According to quantum mechanics, the state of the particle is described by the wavefunction Ne^{ikx} (Topic 5), where N is the (real) normalization factor. Such a wavefunction corresponds to a well-defined linear momentum (its eigenvalue is $k\hbar$), but where is the particle located?

To answer this latter question, we use Postulate II (Topic 5) to calculate the probability density:

$$|\psi|^2 = (Ne^{ikx})^*(Ne^{ikx}) = N^2(e^{-ikx})(e^{ikx}) = N^2 \qquad (8.1)$$

This probability density is independent of x; so, wherever we look on the x-axis, there is an equal probability of finding the particle (Fig. 8.1). In other words, if the wavefunction of the

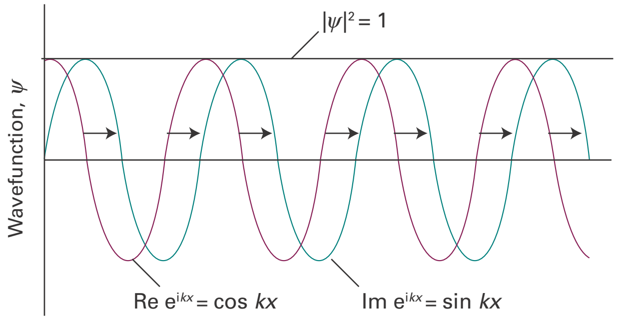


Figure 8.1 The square modulus of a wavefunction corresponding to a definite state of linear momentum is a constant, so it corresponds to a uniform probability of finding the particle anywhere.

particle is given by Ne^{ikx}, then we cannot predict where we will find the particle. The extraordinary conclusion is that if we know the linear momentum precisely, then we can say nothing about the position. This **complementarity** of certain pairs of observables, in this case linear momentum and position, pervades the whole of quantum mechanics.

Brief illustration 8.1 Uncertainty in position and momentum 1

If the wavefunction of the particle is given by $N \cos kx$, then the probability density $N^2 \cos^2 kx$ vanishes at particular locations (values of x such that kx is an odd multiple of $\pi/2$) and, although we cannot specify precisely where the particle is located we do know locations where it is *not* located. We also know (Topic 7) that measurements of the linear momentum will result in $+k\hbar$ one-half of the time and $-k\hbar$ the other half of the time. Therefore, compared to the wavefunction Ne^{ikx}, we see that by relinquishing the certainty in knowing the linear momentum (two values are possible rather than just one) we have obtained some certainty in knowing the location of the particle.

Self-test 8.1 Repeat the analysis for the wavefunction $N \cos 2kx$.

Answer: For momentum: $+2k\hbar$ and $-2k\hbar$, each half of the time. Though there are now twice as many locations where the particle is *not* located, the uncertainty in the position remains the same because the range of space is infinite.

How do we recognize complementary observables and what are their consequences? Can we specify the energy of a molecule at the same time, for instance, as its dipole moment or are they complementary too? These are some of the questions we address in this Topic.

8.2 The Heisenberg uncertainty principle

We have seen that if we know the linear momentum of a particle precisely, then we can say nothing about its location. But what of the opposite problem: can we know the linear momentum of a particle if we know its position precisely? That we cannot can be deduced as follows.

If we know that the particle is at a definite location, its wavefunction must be large there and zero everywhere else (Fig. 8.2). Such a wavefunction can be created by superimposing a large number of harmonic (sine and cosine) functions, or, equivalently, a number of e^{ikx} functions. In other words, we can create a sharply localized wavefunction, called a **wavepacket**, by forming a linear combination of wavefunctions that correspond to many different linear momenta. The superposition of a few harmonic functions gives a wavefunction that spreads over a range of locations (Fig. 8.3). However, as the number of wavefunctions in the superposition increases, the wavepacket becomes sharper on account of the more complete interference between the positive and negative regions of the individual waves. When an infinite number of components are used, the wavepacket is a sharp, infinitely narrow spike, which corresponds to perfect localization of the particle. Now the particle is perfectly localized. However, we have lost all information about its momentum because a measurement of the momentum will give a result corresponding to any one of the infinite number of waves in the superposition, and which one it will give is unpredictable

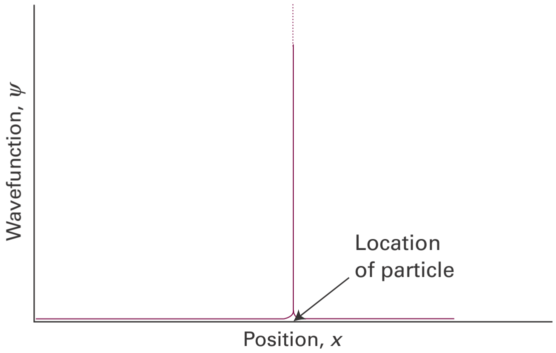


Figure 8.2 The wavefunction for a particle at a well-defined location is a sharply spiked function which has zero amplitude everywhere except at the particle's position.

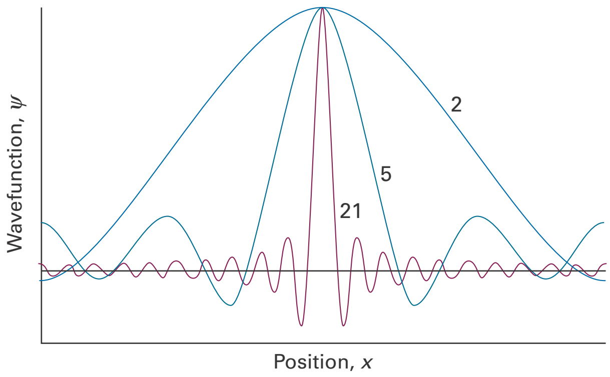


Figure 8.3 The wavefunction for a particle with an ill-defined location can be regarded as the linear combination of several wavefunctions of definite wavelength that interfere constructively in one place but destructively elsewhere. As more waves are used in the superposition (as given by the numbers attached to the curves), the location becomes more precise at the expense of uncertainty in the particle's momentum. An infinite number of waves are needed in the superposition to construct the wavefunction of the perfectly localized particle.

(Postulate V). Hence, if we know the location of the particle precisely (implying that its wavefunction is a superposition of an infinite number of momentum eigenfunctions), then its momentum is completely unpredictable.

The conclusion that the linear momentum and position of a particle cannot be known simultaneously is summarized by the **Heisenberg uncertainty principle**, proposed by Werner Heisenberg in 1927:

> It is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle.

Heisenberg was able to go beyond this qualitative statement and give the principle a precise quantitative form:

$$\Delta p \Delta q \geq \hbar/2 \qquad \text{Heisenberg uncertainty principle} \qquad (8.2)$$

In this expression Δp is the 'uncertainty' in the linear momentum parallel to the axis q, and Δq is the uncertainty in position along that axis. These 'uncertainties' are precisely defined, for they are the root mean square deviations of the properties from their mean values:

$$\Delta X = \{\langle X^2 \rangle - \langle X \rangle^2\}^{1/2} \qquad \textit{Definition} \qquad \text{Uncertainty in X} \qquad (8.3)$$

If there is complete certainty about the position of the particle ($\Delta q = 0$), then the only way that eqn 8.2 can be satisfied is for $\Delta p = \infty$, which implies complete uncertainty about the momentum. Conversely, if the momentum parallel to an axis is known exactly ($\Delta p = 0$), then the position along that axis must be completely uncertain ($\Delta q = \infty$).

The p and q that appear in eqn 8.2 refer to the same direction in space. Therefore, whereas simultaneous specification of the position on the x-axis and momentum parallel to the x-axis are restricted by the uncertainty relation, simultaneous location of position on x and momentum parallel to y or z are not restricted. Table 8.1 summarizes the restrictions that the uncertainty principle implies.

Table 8.1 Constraints of the uncertainty principle*

Variable 2	Variable 1					
	x	y	z	p_x	p_y	p_z
x				▨		
y					▨	
z						▨
p_x	▨					
p_y		▨				
p_z			▨			

* Pairs of observables that cannot be determined simultaneously with arbitrary precision are marked with a blue rectangle; all others are unrestricted.

Example 8.1 Calculating the uncertainty in linear momentum

Calculate the uncertainty in the linear momentum of an electron described by the normalized wavefunction $(2/L)^{1/2} \times \sin(\pi x/L)$ in a region of length L.

Method The uncertainty Δp is given by eqn 8.3. We need to compute the expectation values $\langle p^2 \rangle$ and $\langle p \rangle$. Use the Integrals T.2 and T.7 listed in the *Resource section*.

Answer The expectation value of the momentum operator, $\hat{p} = (\hbar/\mathrm{i})\mathrm{d}/\mathrm{d}x$, is

$$\begin{aligned}\langle p \rangle &= \int \psi^* \hat{p}\, \psi \,\mathrm{d}x = \frac{2}{L}\int_0^L \sin(\pi x/L)\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\sin(\pi x/L)\,\mathrm{d}x \\ &= \frac{2\hbar\pi}{\mathrm{i}L^2}\int_0^L \sin(\pi x/L)\cos(\pi x/L)\,\mathrm{d}x \\ &= \frac{2\hbar\pi}{\mathrm{i}L^2} \times \frac{1}{(2\pi/L)}\sin^2(\pi x/L)\Big|_0^L = 0\end{aligned}$$

The expectation value of the momentum squared operator, $\hat{p}^2 = -\hbar^2(\mathrm{d}^2/\mathrm{d}x^2)$, is

$$\begin{aligned}\langle p^2 \rangle &= \int \psi^* \hat{p}^2 \psi \,\mathrm{d}x = -\frac{2\hbar^2}{L}\int_0^L \sin(\pi x/L)\frac{\mathrm{d}^2}{\mathrm{d}x^2}\sin(\pi x/L)\,\mathrm{d}x \\ &= \frac{2\hbar^2}{L}\left(\frac{\pi}{L}\right)^2 \int_0^L \sin(\pi x/L)\sin(\pi x/L)\,\mathrm{d}x \\ &= \frac{h^2}{2L^3}\left\{\frac{x}{2} - \frac{\sin 2\pi x/L}{4\pi/L}\right\}\Bigg|_0^L = \frac{h^2}{4L^2}\end{aligned}$$

We have used $\hbar = h/2\pi$. Therefore the uncertainty in the linear momentum is

$$\Delta p = \{\langle p^2 \rangle - \langle p \rangle^2\}^{1/2} = \left\{\frac{h^2}{4L^2} - 0^2\right\}^{1/2} = \frac{h}{2L}\left(\text{or } \frac{\pi\hbar}{L}\right)$$

Self-test 8.2 Calculate the uncertainty in the position of the electron in the same system and proceed to confirm that the Heisenberg uncertainty principle is satisfied.

Answer: $\Delta x = 0.181L, \Delta p \Delta x = 1.14 \times \hbar/2 > \hbar/2$

Brief illustration 8.2 Uncertainty in position and momentum 2

Suppose the speed of a projectile of mass 1.0 g is known to within 1 μm s^{-1}. We can estimate the uncertainty Δp from $m\Delta v$, where Δv is the uncertainty in the speed and is taken to be 1 μm s^{-1}. The minimum uncertainty in its position can be estimated using eqn 8.2:

$$\Delta q = \frac{\hbar}{2m\Delta v}$$

$$= \frac{1.055\times10^{-34}\,\mathrm{J\,s}}{2\times(1.0\times10^{-3}\,\mathrm{kg})\times(1\times10^{-6}\,\mathrm{m\,s^{-1}})} = 5\times10^{-26}\,\mathrm{m}$$

where we have used $1\,\mathrm{J} = 1\,\mathrm{kg\,m^2\,s^{-2}}$. The uncertainty is completely negligible for all practical purposes concerning macroscopic objects. However, if the mass is that of an electron, then the same uncertainty in speed implies an uncertainty in position far larger than the diameter of an atom (the analogous calculation gives $\Delta q = 60\,\mathrm{m}$); so the concept of a trajectory, the simultaneous possession of a precise position and momentum, is untenable.

Self-test 8.3 Estimate the minimum uncertainty in the speed of an electron in a one-dimensional region of length $2a_0$ where $a_0 = 53\,\mathrm{pm}$ (the Bohr radius).

Answer: $547\,\mathrm{km\,s^{-1}}$

8.3 Commutation and complementarity

The Heisenberg uncertainty principle is a special case of a very general form of an uncertainty principle developed by H.P. Robertson in 1929. The latter applies to any pair of observables called **complementary observables**, which are defined in terms of the properties of their operators. Specifically, two observables Ω_1 and Ω_2 are complementary if

$$\hat{\Omega}_1\hat{\Omega}_2\psi \neq \hat{\Omega}_2\hat{\Omega}_1\psi \quad \textit{Definition} \quad \text{Complementary observables} \quad (8.4)$$

When the effect of two operators depends on their order (as this equation implies), we say that they do not **commute**. The different outcomes of the effect of applying $\hat{\Omega}_1$ and $\hat{\Omega}_2$ in a different order is expressed by introducing the **commutator** of the two operators, which is defined as

$$[\hat{\Omega}_1, \hat{\Omega}_2] = \hat{\Omega}_1\hat{\Omega}_2 - \hat{\Omega}_2\hat{\Omega}_1 \quad \textit{Definition} \quad \text{Commutator} \quad (8.5)$$

If the two operators do commute, then their commutator is zero.

Example 8.2 Demonstrating non-commutativity and evaluating a commutator

Show that the operators for position and momentum do not commute and therefore that these observables are complementary. Find their commutator.

Method Consider the effect of $\hat{x}\hat{p}$ on a wavefunction ψ (that is, the effect of $\hat{p}$ followed by the effect on the outcome of multiplication by x), then the effect of $\hat{p}\hat{x}$ on the same function (that is, the effect of multiplication by x followed by the effect of $\hat{p}$ on the outcome). Finally, take the difference of the two results.

Answer The effect of $\hat{x}\hat{p}$ on ψ is

$$\hat{x}\hat{p}\psi = x\times\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\psi}{\mathrm{d}x}$$

The effect of $\hat{p}\hat{x}$ on the same function is

$$\hat{p}\hat{x}\psi = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}x\psi = \frac{\hbar}{\mathrm{i}}\left(\psi + x\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)$$

(For this step we have used the standard rule about differentiating a product of functions.) The second expression is clearly different from the first, so the two operators do not commute. Their commutator is calculated by subtracting the second of these two equations from the first:

$$(\hat{x}\hat{p} - \hat{p}\hat{x})\psi = \frac{\hbar}{\mathrm{i}}\left(x\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) - \frac{\hbar}{\mathrm{i}}\left(\psi + x\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) \overset{-1/\mathrm{i}=\mathrm{i}}{\widehat{=}} \mathrm{i}\hbar\psi$$

Because this relation is true for any ψ, it follows that $[\hat{x}, \hat{p}] = \mathrm{i}\hbar$. This relation is valid for linear momentum along the x-axis (that is, when $\hat{p}$ is actually $\hat{p}_x$). The same kind of calculation can be used to deduce that $[\hat{x}, \hat{p}_y] = 0$ and $[\hat{x}, \hat{p}_z] = 0$.

Self-test 8.4 Do the operators for potential energy and kinetic energy commute in general? If not, evaluate their commutator.

Answer: No: $[\hat{V}, \hat{E}_\mathrm{k}] = (\hbar^2/2m)(\mathrm{d}^2V/\mathrm{d}x^2 + 2(\mathrm{d}V/\mathrm{d}x)\mathrm{d}/\mathrm{d}x)$

We can conclude from the calculation in Example 8.2 that the commutator of the operators for position and linear momentum parallel to the same axis is

$$[\hat{x}, \hat{p}_x] = \mathrm{i}\hbar \quad \text{Commutator of position and linear momentum} \quad (8.6)$$

with similar expressions for other axes. This commutator is of such vital significance in quantum mechanics that it is taken as a fundamental distinction between classical mechanics and quantum mechanics. In fact, rather than giving the explicit forms of the operators for position and linear momentum in Topic 6 we could have stated Postulate III as:

> For every observable property Ω of a system there is a corresponding hermitian operator $\hat{\Omega}$ built from position and linear momentum operators that satisfy the commutation relation in eqn 8.6.

With the concept of the commutator established, the most general form of the uncertainty principle can be given. For *any* two pairs of observables, Ω_1 and Ω_2, the uncertainties (to be precise, the root mean square deviations of their values from the mean) in simultaneous determinations are related by

$$\Delta\Omega_1\Delta\Omega_2 \geq \frac{1}{2}\left|\langle[\hat{\Omega}_1,\hat{\Omega}_2]\rangle\right| \tag{8.7}$$

General form **Uncertainty principle**

where the 'modulus' notation |…| means to take the magnitude of the term the bars enclose (see *The chemist's toolkit* 5.1). The modulus ensures that the product of uncertainties has a real, non-negative value.

When we identify the observables in eqn 8.7 with x and p_x and use eqn 8.6 for their commutator, we obtain eqn 8.2, the specific case of the uncertainty principle for position and momentum.

Example 8.3 Determining the complementarity of two observables

Can the electric dipole moment and the energy of a molecule be specified simultaneously? Take the x-component of the electric dipole moment operator to be $\mu = -ex\times$.

Method First, determine if the electric dipole moment and the energy are complementary observables by evaluating the commutator, eqn 8.5, of the operators corresponding to the observables. Then use the general form of the uncertainty principle, eqn 8.7, to determine if the observables can be specified simultaneously. That is, determine whether the product of their uncertainties is zero or not.

Answer We need to evaluate

$$[\hat{x},\hat{H}] = [\hat{x},\hat{E}_\mathrm{k}+\hat{V}] = [\hat{x},\hat{E}_\mathrm{k}]+[\hat{x},\hat{V}]$$

The potential energy operator commutes with x because they are both multiplicative, and $xV(x) = V(x)x$. To decide whether the kinetic energy operator commutes with x we need to evaluate the following expression:

$$[\hat{x},\hat{E}_\mathrm{k}]\psi = -\frac{\hbar^2}{2m_\mathrm{e}}\left(x\frac{\mathrm{d}^2}{\mathrm{d}x^2}-\frac{\mathrm{d}^2}{\mathrm{d}x^2}x\right)\psi = -\frac{\hbar^2}{2m_\mathrm{e}}\left(x\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}-\frac{\mathrm{d}^2}{\mathrm{d}x^2}x\psi\right)$$

To do so, we note that

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}x\psi = \frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\mathrm{d}}{\mathrm{d}x}x\psi\right) = \frac{\mathrm{d}}{\mathrm{d}x}\left(\psi + x\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)$$
$$= \frac{\mathrm{d}\psi}{\mathrm{d}x}+\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}+x\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}\right) = 2\frac{\mathrm{d}\psi}{\mathrm{d}x}+x\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}$$

It then follows that

$$[\hat{x},\hat{E}_\mathrm{k}]\psi = -\frac{\hbar^2}{2m_\mathrm{e}}\times\left(-2\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) = \frac{\hbar^2}{m_\mathrm{e}}\frac{\mathrm{d}\psi}{\mathrm{d}x} \overset{(\hbar/\mathrm{i})\mathrm{d}/\mathrm{d}x=\hat{p}_x}{=} \frac{\mathrm{i}\hbar}{m_\mathrm{e}}\hat{p}_x\psi$$

and therefore that for all wavefunctions

$$[\hat{x},\hat{E}_\mathrm{k}] = \frac{\mathrm{i}\hbar}{m_\mathrm{e}}\hat{p}_x$$

Hence,

$$[\hat{x},\hat{H}] = \frac{\mathrm{i}\hbar}{m_\mathrm{e}}\hat{p}_x$$

Because the electric dipole moment operator does not commute with the hamiltonian, in general the electric dipole moment and the energy are complementary observables. However, eqn 8.7 tells us that the restriction on their simultaneous determination is

$$\Delta\mu\Delta E = -e\Delta x\Delta E \geq -\frac{1}{2}e\left|\langle[\hat{x},\hat{H}]\rangle\right|$$
$$\geq -\frac{1}{2}e\left|\left\langle\frac{\mathrm{i}\hbar}{m_\mathrm{e}}\hat{p}_x\right\rangle\right| = -\frac{\hbar e}{2m_\mathrm{e}}\langle\hat{p}_x\rangle$$

Therefore, provided the electron has no net linear momentum (so $\langle\hat{p}_x\rangle = 0$) there will be no restriction on the simultaneous determination of the electric dipole moment and the energy even though the corresponding operators are complementary.

Self-test 8.5 Can the potential and kinetic energies be simultaneously specified for an electron undergoing oscillatory motion in one dimension x with a potential energy proportional to x^2?

Answer: No: $[\hat{x}^2,\hat{E}_\mathrm{k}] = (\hbar/m_\mathrm{e})(\hbar+2x\mathrm{i}\hat{p}_x)$

The realization that some observables are complementary allows us to make considerable progress with the calculation of atomic and molecular properties; but it does away with some of the most cherished concepts of classical physics.

Checklist of concepts

☐ 1. The **Heisenberg uncertainty principle** states that it is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle.

☐ 2. Two observables are **complementary** if their corresponding operators do not commute.

☐ 3. The general form of the uncertainty principle provides a quantitative measure of our ability to specify precisely and simultaneously any two observables.

Checklist of equations

Property	Equation	Comment	Equation number
Heisenberg uncertainty principle	$\Delta p \Delta q \geq \hbar/2$	p and q parallel	8.2
Uncertainty	$\Delta X = \{\langle X^2 \rangle - \langle X \rangle^2\}^{1/2}$	Specifically, the root mean square deviation	8.3
Commutator	$\left[\hat{\Omega}_1, \hat{\Omega}_2\right] = \hat{\Omega}_1 \hat{\Omega}_2 - \hat{\Omega}_2 \hat{\Omega}_1$	Definition	8.5
	$[\hat{x}, \hat{p}] = \mathrm{i}\hbar$	p and x parallel	8.6
Uncertainty principle	$\Delta \Omega_1 \Delta \Omega_2 \geq \frac{1}{2} \langle [\hat{\Omega}_1, \hat{\Omega}_2] \rangle$	General form	8.7

Focus 2 on The principles of quantum mechanics

Topic 4 The emergence of quantum theory

Discussion questions

4.1 Summarize the evidence that led to the introduction of quantum mechanics.

4.2 Explain the meaning and consequences of wave–particle duality.

Exercises

4.1(a) Calculate the size of the quantum involved in the excitation of (i) a molecular vibration of period 20 fs, (ii) a pendulum of period 2.0 s. Express the results in joules and kilojoules per mole.

4.1(b) Calculate the size of the quantum involved in the excitation of (i) a molecular vibration of period 3.2 fs, (ii) a balance wheel of period 1.0 ms. Express the results in joules and kilojoules per mole.

4.2(a) The work function for metallic caesium is 2.14 eV. Calculate the kinetic energy and the speed of the electrons ejected by light of wavelength (i) 580 nm, (ii) 250 nm.

4.2(b) The work function for metallic rubidium is 2.09 eV. Calculate the kinetic energy and the speed of the electrons ejected by light of wavelength (i) 520 nm, (ii) 355 nm.

4.3(a) In an experiment to study the photoelectric effect, a photon of radiation of wavelength 465 nm was found to eject an electron from a metal with a kinetic energy of 2.11 eV. What is the maximum wavelength capable of ejecting an electron from the metal?

4.3(b) When light of wavelength 195 nm strikes a certain metal surface, electrons are ejected with a speed of $1.23\times10^6\,\mathrm{m\,s^{-1}}$. Calculate the speed of electrons ejected from the metal surface by light of wavelength 255 nm.

4.4(a) In an X-ray photoelectron experiment, a photon of wavelength 150 pm ejects an electron from the inner shell of an atom and it emerges with a speed of $2.14\times10^7\,\mathrm{m\,s^{-1}}$. Calculate the binding energy of the electron.

4.4(b) In an X-ray photoelectron experiment, a photon of wavelength 121 pm ejects an electron from the inner shell of an atom and it emerges with a speed of $5.69\times10^7\,\mathrm{m\,s^{-1}}$. Calculate the binding energy of the electron.

4.5(a) Calculate the energy per photon and the energy per mole of photons for radiation of wavelength (i) 620 nm (red), (ii) 570 nm (yellow), (iii) 380 nm (blue).

4.5(b) Calculate the energy per photon and the energy per mole of photons for radiation of wavelength (i) 188 nm (ultraviolet), (ii) 125 pm (X-ray), (iii) 1.00 cm (microwave).

4.6(a) A sodium lamp emits yellow light of wavelength 590 nm. How many photons does it emit each second if its power is (i) 10 W, (ii) 250 W?

4.6(b) A laser used to read CDs emits red light of wavelength 700 nm. How many red photons does it emit each second if its power is (i) 0.25 W, (ii) 1.5 mW?

4.7(a) Calculate the de Broglie wavelength of (i) a mass of 2 g travelling at $1\,\mathrm{cm\,s^{-1}}$, (ii) the same, travelling at $250\,\mathrm{km\,s^{-1}}$, (iii) a He atom travelling at $1000\,\mathrm{m\,s^{-1}}$ (a typical speed at room temperature).

4.7(b) Calculate the de Broglie wavelength of an electron accelerated from rest through a potential difference of (i) 100 V, (ii) 15 kV, (iii) 250 kV.

4.8(a) Electron diffraction makes use of electrons with wavelengths comparable to bond lengths. To what speed must an electron be accelerated for it to have a wavelength of 100 pm? What accelerating potential difference is needed?

4.8(b) Could *proton diffraction* be an interesting technique for the investigation of molecular structure? To what speed must a proton be accelerated for it to have a wavelength of 100 pm? What accelerating potential difference is needed?

4.9(a) The impact of photons on matter exerts a force that can move it, but the effect of a single photon is insignificant except when it strikes an atom or subatomic particle. Calculate the speed to which a stationary electron would be accelerated if it absorbed a photon of 150 nm radiation.

4.9(b) Similarly, calculate the speed to which a stationary H atom would be accelerated if it absorbed a photon of 100 nm radiation.

Problems

4.1 The Planck distribution is given in eqn 4.3. (a) Plot the Planck distribution for ρ as a function of wavelength (take $T=298\,\mathrm{K}$). (b) Show mathematically that as $\lambda\to0$, $\rho\to0$ and therefore that the 'ultraviolet catastrophe' is avoided. (c) Show that for long wavelengths ($hc/\lambda kT\ll1$), the Planck distribution reduces to the Rayleigh–Jeans law, the classical expression in eqn 4.2.

4.2 (a) Derive Wien's displacement law (eqn 4.1) and deduce an expression for the constant as a multiple of the second radiation constant, $c_2=hc/k$. (b) Values of $\lambda_{\max}$ from a small pinhole in an electrically heated container were determined at a series of temperatures, and the results are given below. Deduce a value for Planck's constant using the values of c_2 and k.

θ/°C	1000	1500	2000	2500	3000	3500
$\lambda_{\max}$/nm	2181	1600	1240	1035	878	763

4.3‡ The temperature of the Sun's surface is approximately 5800 K. On the assumption that the human eye evolved to be most sensitive at the wavelength of light corresponding to the maximum in the Sun's radiant energy distribution, determine the colour of light to which the eye is the most sensitive.

‡ This problem was supplied by Charles Trapp and Carmen Giunta.

4.4 Calculate the value of Planck's constant given that the following kinetic energies were observed for photoejected electrons irradiated by radiation of the wavelengths noted.

λ/nm	320	330	345	360	385
E_k/eV	1.17	1.05	0.885	0.735	0.511

Topic 5 The wavefunction

Discussion questions

5.1 Discuss the relationship between probability amplitude and probability density.

5.2 Describe the constraints that the Born interpretation puts on acceptable wavefunctions.

5.3 What are the advantages of working with normalized wavefunctions?

Exercises

5.1(a) Consider a time-independent wavefunction of a particle moving in three-dimensional space. Identify the variables upon which the wavefunction depends.
5.1(b) Consider a time-dependent wavefunction of a particle moving in two-dimensional space. Identify the variables upon which the wavefunction depends.

5.2(a) Consider a time-independent wavefunction of a hydrogen atom. Identify the variables upon which the wavefunction depends. Use spherical polar coordinates.
5.2(b) Consider a time-dependent wavefunction of a helium atom. Identify the variables upon which the wavefunction depends. Use spherical polar coordinates.

5.3(a) An unnormalized wavefunction for a light atom rotating around a heavy atom to which it is bonded is $\psi(\phi) = e^{i\phi}$ with $0 \le \phi \le 2\pi$. Normalize this wavefunction (to 1).

5.3(b) An unnormalized wavefunction for an electron in a carbon nanotube of length L is $\sin(2\pi x/L)$. Normalize this wavefunction (to 1).

5.4(a) For the system described in Exercise 5.3(a), what is the probability of finding the light atom in the volume element $d\phi$ at $\phi = \pi$?
5.4(b) For the system described in Exercise 5.3(b), what is the probability of finding the electron in the range dx at $x = L/2$?

5.5(a) For the system described in Exercise 5.3(a), what is the probability of finding the light atom between $\phi = \pi/2$ and $\phi = 3\pi/2$?
5.5(b) For the system described in Exercise 5.3(b), what is the probability of finding the electron between $x = L/4$ and $x = 3L/4$?

Problems

5.1 Suppose that the normalized wavefunction for an electron in a carbon nanotube of length $L = 10.0$ nm is: $\psi = (2/L)^{1/2} \sin(\pi x/L)$. Calculate the probability that the electron is (a) between $x = 4.95$ nm and 5.05 nm, (b) between $x = 7.95$ nm and 9.05 nm, (c) between $x = 9.90$ nm and 10.00 nm, (d) in the left half of the box, (e) in the central third of the box.

5.2 The normalized wavefunction for the electron in a hydrogen atom is $\psi = (1/\pi a_0^3)^{1/2} e^{-r/a_0}$, where $a_0 = 53$ pm (the Bohr radius). (a) Calculate the probability that the electron will be found somewhere within a small sphere of radius 1.0 pm centred on the nucleus. (b) Now suppose that the same sphere is located at $r = a_0$. What is the probability that the electron is inside it?

5.3 A hydrogen atom attached to a metallic surface is undergoing oscillatory motion so that the state of the atom is described by a wavefunction that is proportional to the square of the atom's displacement from the metallic surface. Assume that the motion of the H atom is constrained to one dimension between $x = 0$ and $x = \pi$ and that its state is described by the unnormalized wavefunction $\psi(x) = x^2$. If the probability of finding the atom between $x = 0$ and $x = a$ is $\frac{1}{2}$, what is the value of a?

5.4 A particle free to move along one dimension x (with $0 \le x < \infty$) is described by the unnormalized wavefunction $\psi(x) = e^{-ax}$ with $a = 2\,\text{m}^{-1}$. What is the probability of finding the particle at a distance $x \ge 1$ m?

5.5 The rotation of a light atom around a heavier atom to which it is bonded can be described quantum mechanically. The unnormalized wavefunctions for a light atom confined to move on a circle (with a heavier atom at the circle's centre) are $\psi(\phi) = e^{-im\phi}$, where $m = 0, \pm1, \pm2, \pm3, \ldots$ and $0 \le \phi \le 2\pi$. Determine $\langle \phi \rangle$.

5.6 Atoms in a chemical bond vibrate around the equilibrium bond length. An atom undergoing vibrational motion is described by the wavefunction $\psi(x) = Ne^{-x^2/2a^2}$, where a is a constant and $-\infty < x < \infty$. (a) Normalize this function. (b) Calculate the probability of finding the particle in the range $-a \le x \le a$. *Hint*: The integral encountered in part (b) is the error function; see Integral G.6 of the *Resource section*. Its numerical values are provided in most mathematical software packages.

5.7 Suppose that the state of the vibrating atom in Problem 5.6 is described by the wavefunction $\psi(x) = Nxe^{-x^2/2a^2}$. Where is the most probable location of the particle?

5.8 Normalize the following wavefunctions: (a) $\sin(n\pi x/L)$ in the range $0 \le x \le L$, where $n = 1, 2, 3, \ldots$ (this wavefunction can be used to describe delocalized electrons in a linear polyene); (b) a constant in the range $-L \le x \le L$; (c) $e^{-r/a}$ in three-dimensional space (this wavefunction can be used to describe the electron in the ion He^+); (d) $xe^{-r/2a}$ in three-dimensional space. *Hint*: The volume element in three dimensions is $d\tau = r^2 dr \sin\theta \, d\theta \, d\phi$, with $0 \le r < \infty$, $0 \le \theta \le \pi$, $0 \le \phi \le 2\pi$.

Topic 6 Extracting information from the wavefunction

Discussion questions

6.1 Suggest how the general shape of a wavefunction can be predicted without solving the Schrödinger equation explicitly.

6.2 Describe the relationship between operators and observables in quantum mechanics.

Exercises

6.1(a) Construct the potential energy operator of a particle subjected to a harmonic oscillator potential (Topic 2).
6.1(b) Construct the potential energy operator of a particle subjected to a Coulombic potential.

6.2(a) Complex functions of the form e^{ikx} can be used to model the wavefunctions of particles in a linear accelerator. Show that any linear combination of the complex functions e^{2ix} and e^{-2ix} is an eigenfunction of the operator d^2/dx^2 and identify its eigenvalue.
6.2(b) Functions of the form sin nx can be used to model the wavefunctions of electrons in a carbon nanotube. Show that any linear combination of the functions sin $3x$ and cos $3x$ is an eigenfunction of the operator d^2/dx^2 and identify its eigenvalue.

6.3(a) The momentum operator is proportional to d/dx. Which of the following functions are eigenfunctions of d/dx? (i) e^{ikx}, (ii) e^{ax^2}, (iii) x, (iv) x^2, (v) $ax+b$, (vi) $\sin(x+3a)$. Give the corresponding eigenvalue where appropriate.
6.3(b) The kinetic energy operator is proportional to d^2/dx^2. Which of the following functions are eigenfunctions of d^2/dx^2? (i) e^{ax}, (ii) e^{-ax^2}, (iii) k, (iv) kx^2, (v) $ax+b$, (vi) $\cos(kx+5)$. Give the corresponding eigenvalue where appropriate.

6.4(a) Confirm that the kinetic energy operator, $-(\hbar^2/2m)d^2/dx^2$, is Hermitian.
6.4(b) When we discuss rotational motion, we shall see that the operator corresponding to the angular momentum of a particle is $(\hbar/i)d/d\phi$, where ϕ is an angle. Is this operator Hermitian?

6.5(a) You might come across an operator of the form $\hat{x}+ia\hat{p}_x$, where a is a real constant, and wonder if it corresponds to an observable. Could it?
6.5(b) Likewise, you might wonder if $\hat{x}^2-ia\hat{E}_k$, where a is a real constant, corresponds to an observable. Could it?

Problems

6.1 Write the time-independent Schrödinger equations for (a) an electron moving in one dimension about a stationary proton and subjected to a Coulombic potential, (b) a free particle, (c) a particle subjected to a constant, uniform force.

6.2 Construct quantum mechanical operators for the following observables: (a) kinetic energy in one and in three dimensions, (b) the inverse separation, $1/x$, (c) electric dipole moment in one dimension, (d) the mean square deviations of the position and momentum of a particle (in one dimension) from the mean values.

6.3 Determine which of the following functions are eigenfunctions of the inversion operator $\hat{\imath}$ (which has the effect of making the replacement $x \to -x$): (a) x^3-kx, (b) cos kx, (c) x^2+3x-1. State the eigenvalue of $\hat{\imath}$ where relevant.

6.4 Show that the product of a Hermitian operator with itself is also a Hermitian operator.

Topic 7 Predicting the outcome of experiments

Discussion question

7.1 Describe how a wavefunction determines the dynamical properties of a system and how those properties may be predicted.

Exercises

7.1(a) Functions of the form $\sin(n\pi x/L)$ can be used to model the wavefunctions of electrons in a carbon nanotube of length L. Show that the wavefunctions $\sin(n\pi x/L)$ and $\sin(m\pi x/L)$, where $n \neq m$, are orthogonal for a particle confined to the region $0 \le x \le L$.
7.1(b) Functions of the form $\cos(n\pi x/L)$ can be used to model the wavefunctions of electrons in metals. Show that the wavefunctions $\cos(n\pi x/L)$ and $\cos(m\pi x/L)$, where $n \neq m$, are orthogonal for a particle confined to the region $0 \le x \le L$.

7.2(a) A light atom rotating around a heavy atom to which it is bonded is described by a wavefunction of the form $\psi(\phi)=e^{im\phi}$ with $0 \le \phi \le 2\pi$ and m an integer. Show that the $m=+1$ and $m=+2$ wavefunctions are orthogonal.
7.2(b) Repeat Exercise 7.2(a) for the $m=+1$ and $m=-1$ wavefunctions.

7.3(a) An electron in a carbon nanotube of length L is described by the wavefunction $\psi(x)=\sin(2\pi x/L)$. Compute the expectation value of the position of the electron.

7.3(b) An electron in a carbon nanotube of length L is described by the wavefunction $\psi(x) = (2/L)^{1/2} \sin(\pi x/L)$. Compute the expectation value of the kinetic energy of the electron.

7.4(a) An electron in a one-dimensional metal of length L is described by the wavefunction $\psi(x) = \sin(\pi x/L)$. Compute the expectation value of the momentum of the electron.

7.4(b) A light atom rotating around a heavy atom to which it is bonded is described by a wavefunction of the form $\psi(\phi) = e^{i\phi}$ with $0 \le \phi \le 2\pi$. If the operator corresponding to angular momentum is given by $(\hbar/i)d/d\phi$, compute the expectation value of the angular momentum of the light atom.

Problems

7.1 A particle freely moving in one dimension x with $0 \le x < \infty$ is in a state described by the wavefunction $\psi(x) = a^{1/2}e^{-ax/2}$, where a is a constant. Determine the expectation value of the position operator.

7.2 The wavefunction of an electron in a linear accelerator is $\psi = (\cos\chi)e^{ikx} + (\sin\chi)e^{-ikx}$, where χ (chi) is a parameter. What is the probability that the electron will be found with a linear momentum (a) $+k\hbar$, (b) $-k\hbar$? What form would the wavefunction have if it were 90 per cent certain that the electron had linear momentum $+k\hbar$?

7.3 Evaluate the kinetic energy of the electron with wavefunction given in Problem 7.2.

7.4 Calculate the average linear momentum of a particle described by the following wavefunctions: (a) e^{ikx}, (b) $\cos kx$, (c) e^{-ax^2}, where in each one x ranges from $-\infty$ to $+\infty$.

7.5 (a) Two (unnormalized) excited-state wavefunctions of the H atom are (i) $\psi = (2 - r/a_0)e^{-r/a_0}$ and (ii) $\psi = r\sin\theta\cos\phi\, e^{-r/2a_0}$. Normalize both functions to 1. (b) Confirm that these two functions are mutually orthogonal.

7.6 Evaluate the expectation values of r and r^2 for a hydrogen atom with wavefunctions given in Problem 7.5.

7.7 Calculate (a) the mean potential energy and (b) the mean kinetic energy of an electron in the hydrogen atom whose state is described by the wavefunction given in Problem 5.2.

7.8 Suppose that the wavefunction of an electron in a carbon nanotube is a linear combination of $\cos nx$ functions. Use mathematical software to construct superpositions of cosine functions and determine the probability that a given momentum will be observed. If you plot the superposition (which you should), set $x = 0$ at the centre of the screen and build the superposition there. Evaluate the root mean square location of the wavepacket, $\langle x^2\rangle^{1/2}$.

Topic 8 The uncertainty principle

Discussion questions

8.1 Account for the uncertainty relation between position and linear momentum in terms of the shape of the wavefunction.

8.2 Describe the properties of wavepackets in terms of the Heisenberg uncertainty principle.

Exercises

8.1(a) The speed of a certain proton is 6.1×10^6 m s^{-1}. If the uncertainty in its momentum is to be reduced to 0.0100 per cent, what uncertainty in its location must be tolerated?

8.1(b) The speed of a certain electron is 1000 km s^{-1}. If the uncertainty in its momentum is to be reduced to 0.0010 per cent, what uncertainty in its location must be tolerated?

8.2(a) Calculate the minimum uncertainty in the speed of a ball of mass 500 g that is known to be within 1.0 μm of a certain point on a bat. What is the minimum uncertainty in the position of a bullet of mass 5.0 g that is known to have a speed somewhere between 350.000 00 m s^{-1} and 350.000 01 m s^{-1}?

8.2(b) An electron in a nanoparticle is confined to a region of length 0.10 nm. What are the minimum uncertainties in (i) its speed, (ii) its kinetic energy?

8.3(a) Evaluate the commutators (i) $[\hat{x}, \hat{y}]$, (ii) $[\hat{p}_x, \hat{p}_y]$, (iii) $[\hat{x}, \hat{p}_x]$, (iv) $[\hat{x}^2, \hat{p}_x]$, (v) $[\hat{x}^n, \hat{p}_x]$.

8.3(b) Evaluate the commutators (i) $[(1/\hat{x}), \hat{p}_x]$, (ii) $[(1/\hat{x}), \hat{p}_x^2]$, (iii) $[\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{y}\hat{p}_z - \hat{z}\hat{p}_y]$, (iv) $[\hat{x}^2(\partial^2/\partial y^2), \hat{y}(\partial/\partial x)]$.

Problems

8.1 An atom undergoing vibrational motion is described by the wavefunction $\psi(x) = (2a/\pi)^{1/4}e^{-ax^2}$, where a is a constant and $-\infty < x < \infty$. Verify that the value of the product $\Delta p\Delta x$ is consistent with the predictions from the uncertainty principle.

8.2 Confirm the following properties of commutators: (a) $[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$; (b) $[\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}]$; (c) $[\hat{A}^2, \hat{B}] = \hat{A}[\hat{A}, \hat{B}] + [\hat{A}, \hat{B}]\hat{A}$.

8.3 Evaluate the commutators (a) $[\hat{H}, \hat{p}_x]$ and (b) $[\hat{H}, \hat{x}]$ where $\hat{H} = \hat{p}_x^2/2m + \hat{V}(x)$. Choose (i) $V(x) = V$, a constant, (ii) $V(x) = \frac{1}{2}k_f x^2$.

8.4 Evaluate the limitation on the simultaneous specification of the following observables: (a) the position and momentum of a particle in one dimension; (b) the three components of linear momentum of a particle; (c) the kinetic energy and potential energy of a particle in one dimension; (d) the electric dipole moment and the total energy of a one-dimensional system; (e) the kinetic energy and the position of a particle in one dimension.

Integrated activities

F2.1 Compare the results of experimental measurements of an observable when the wavefunction is (a) an eigenfunction of the corresponding operator, (b) a superposition of eigenfunctions of that operator.

F2.2 Show that the expectation value of an operator that can be written as the square of a Hermitian operator is positive.

F2.3 (a) Given that any operators used to represent observables must satisfy the commutation relation in eqn 8.6, what would be the operator for position if the choice had been made to represent linear momentum parallel to the x-axis by multiplication by the linear momentum? These different choices are all valid 'representations' of quantum mechanics. (b) With the identification of $\hat{x}$ in this representation, what would be the operator for $1/x$? *Hint*: Think of $1/x$ as x^{-1}.

F2.4$^{\mathrm{LG}}$ Use mathematical software, a spreadsheet, or the *Living graphs* (labelled $^{\mathrm{LG}}$) on the website of this book to construct superpositions of cosine functions as

$$\psi(x)=\frac{1}{N}\sum_{k=1}^{N}\cos(k\pi x)$$

where the constant $1/N$ is introduced to keep the superpositions with the same overall magnitude. Explore how the probability density $\psi^2(x)$ changes with the value of N.

Mathematical background 2 Differential equations

A **differential equation** is a relation between a function and its derivatives, as in

$$a\frac{\mathrm{d}^2f}{\mathrm{d}x^2}+b\frac{\mathrm{d}f}{\mathrm{d}x}+cf=0 \qquad \text{(MB2.1)}$$

where f is a function of the variable x and the factors a, b, c may be either constants or functions of x. If the unknown function depends on only one variable, as in this example, the equation is called an **ordinary differential equation**; if it depends on more than one variable, as in

$$a\frac{\partial^2f}{\partial x^2}+b\frac{\partial^2f}{\partial y^2}+cf=0 \qquad \text{(MB2.2)}$$

it is called a **partial differential equation**. Here, f is a function of x and y, and the factors a, b, c may be either constants or functions of both variables. Note the change in symbol from d to ∂ to signify a *partial derivative* (see *Mathematical background* 1).

MB2.1 The structure of differential equations

The **order** of the differential equation is the order of the highest derivative that occurs in it: both examples above are second-order equations. Only rarely in science is a differential equation of order higher than 2 encountered.

A **linear differential equation** is one for which, if f is a solution, then so is constant × f. Both examples above are linear. If the 0 on the right were replaced by a different number or a function other than f, then they would cease to be linear.

Solving a differential equation means something different from solving an algebraic equation. In the latter case, the solution is a value of the variable x (as in the solution $x=2$ of the quadratic equation $x^2-4=0$). The solution of a differential equation is the entire function that satisfies the equation, as in

$$\frac{\mathrm{d}^2f}{\mathrm{d}x^2}+f=0, \quad f(x)=A\sin x+B\cos x \qquad \text{(MB2.3)}$$

with A and B constants. The process of finding a solution of a differential equation is called **integrating** the equation. The solution in eqn MB2.3 is an example of a **general solution** of a differential equation; that is, it is the most general solution of the equation and is expressed in terms of a number of constants (A and B in this case). When the constants are chosen to accord with certain specified **initial conditions** (if one variable is the time) or certain **boundary conditions** (to fulfil certain spatial restrictions on the solutions), we obtain the **particular solution** of the equation. The particular solution of a first-order differential equation requires one such condition; a second-order differential equation requires two.

Brief illustration MB2.1 Particular solutions

If we are informed that $f(0)=0$, then because from eqn MB2.3 it follows that $f(0)=B$, we can conclude that $B=0$. That still leaves A undetermined. If we are also told that $\mathrm{d}f/\mathrm{d}x=2$ at $x=0$ (that is, $f'(0)=2$, where the prime denotes a first derivative), then because the general solution (but with $B=0$) implies that $f'(x)=A\cos x$, we know that $f'(0)=A$, and therefore $A=2$. The particular solution is therefore $f(x)=2\sin x$. Figure MB2.1 shows a series of particular solutions corresponding to different boundary conditions.

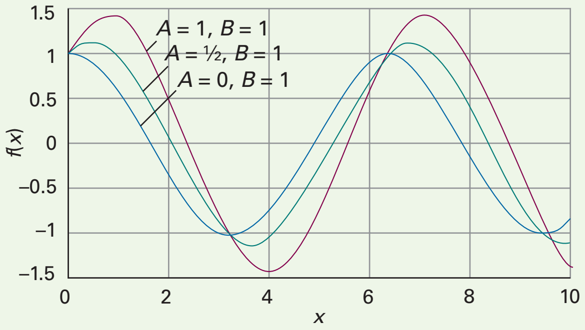


Figure MB2.1 The solution of the differential equation in *Brief illustration* MB2.1 with three different boundary conditions (as indicated by the resulting values of the constants *A* and *B*).

MB2.2 The solution of ordinary differential equations

The first-order linear differential equation

$$\frac{\mathrm{d}f}{\mathrm{d}x}+af=0 \qquad \text{(MB2.4a)}$$

with a a function of x or a constant can be solved by direct integration. To proceed, we use the fact that the quantities df and dx (called *differentials*) can be treated algebraically like any quantity and rearrange the equation into

$$\frac{\mathrm{d}f}{f}=-a\mathrm{d}x \qquad \text{(MB2.4b)}$$

and integrate both sides. For the left-hand side, we use the familiar result $\int \mathrm{d}y/y=\ln y+\text{constant}$. After pooling all the constants into a single constant C, we obtain:

$$\ln f(x)=-\int a\,\mathrm{d}x+C \qquad \text{(MB2.4c)}$$

Brief illustration MB2.2 The solution of a first-order equation

Suppose that in eqn MB2.4a the factor $a=2x$; then the general solution, eqn MB2.4c, is

$$\ln f(x)=-2\int x\,\mathrm{d}x+C=-x^2+C$$

(We have absorbed the constant of integration into the constant C.) Therefore

$$f(x)=N\mathrm{e}^{-x^2},\quad N=\mathrm{e}^C$$

If we are told that $f(0)=1$, then we can infer that $N=1$ and therefore that $f(x)=\mathrm{e}^{-x^2}$.

Even the solutions of first-order differential equations quickly become more complicated. A nonlinear first-order equation of the form

$$\frac{\mathrm{d}f}{\mathrm{d}x}+af=b \tag{MB2.5a}$$

with a and b functions of x (or constants) has a solution of the form

$$f(x)\mathrm{e}^{\int a\,\mathrm{d}x}=\int \mathrm{e}^{\int a\,\mathrm{d}x}b\,\mathrm{d}x+C \tag{MB2.5b}$$

as may be verified by differentiation. Mathematical software packages can often perform the required integrations.

Second-order differential equations are in general much more difficult to solve than first-order equations. One powerful approach commonly used to lay siege to second-order differential equations is to express the solution as a power series:

$$f(x)=\sum_{n=0}^{\infty}c_n x^n \tag{MB2.6}$$

and then to use the differential equation to find a relation between the coefficients. This approach results, for instance, in the Hermite polynomials that form part of the solution of the Schrödinger equation for the harmonic oscillator (Topic 12). Many of the second-order differential equations that occur in this text are tabulated in compilations of solutions or can be solved with mathematical software, and the specialized techniques that are needed to establish the form of the solutions may be found in mathematical texts.

MB2.3 The solution of partial differential equations

The only partial differential equations that we need to solve are those that can be separated into two or more ordinary differential equations by the technique known as **separation of variables**. To discover if the differential equation in eqn MB2.2 can be solved by this method we suppose that the full solution can be factored into functions that depend only on x or only on y, and write $f(x,y)=X(x)Y(y)$. At this stage there is no guarantee that the solution can be written in this way. Substituting this trial solution into the equation and recognizing that

$$\frac{\partial^2 XY}{\partial x^2}=Y\frac{\mathrm{d}^2X}{\mathrm{d}x^2}\quad \frac{\partial^2 XY}{\partial y^2}=X\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}$$

we obtain

$$aY\frac{\mathrm{d}^2X}{\mathrm{d}x^2}+bX\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}+cXY=0$$

We are using d instead of ∂ at this stage to denote differentials because each of the functions X and Y depend on one variable, x and y, respectively. Division through by XY turns this equation into

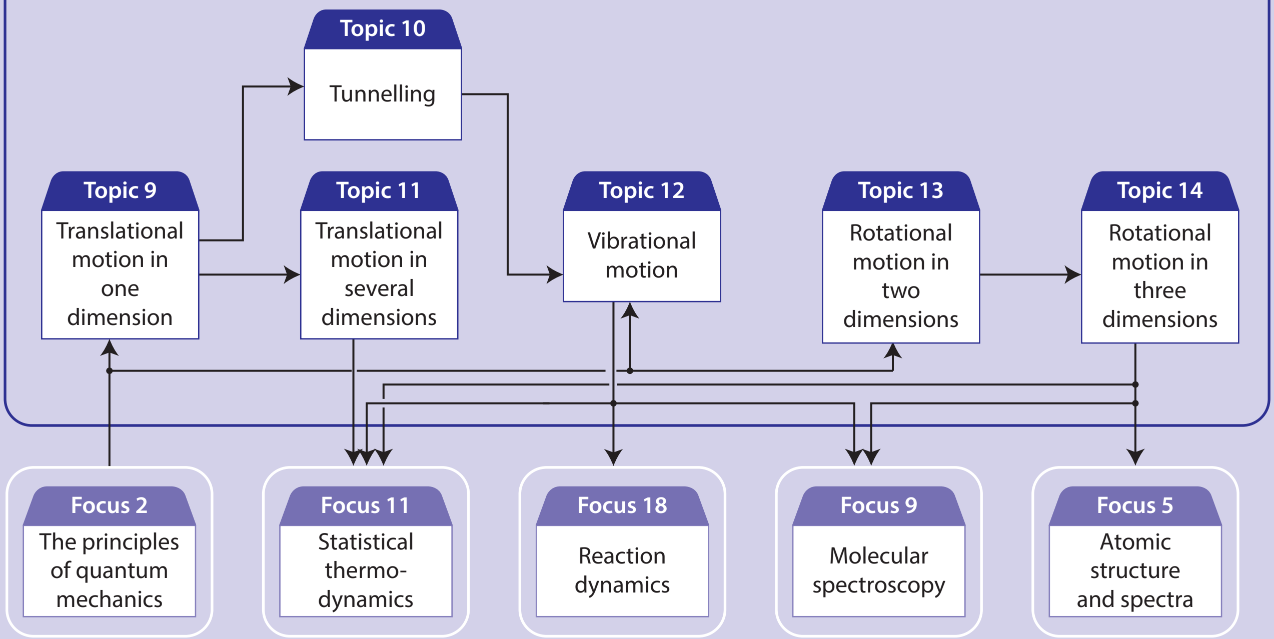
$$\frac{a}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2}+\frac{b}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}+c=0$$

Now suppose that a is a function only of x, b a function of y, and c a constant. (There are various other possibilities that permit the argument to continue.) Then the first term depends only on x and the second only on y. If x is varied, only the first term can change. But as the other two terms do not change and the sum of the three terms is a constant (0), even that first term must be a constant. The same is true of the second term. Therefore because each term is equal to a constant, we can write

$$\frac{a}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2}=c_1\quad \frac{b}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}=c_2\quad \text{with } c_1+c_2=-c$$

We now have two ordinary differential equations to solve by the techniques described in Section MB2.2. An example of this procedure is given in Topic 11, for a particle in a two-dimensional region.

FOCUS 3 ON The quantum mechanics of motion



One central feature of physical chemistry is its role in building models of atomic and molecular behaviour to explain observed phenomena. A prime example of this procedure is the approach developed in this group of Topics, where we solve the Schrödinger equations associated with simple models for translation, vibration, and rotation of particles. The key result is that only certain wavefunctions and energies are acceptable, and they are labelled by 'quantum numbers'. Insights derived from judicious application of the models developed here inform our understanding of structure (see, for example, *Atomic structure and spectra* and *Molecular spectroscopy*) and are starting points for the discussion of thermodynamics, as we see in *Statistical thermodynamics*.

Our model of translational motion is the 'particle in a box', a particle freely moving in one dimension between two impenetrable walls (**Topic 9**). The need for the wavefunction to satisfy certain conditions results in the quantization of energy. Quantum mechanics reveals another non-classical phenomenon: when the potential energy at the walls of the box is finite, the particle can pass into or through the walls even if classically it does not have enough energy to pass over the barrier. This behaviour, known as 'tunnelling' (**Topic 10**), explains a wide range of chemical and physical processes, such as proton and electron transfer. A natural and useful extension of this material is to translation in three dimensions (**Topic 11**).

A widely adopted model of vibrational motion in molecules is the 'harmonic oscillator' (**Topic 12**), in which the particle oscillates around an equilibrium position. The energy levels of a harmonic oscillator are quantized and, once again, we encounter tunnelling into classically forbidden regions.

The 'particle on a ring' (**Topic 13**) and the 'particle on a sphere' (**Topic 14**) are models for rotational motion in two and three dimensions, respectively. Here we encounter a new phenomenon: not only is the energy quantized but so too is the angular momentum.

What is the impact of this material?

Quantum mechanical effects in nanomaterials can render the properties of an assembly dependent on its size. In *Impact* 3.1, we focus on the origins and consequences of these effects in nanocrystals and quantum dots.

To read more about the impact of this material, scan the QR code, or go to http://bcs.whfreeman.com/webpub/chemistry/qmc2e/impact/qchem_impact3.html.

TOPIC 9

Translational motion in one dimension

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➤ Why do you need to know this material?

The application of quantum theory to one of the basic types of motion of particles, namely translation, reveals a number of non-classical features in a simple manner. These features are necessary for understanding a variety of microscopic phenomena, including conduction of electricity and properties of nanomaterials. They also reveal the origin of quantization, which has consequences throughout chemistry.

➤ What is the key idea?

The translational energy levels of a particle confined to a finite region of space are quantized.

➤ What do you need to know already?

You should know that the wavefunction is the solution of the Schrödinger equation (Topic 6) and be familiar with the techniques of deriving dynamical properties from the wavefunction by using operators corresponding to the observables (Topics 6 and 7).

This Topic presents the essential features of the solutions of the Schrödinger equation for one of the basic types of motion, namely translation. We shall see that only certain wavefunctions and their corresponding energies are acceptable; hence, quantization emerges as a natural consequence of the Schrödinger equation and the conditions imposed on it.

9.1 Free motion

The Schrödinger equation for a particle of mass m moving in one dimension is

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}+V(x)\psi(x)=E\psi(x) \quad \textit{One dimension, time-independent} \quad \text{Schrödinger equation} \qquad (9.1)$$

For a particle that is moving in the absence of any external forces, the potential energy is a constant, which can be chosen to be zero. The equation therefore becomes

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}=E\psi(x) \quad \textit{One dimension} \quad \text{Schrödinger equation for free motion} \qquad (9.2)$$

The general solutions of this equation are

$$\psi_k=A\mathrm{e}^{\mathrm{i}kx}+B\mathrm{e}^{-\mathrm{i}kx} \qquad E_k=\frac{k^2\hbar^2}{2m} \qquad (9.3)$$

with A and B constants, as may be verified by substitution. Note that we are now labelling both the wavefunctions and the energies (that is, the eigenfunctions and eigenvalues of $\hat{H}$) with the index k. The wavefunctions in eqn 9.3 are continuous, have continuous slope everywhere, are single-valued, and do not go to infinity, and so—in the absence of any other information—are acceptable for all values of k. Because the energy of the particle is proportional to k^2, all values of the energy are permitted. *It follows that the translational energy of a free particle is not quantized.*

The values of the constants A and B depend on how the state of motion of the particle is prepared:

- If it is shot towards positive x, then its linear momentum is $+k\hbar$ (see Topic 6), and its wavefunction is proportional to e^{ikx}. In this case $B=0$ and A is a normalization factor.
- If it is shot in the opposite direction, towards negative x, then its linear momentum is $-k\hbar$ and its wavefunction is proportional to e^{-ikx}. In this case, $A=0$ and B is the normalization factor.

Although the wavefunction for a free particle, $e^{\pm ikx}$, is not square-integrable in a region of infinite length ($\psi^*\psi$ is a constant, and its integral over all space is therefore infinite), we can get round this problem by assuming that the particle is in a finite region of length L, normalizing the wavefunction, and then, at the end of any subsequent calculation using the wavefunction, allowing L to become infinite (see Problem 9.5).

Brief illustration 9.1 The wavefunction of a freely moving particle

An electron at rest that is shot out of an accelerator towards positive x through a potential difference of 1.0 V acquires a kinetic energy of 1.0 eV or 1.6×10^{-19} J. The wavefunction for such a particle is given by eqn 9.3 with $B=0$ and k given by rearranging eqn 9.3 into

$$k=\left(\frac{2m_eE_k}{\hbar^2}\right)^{1/2}=\left(\frac{2\times(9.109\times10^{-31}\,\text{kg})\times(1.6\times10^{-19}\,\text{J})}{(1.055\times10^{-34}\,\text{J s})^2}\right)^{1/2}$$
$$=5.1\times10^{9}\,\text{m}^{-1}$$

or 5.1 nm^{-1} (with 1 nm = 10^{-9} m). Therefore the wavefunction is $\psi(x)=Ae^{5.1ix/\text{nm}}$.

Self-test 9.1 Write the wavefunction for an electron travelling to the left (negative x) after being accelerated through a potential difference of 10 kV.

Answer: $\psi(x)=Be^{-510ix/\text{nm}}$

The probability density $|\psi|^2$ is uniform if the particle is in either of the pure momentum states e^{ikx} or e^{-ikx}. According to the Born interpretation (Topic 5), nothing further can be said about the location of the particle. That conclusion is consistent with the uncertainty principle, because if the momentum is certain, then the position cannot be specified (the operators corresponding to x and p do not commute and thus correspond to complementary observables, Topic 8).

A final point in this connection is that the wavefunctions e^{ikx} and e^{-ikx} illustrate a general feature of quantum mechanics: a particle with net motion is described by a complex wavefunction (complex in the sense of depending on $i=(-1)^{1/2}$ and having both real and imaginary parts). A wavefunction that is purely real corresponds to zero net motion. For instance, if $\psi(x)=\cos kx$, then the expectation value of the linear momentum is zero ($\langle p\rangle=0$, Topic 7).

9.2 Confined motion: the particle in a box

In this section, we consider a **particle in a box**, in which a particle of mass m is confined to a finite region of space between two impenetrable walls. The potential energy is zero inside the box but rises abruptly to infinity at the walls at $x=0$ and $x=L$ (Fig. 9.1). The potential energy of the particle is given by

$$\begin{aligned}&\text{For } x\le 0 \text{ and } x\ge L: && V=\infty\\ &\text{For } 0<x<L: && V=0\end{aligned}$$

When the particle is between the walls, the Schrödinger equation is the same as for a free particle (eqn 9.2), so the general solutions given in eqn 9.3 are also the same. However, it will prove convenient to use $e^{\pm ikx}=\cos kx\pm i\sin kx$ to write

$$\begin{aligned}\psi_k(x)&=Ae^{ikx}+Be^{-ikx}=A(\cos kx+i\sin kx)+B(\cos kx-i\sin kx)\\&=(A+B)\cos kx+(A-B)i\sin kx\end{aligned}$$

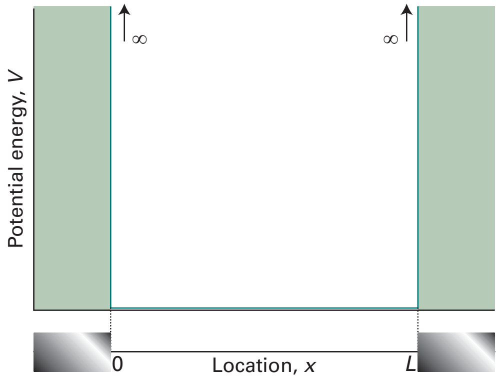


Figure 9.1 A particle in a one-dimensional region with impenetrable walls. Its potential energy is zero between $x=0$ and $x=L$, and rises abruptly to infinity as soon as it touches the walls.

If we write $C=(A-B)\mathrm{i}$ and $D=A+B$ the general solutions take the form

$$\psi_k(x)=C\sin kx+D\cos kx \qquad \text{General solution for } 0<x<L \tag{9.4}$$

At the walls and outside the box the wavefunctions must be zero as the particle will not be found in a region where its potential energy is infinite:

$$\text{For } x\leq 0 \text{ and } x\geq L, \qquad \psi_k(x)=0 \tag{9.5}$$

At this point, there are no restrictions on the value of k and all solutions appear to be acceptable.

(a) The acceptable solutions

The requirement of the continuity of the wavefunction (Topic 5) implies that $\psi_k(x)$ as given by eqn 9.4 must be zero at the walls, for it must match the wavefunction (eqn 9.5) inside the material of the walls where the functions meet. That is, the wavefunction must satisfy the following two **boundary conditions**, or constraints on the function at certain locations:

$$\psi_k(0)=0 \quad \text{and} \quad \psi_k(L)=0 \qquad \text{Boundary conditions} \tag{9.6}$$

As we show in the following *Justification*, the requirement that the wavefunction satisfy these boundary conditions implies that only certain wavefunctions are acceptable and that the only permitted wavefunctions and energies of the particle are

$$\psi_n(x)=C\sin\left(\frac{n\pi x}{L}\right) \qquad n=1,2,\ldots \tag{9.7a}$$

$$E_n=\frac{n^2h^2}{8mL^2} \qquad n=1,2,\ldots \tag{9.7b}$$

where C is an as yet undetermined constant. Note that the wavefunctions and energy are now labelled with the dimensionless integer n instead of the quantity k.

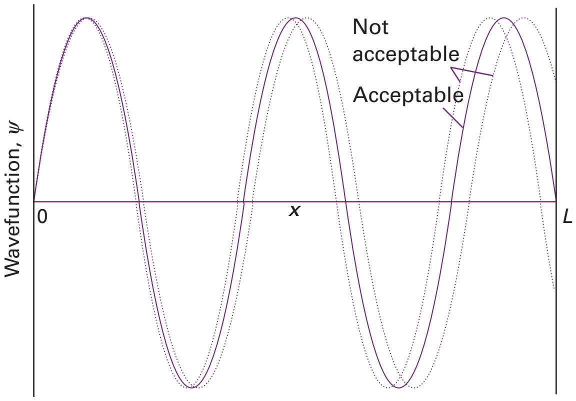


Figure 9.2 An acceptable wavefunction must have a de Broglie wavelength such that the wave fits into the box.

Justification 9.1 The energy levels and wavefunctions of a particle in a one-dimensional box

For an informal demonstration of quantization, we consider each wavefunction to be a de Broglie wave that fits into the container in the sense that an integral number of half-wavelengths (one bulge, two bulges, …, Fig. 9.2) is equal to the length of the box:

$$n\times\frac{1}{2}\lambda=L \qquad n=1,2,\ldots$$

and therefore

$$\lambda=\frac{2L}{n} \quad \text{with} \quad n=1,2,\ldots$$

According to the de Broglie relation, these wavelengths correspond to the momenta

$$p=\frac{h}{\lambda}=\frac{nh}{2L}$$

The particle has only kinetic energy inside the box (where $V=0$), so the permitted energies are

$$E=\frac{p^2}{2m}=\frac{n^2h^2}{8mL^2} \quad \text{with} \quad n=1,2,\ldots$$

as in eqn 9.7b.

A more formal and more widely applicable approach is as follows. From the boundary condition $\psi_k(0)=0$ and the fact that, from eqns 9.4 and 9.5, $\psi_k(0)=D$ (because $\sin 0=0$ and $\cos 0=1$), we can conclude that $D=0$. It follows that the wavefunction must be of the form

$$\psi_k(x)=C\sin kx$$

From the second boundary condition, $\psi_k(L)=0$, we know that $\psi_k(L)=C\sin kL=0$. We could take $C=0$, but doing so would give $\psi_k(x)=0$ for all x, which would conflict with the Born interpretation (the particle must be somewhere). The alternative is to require that kL be chosen so that $\sin kL=0$. This condition is satisfied if

$$kL=n\pi \qquad n=1,2,\ldots$$

The value $n=0$ is ruled out, because it implies $k=0$ and $\psi_k(x)=0$ everywhere (because $\sin 0=0$), which is unacceptable. Negative values of n merely change the sign of $\sin kL$ (because $\sin(-x)=-\sin x$) and do not result in new solutions. The wavefunctions are therefore

$$\psi_n(x)=C\sin(n\pi x/L) \quad n=1,2,\ldots$$

At this stage we have begun to label the solutions with the index n instead of k. Because k and E_k are related by eqn 9.3, and k and n are related by $kL=n\pi$, it follows that the energy of the particle is limited to $E_n=n^2h^2/8mL^2$, the values obtained by the informal procedure and stated in eqn 9.7.

We conclude that the energy of the particle in a one-dimensional box is quantized and that this quantization arises from the boundary conditions that ψ must satisfy. This is a general conclusion: *the need to satisfy boundary conditions implies that only certain wavefunctions are acceptable, and hence restricts observables to discrete values.* So far, only energy has been quantized; shortly we shall see that other physical observables may also be quantized.

We need to determine the constant C in eqn 9.7. To do so, we normalize the wavefunction to 1 by using Integral T.2 given in the *Resource section* and used in Example 5.2. Because the wavefunction is zero outside the range $0 \le x \le L$, we use

$$\int_0^L \psi^2 \mathrm{d}x = C^2 \overbrace{\int_0^L \sin^2 \frac{n\pi x}{L}\mathrm{d}x}^{L/2} = C^2 \times \frac{L}{2} = 1, \qquad \text{so } C = \left(\frac{2}{L}\right)^{1/2}$$

for all n. Therefore, the complete solution for the particle in a box is

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \quad \text{for } 0 \le x \le L$$

$$\psi_n(x) = 0 \quad \text{for } x < 0 \text{ and } x > L$$

One-dimensional box Wavefunctions (9.8a)

$$E_n = \frac{n^2 h^2}{8mL^2} \qquad n = 1, 2, \ldots$$

One-dimensional box Energy levels (9.8b)

Brief illustration 9.2 The energy of a particle in a box

A long carbon nanotube can be modelled as a one-dimensional structure and its electrons described by particle-in-a-box wavefunctions. The lowest energy of an electron in a carbon nanotube of length 100 nm is given by eqn 9.8b with $n = 1$:

$$E_1 = \frac{(1)^2 \times (6.626 \times 10^{-34}\,\mathrm{J\,s})^2}{8 \times (9.109 \times 10^{-31}\,\mathrm{kg}) \times (100 \times 10^{-9}\,\mathrm{m})^2} = 6.02 \times 10^{-24}\,\mathrm{J}$$

and its wavefunction is

$$\psi_1(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right)$$

Self-test 9.2 What are the energy and wavefunction for the next-higher energy electron of the system described in this *Brief illustration*?

Answer: $E_2 = 2.41 \times 10^{-23}$ J, $\psi_2(x) = (2/L)^{1/2} \sin(2\pi x/L)$

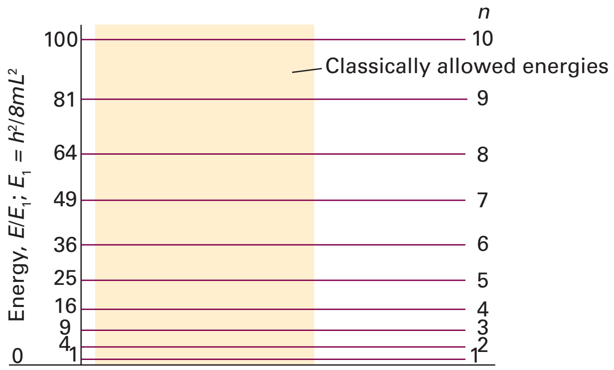


Figure 9.3 The allowed energy levels for a particle in a box. Note that the energy levels increase as n^2, and that their separation increases as the quantum number increases.

As we have seen, the energies and wavefunctions are labelled with the quantum number n. A **quantum number** is an integer (in some cases, as we see in Topic 19, a half-integer) that labels the state of the system. For a particle in a one-dimensional box there are an infinite number of acceptable solutions, and the quantum number n specifies the one of interest (Fig. 9.3). As well as acting as a label, a quantum number can often be used to calculate the energy corresponding to the state and to write down the wavefunction explicitly (in the present example, by using the relations in eqn 9.8). A list of the quantum numbers commonly encountered in quantum mechanics is collected in the *Resource Section* at the end of the text.

(b) The properties of the wavefunctions

Figure 9.4 shows some of the wavefunctions of a particle in a one-dimensional box: they are all sine functions with the same amplitude but different wavelengths. Shortening the wavelength results in a sharper average curvature of the wavefunction and therefore an increase in the kinetic energy of the particle (its only source of energy because $V = 0$ inside the box). Note that the number of **nodes**, which are points where the wavefunction passes *through* zero (not merely reaching zero, as at the walls), also increases as n increases, and that the wavefunction ψ_n has $n - 1$ nodes. Increasing the number of nodes between walls of a given separation increases the average curvature of the wavefunction and hence the kinetic energy of the particle.

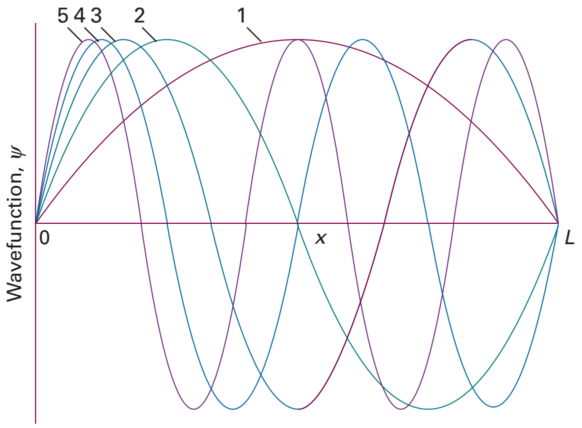


Figure 9.4 The first five normalized wavefunctions of a particle in a box. Each wavefunction is a standing wave, and successive functions possess one more half-wave and a correspondingly shorter wavelength.

Brief illustration 9.3 The nodes in a particle-in-a-box wavefunction

The wavefunction for a particle in a one-dimensional box with $n=2$ has a node where $\sin(2\pi x/L)=0$, that is at $x=L/2$. Its location can also be identified by inspection of Fig. 9.4, where we see that $\psi_2(x)$ passes through zero at the centre of the box.

Self-test 9.3 Locate the nodes for a particle in a one-dimensional box with $n=3$.

Answer: $x=L/3, 2L/3$

The probability density for a particle in a one-dimensional box is

$$\psi_n^2(x)=\frac{2}{L}\sin^2\left(\frac{n\pi x}{L}\right) \tag{9.9}$$

and varies with position. The non-uniformity in the probability density is pronounced when n is small (Fig. 9.5). The most probable locations of the particle correspond to the maxima in the probability density.

Brief illustration 9.4 The most probable locations of a particle in a box

A particle in a box with $n=2$ has a probability density given by

$$\psi_2^2(x)=\frac{2}{L}\sin^2\left(\frac{2\pi x}{L}\right)$$

The most probable locations occur where $\sin^2(2\pi x/L)=1$, that is, at $x=L/4$ and $3L/4$.

Self-test 9.4 Determine the most likely locations of a particle in a one-dimensional box with $n=3$.

Answer: $x=L/6, L/2, 5L/6$

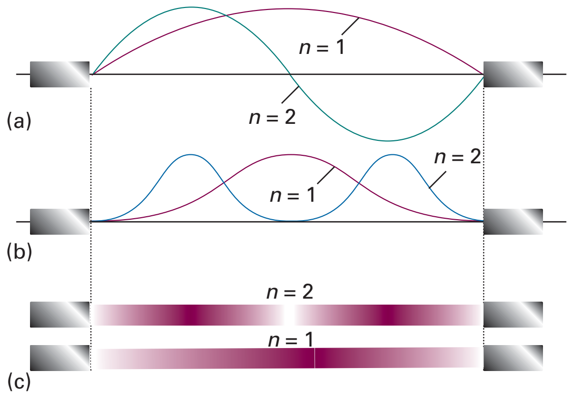


Figure 9.5 (a) The first two wavefunctions, (b) the corresponding probability densities, and (c) a representation of the probability density in terms of the darkness of shading.

The probability density $\psi^2(x)$ becomes more uniform as n increases, provided we ignore the fine detail of the increasingly rapid oscillations (Fig. 9.6). The probability density at high quantum numbers reflects the classical result that a particle bouncing between the walls spends, on the average, equal times at all points. That the quantum result corresponds to the classical prediction at high quantum numbers is an illustration of the **correspondence principle**, which states that classical mechanics emerges from quantum mechanics as high quantum numbers are reached.

Example 9.1 Determining the probability of finding the particle in a finite region

The wavefunctions of an electron in a conjugated polyene can be approximated by particle-in-a-box wavefunctions. What is the probability, P, of locating the electron between $x=0$ (the left-hand end of a molecule) and $x=0.2\,\text{nm}$ in its lowest energy state in a conjugated molecule of length 1.0 nm?

Method According to the Born interpretation, $\psi(x)^2\mathrm{d}x$ is the probability of finding the particle in the small region $\mathrm{d}x$ located at x; therefore, the total probability of finding the electron in the specified region is the integral of $\psi(x)^2\mathrm{d}x$ over that region, as given in eqn 5.5. We use the model of a particle in a box to describe the electron in the conjugated polyene. The wavefunction of the electron is given in eqn 9.8 with $n=1$. Use Integral T.2 listed in the *Resource section*.

Answer The probability of finding the particle in a region between $x=0$ and $x=l$ is

$$P=\int_0^l \psi_n^2\mathrm{d}x=\frac{2}{L}\int_0^l \sin^2\left(\frac{n\pi x}{L}\right)\mathrm{d}x=\frac{l}{L}-\frac{1}{2n\pi}\sin\left(\frac{2\pi nl}{L}\right)$$

Now set $n=1$, $L=1.0\,\text{nm}$, and $l=0.2\,\text{nm}$, which gives $P=0.05$. The result corresponds to a chance of 1 in 20 of finding the electron in the region. As n becomes infinite, the sine term, which is multiplied by $1/n$, makes no contribution to P and the classical result for a uniformly distributed particle, $P=l/L$, is obtained.

Self-test 9.5 Calculate the probability that an electron in the state with $n=1$ will be found between $x=0.25L$ and $x=0.75L$ in a conjugated molecule of length L (with $x=0$ at the left-hand end of the molecule).

Answer: $P=0.82$

(c) The properties of observables

The linear momentum of a particle in a box is not well defined because the wavefunction $\sin kx$ is not an eigenfunction of the linear momentum operator. However, each wavefunction is a linear combination of the linear momentum eigenfunctions e^{ikx} and e^{-ikx}. Then, because $\sin x=(e^{ix}-e^{-ix})/2i$, we can write

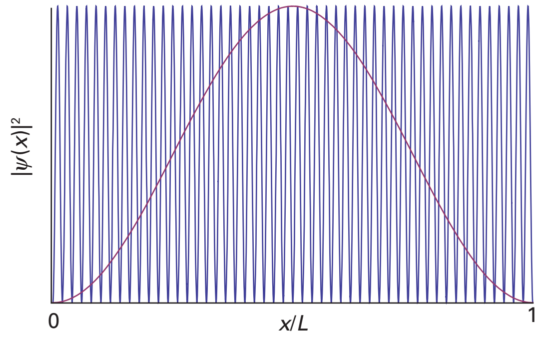


Figure 9.6 The probability density $\psi^2(x)$ for large quantum number (here $n=50$, blue, compared with $n=1$, red). Notice that for high n the probability density is nearly uniform, provided we ignore the fine detail of the increasingly rapid oscillations.

$$\psi_n(x)=\left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)=\frac{1}{2\mathrm{i}}\left(\frac{2}{L}\right)^{1/2}(\mathrm{e}^{\mathrm{i}kx}-\mathrm{e}^{-\mathrm{i}kx})\qquad k=\frac{n\pi}{L} \tag{9.10}$$

It follows (Topic 7) that measurement of the linear momentum will give the value $+k\hbar$ for half the measurements of momentum and $-k\hbar$ for the other half. This detection of opposite directions of travel with equal probability is the quantum mechanical version of the classical picture that a particle in a one-dimensional box rattles from wall to wall and in any given period spends half its time travelling to the left and half travelling to the right.

Brief illustration 9.5 The expectation value of linear momentum

The measurement of the linear momentum for a particle in a box with quantum number n will give $+k\hbar$ for half the measurements and $-k\hbar$ for the other half (where $k=n\pi/L$). Therefore, the expectation value of the linear momentum is zero. This result can also be obtained more formally from

$$\langle p\rangle=\int_0^L \psi_n\hat{p}\psi_n\mathrm{d}x=\frac{2}{L}\int_0^L \sin\frac{n\pi x}{L}\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right)\sin\frac{n\pi x}{L}\mathrm{d}x=0$$

where we have used Integral T.7 listed in the *Resource section*.

Self-test 9.6 What is the expectation value of p^2 of a particle in a one-dimensional box with quantum number n?

Answer: $\langle p^2\rangle=n^2h^2/4L^2$

Because n cannot be zero, the lowest energy that the particle may possess is not zero (as would be allowed by classical mechanics, corresponding to a stationary particle) but

$$E_1=\frac{h^2}{8mL^2}\qquad \textit{Particle in a box}\quad \text{Zero-point energy} \tag{9.11}$$

This lowest, irremovable energy is called the **zero-point energy**. The physical origin of the zero-point energy can be explained in two ways:

- The Heisenberg uncertainty principle requires a particle to possess kinetic energy if it is confined to a finite region: the location of the particle is not completely indefinite ($\Delta x\neq\infty$), so the uncertainty in its momentum cannot be precisely zero ($\Delta p\neq 0$). Because $\Delta p=(\langle p^2\rangle-\langle p\rangle^2)^{1/2}=\langle p^2\rangle^{1/2}$ in this case, $\Delta p\neq 0$ implies that $\langle p^2\rangle\neq 0$, which implies that the particle must always have nonzero kinetic energy.
- If the wavefunction is to be zero at the walls, but smooth, continuous, and not zero everywhere, then it must be curved, and curvature in a wavefunction implies the possession of kinetic energy.

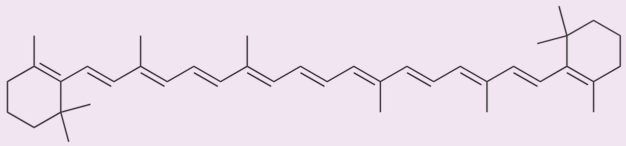
The separation between adjacent energy levels with quantum numbers n and $n+1$ is

$$E_{n+1}-E_n=\frac{(n+1)^2h^2}{8mL^2}-\frac{n^2h^2}{8mL^2}=(2n+1)\frac{h^2}{8mL^2} \tag{9.12}$$

This separation decreases as the length of the container increases, and is very small when the container has macroscopic dimensions. The separation of adjacent levels becomes zero when the walls are infinitely far apart. Atoms and molecules free to move in normal laboratory-sized vessels may therefore be treated as though their translational energy is not quantized.

Example 9.2 Estimating an absorption wavelength

β-Carotene (**1**) is a linear polyene in which 10 single and 11 double bonds alternate along a chain of 22 carbon atoms. If we take each C—C bond length to be about 140 pm, then the length L of the molecular box in β-carotene is $L=2.94$ nm. Estimate the wavelength of the light absorbed by this molecule from its ground state to the next-higher excited state.



1 β-Carotene

Method For reasons that will be familiar from introductory chemistry, each C atom contributes one p electron to the π-orbitals and each energy level can be occupied by two electrons. Use the particle-in-a-box model to describe the state of the electrons in the polyene and calculate the energy separation between the highest occupied and the lowest unoccupied levels. Use eqn 9.12 and then convert that energy to a wavelength by using the Bohr frequency relation (eqn 4.4).

Answer There are 22 C atoms in the conjugated chain; each contributes one p electron to the levels, so each level up to $n=11$ is occupied by two electrons. The separation in energy between the ground state and the state in which one electron is promoted from $n=11$ to $n=12$ is

$$\begin{aligned}\Delta E &= E_{12}-E_{11}\\ &=(2\times 11+1)\frac{(6.626\times 10^{-34}\,\mathrm{J\,s})^2}{8\times(9.109\times 10^{-31}\,\mathrm{kg})\times(2.94\times 10^{-9}\,\mathrm{m})^2}\\ &=1.60\times 10^{-19}\,\mathrm{J}\end{aligned}$$

It follows from the Bohr frequency condition ($\Delta E = h\nu$) that the frequency of radiation required to cause this transition is

$$\nu=\frac{\Delta E}{h}=\frac{1.60\times 10^{-19}\,\mathrm{J}}{6.626\times 10^{-34}\,\mathrm{J\,s}}=2.41\times 10^{14}\,\mathrm{s}^{-1}$$

or 241 THz (1 THz $=10^{12}$ Hz), corresponding to a wavelength $\lambda=1240$ nm. The experimental value is 603 THz ($\lambda=497$ nm), corresponding to radiation in the visible range of the electromagnetic spectrum. Considering the crudeness of the model we have adopted here, we should be encouraged that the computed and observed frequencies agree to within a factor of 2.5.

Self-test 9.7 Estimate a typical nuclear excitation energy in electronvolts (1 eV $=1.602\times 10^{-19}$ J; 1 GeV $=10^9$ eV) by calculating the first excitation energy of a proton confined to a one-dimensional box with a length equal to the diameter of a nucleus (approximately 1×10^{-15} m, or 1 fm).

Answer: 0.6 GeV

Checklist of concepts

☐ **1.** The translational energy of a free particle is not quantized.

☐ **2.** A particle with net motion is described by a complex wavefunction. A real wavefunction corresponds to zero net motion.

☐ **3.** The need to satisfy boundary conditions implies that only certain wavefunctions are acceptable and therefore restricts observables to discrete values.

☐ **4.** A **quantum number** is an integer (in certain cases, a half-integer) that labels the state of the system.

☐ **5.** **Nodes** are points where the wavefunction passes through zero.

☐ **6.** A particle in a box possesses a **zero-point energy**.

☐ **7.** The **correspondence principle** states that classical mechanics emerges from quantum mechanics as high quantum numbers are reached.

Checklist of equations

Property	Equation	Comment	Equation number
Free-particle wavefunction	$\psi_k = A\mathrm{e}^{\mathrm{i}kx}+B\mathrm{e}^{-\mathrm{i}kx}$	All values of k allowed	9.3
Free-particle energy	$E_k = k^2\hbar^2/2m$	All values of k allowed	9.3
Particle-in-a-box wavefunction	$\psi_n(x)=(2/L)^{1/2}\sin(n\pi x/L)$ for $0\le x\le L$ $\psi_n(x)=0$ for $x<0$ and $x>L$	$n=1, 2, \ldots$	9.8a
Particle-in-a-box energy	$E_n = n^2h^2/8mL^2$	$n=1, 2, \ldots$	9.8b
Zero-point energy for particle in a box	$E_1 = h^2/8mL^2$		9.11

TOPIC 10

Tunnelling

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➤ Why do you need to know this material?

The quantum mechanical phenomenon known as tunnelling is necessary to explain a wide range of chemical and physical processes, including electron and proton transfer reactions and conformational changes in molecules.

➤ What is the key idea?

Tunnelling, the passage of a particle into or through a classically forbidden region, can occur when potential energy barriers do not rise abruptly to infinity.

➤ What do you need to know already?

You need to be familiar with the postulates of quantum theory (Topics 5–7) and the solutions of the Schrödinger equation for the particle in a box (Topic 9).

Topic 9 presents the solution of the Schrödinger equation for a particle confined between two walls with potential energy barriers that rise abruptly to infinity and prevent the particle from being found outside the walls. However, potential barriers do not rise to infinity in real systems and, for potentials such as that shown in Fig. 10.1, particles are able to penetrate into and through regions where classical physics would forbid them to be found. This phenomenon has very important implications for the electronic properties of materials, for the rates of electron transfer reactions (Topic 94), for the properties of acids and bases, and for the techniques currently used to study surfaces.

10.1 The rectangular potential energy barrier

Consider a particle incident from the left on a **rectangular potential energy barrier**, a one-dimensional barrier of constant height and finite width (Fig. 10.2). If the energy of the particle, E, is less than the potential barrier height, V, then according to classical mechanics the particle will be reflected off the potential wall. However, according to quantum theory, when the particle is inside the region representing the barrier, its wavefunction does not decay abruptly to zero but rather varies smoothly and then, on the far side of the barrier, oscillates again. The net result is penetration through the classically forbidden region, the phenomenon known as **tunnelling**.

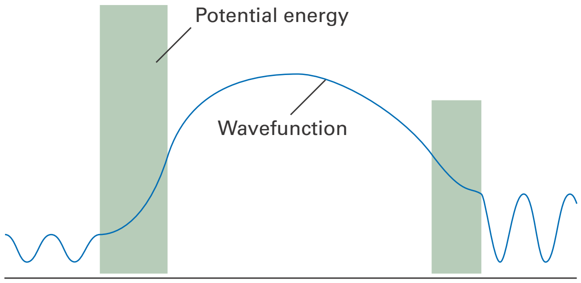


Figure 10.1 Potential energy barriers do not rise abruptly to infinity in real systems. In the arrangement shown here, a particle placed in the well between the potential barriers can penetrate into and through the barriers on either side of the well.

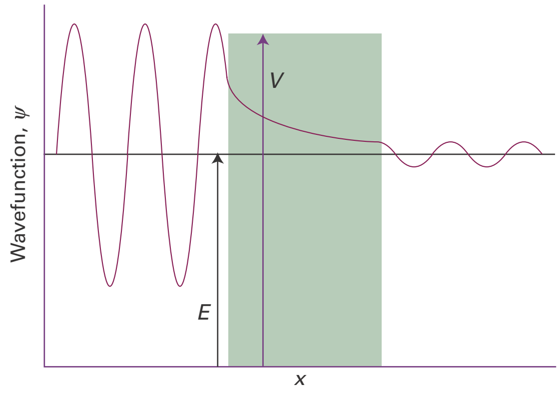


Figure 10.2 A rectangular potential energy barrier of constant height and finite width. A particle incident on the barrier from the left has an oscillating wavefunction, but inside the barrier there are no oscillations (for $E<V$). If the barrier is not too thick, the wavefunction is nonzero at its opposite face, and so oscillations begin again there. (Only the real component of the wavefunction is shown.)

The Schrödinger equation is used to calculate the probability of tunnelling of a particle of mass m incident from the left on a rectangular potential energy that extends from $x=0$ to $x=L$. On the left of the barrier ($x<0$) the wavefunctions are those of a particle with $V=0$, so from eqn 9.3 we can write

$$\psi = Ae^{ikx} + Be^{-ikx} \qquad k\hbar = (2mE)^{1/2} \tag{10.1}$$

Wavefunction left of barrier

Particle in a rectangular barrier

The Schrödinger equation for the region representing the barrier ($0 \le x \le L$), where the potential energy is the constant V, is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V\psi(x) = E\psi(x) \tag{10.2}$$

We shall consider particles that have $E<V$ (so, according to classical physics, the particle has insufficient energy to pass through the barrier), and therefore for which $V-E>0$. The general solutions of this equation are

$$\psi = Ce^{\kappa x} + De^{-\kappa x} \qquad \kappa\hbar = \{2m(V-E)\}^{1/2} \tag{10.3}$$

Wavefunction inside barrier

Particle in a rectangular barrier

as can be verified by differentiating ψ twice with respect to x. The important feature to note is that the two exponentials in eqn 10.3 are now real functions, as distinct from the complex, oscillating functions for the region where $V=0$. To the right of the barrier ($x>L$), where $V=0$ again, the wavefunctions are

$$\psi = A'e^{ikx} \qquad k\hbar = (2mE)^{1/2} \tag{10.4}$$

Wavefunction right of barrier

Particle in a rectangular barrier

Note that to the right of the barrier, the particle can only be moving to the right and therefore terms of the form e^{-ikx} do not contribute to the wavefunction in eqn 10.4.

The complete wavefunction for a particle incident from the left consists of (Fig. 10.3):

- an incident wave (Ae^{ikx} corresponds to positive momentum);
- a wave reflected from the barrier (Be^{-ikx} corresponds to negative momentum, motion to the left);
- the exponentially changing amplitudes inside the barrier (eqn 10.3);
- an oscillating wave (eqn 10.4) representing the propagation of the particle to the right after tunnelling through the barrier successfully.

Physical interpretation

The probability that a particle is travelling towards positive x (to the right) on the left of the barrier ($x<0$) is proportional to $|A|^2$, and the probability that it is travelling to the right on the right of the barrier ($x>L$) is $|A'|^2$. The ratio of these two probabilities, $|A'|^2/|A|^2$, which reflects the probability of the particle tunnelling through the barrier, is called the **transmission probability**, T.

To determine the relationship between $|A'|^2$ and $|A|^2$, we need to investigate the relationships between the coefficients A, B, C, D, and A'. Since the acceptable wavefunctions must be continuous at the edges of the barrier (at $x=0$ and $x=L$, remembering that $e^0=1$),

$$A+B=C+D \qquad Ce^{\kappa L}+De^{-\kappa L}=A'e^{ikL} \tag{10.5a}$$

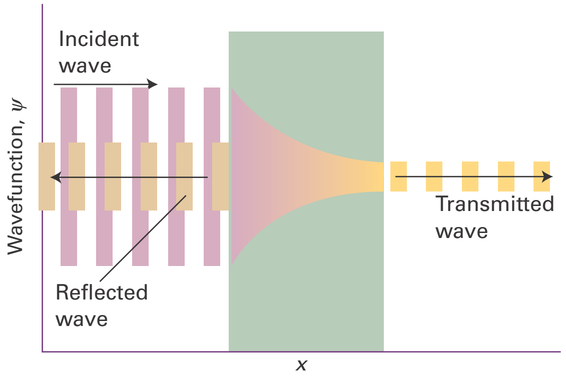


Figure 10.3 When a particle is incident on a barrier from the left, the wavefunction consists of a wave representing linear momentum to the right, a reflected component representing momentum to the left, a varying but not oscillating component inside the barrier, and a (weak) wave representing motion to the right on the far side of the barrier.

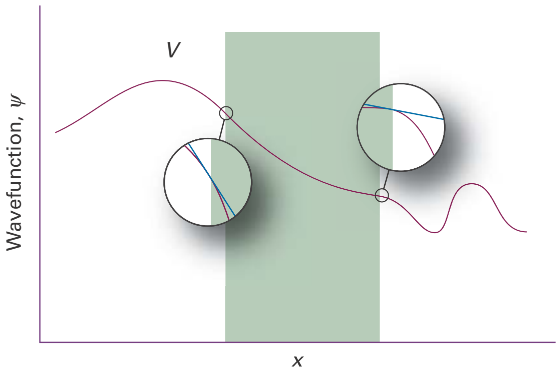


Figure 10.4 The wavefunction and its slope must be continuous at the edges of the barrier. The conditions for continuity enable us to connect the wavefunctions in the three zones and hence to obtain relations between the coefficients that appear in the solutions of the Schrödinger equation.

Their slopes (their first derivatives) must also be continuous there (Fig. 10.4):

$$ikA - ikB = \kappa C - \kappa D \qquad \kappa C e^{\kappa L} - \kappa D e^{-\kappa L} = ikA' e^{ikL} \tag{10.5b}$$

After straightforward but lengthy algebraic manipulations of the above set of equations 10.5 (see Problem 10.1), it turns out that

$$T = \left\{1 + \frac{(e^{\kappa L} - e^{-\kappa L})^2}{16\varepsilon(1-\varepsilon)}\right\}^{-1} \tag{10.6}$$

Rectangular potential barrier

Transmission probability

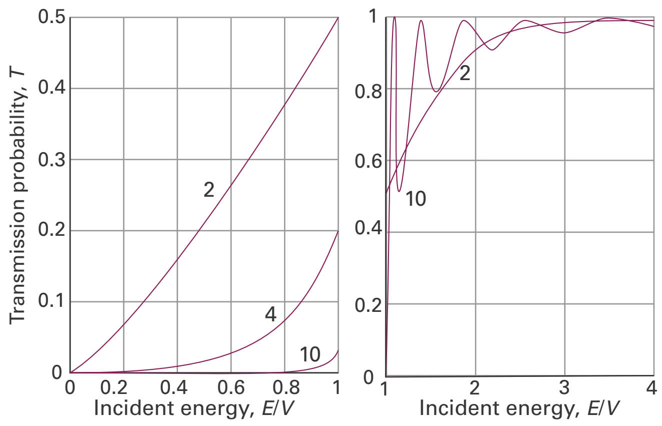


Figure 10.5 The transmission probabilities for passage through a rectangular potential barrier. The horizontal axis is the energy of the incident particle expressed as a multiple of the barrier height. The curves are labelled with the value of $L(2mV)^{1/2}/\hbar$. The graph on the left is for $E < V$ and that on the right for $E > V$. Note that $T > 0$ for $E < V$ whereas classically T would be zero. However, $T < 1$ for $E > V$, whereas classically T would be 1.

where $\varepsilon = E/V$. This function is plotted in Fig. 10.5. The transmission probability for $E > V$ (which you are invited to calculate in Problem 10.2) is shown there too. The transmission probability has the following properties:

Physical interpretation

- $T \approx 0$ for $E \ll V$;
- T increases as E approaches V: the probability of tunnelling increases;
- T approaches, but is still less than, 1 for $E > V$: there is still a probability of the particle being reflected by the barrier even when classically it can pass over it;
- $T \approx 1$ for $E >> V$, as expected classically.

For high, wide barriers (in the sense that $\kappa L \gg 1$), eqn 10.6 simplifies to

$$T \approx 16\varepsilon(1-\varepsilon)e^{-2\kappa L} \tag{10.7}$$

The transmission probability decreases exponentially with the thickness of the barrier and with $m^{1/2}$. It follows that particles of low mass are more able to tunnel through barriers than heavy ones (Fig. 10.6). Tunnelling is very important for electrons and muons ($m_\mu \approx 207m_e$), and moderately important for protons ($m_p \approx 1840m_e$); for heavier particles it is less important.

A number of effects in chemistry (for example, the isotope dependence of some reaction rates) depend on the ability of the proton to tunnel more readily than the deuteron. The very rapid equilibration of proton-transfer reactions is also a manifestation of the ability of protons to tunnel through barriers and transfer quickly from an acid to a base. Tunnelling of protons between acidic and basic groups is also an important feature of the mechanism of some enzyme-catalysed reactions.

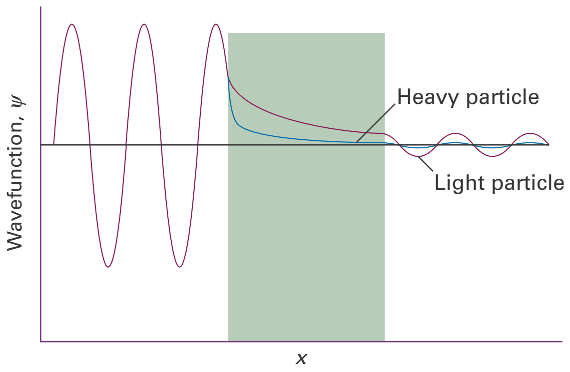


Figure 10.6 The wavefunction of a heavy particle decays more rapidly inside a barrier than that of a light particle. Consequently, a light particle has a greater probability of tunnelling through the barrier.

Brief illustration 10.1 Transmission probabilities for a rectangular barrier

Suppose that a proton of an acidic hydrogen atom is confined to an acid that can be represented by a barrier of height 2.000 eV and length 100 pm. The probability that a proton with energy 1.995 eV (corresponding to 3.195×10^{-19} J) can escape from the acid is computed using eqn 10.6, with $\varepsilon = E/V = 1.995\,\text{eV}/2.000\,\text{eV} = 0.9975$ and $V - E = 0.005$ eV (corresponding to 8.0×10^{-22} J).

$$\kappa = \frac{\{2\times(1.67\times10^{-27}\,\text{kg})\times(8.0\times10^{-22}\,\text{J})\}^{1/2}}{1.055\times10^{-34}\,\text{J s}}$$
$$= 1.55\ldots\times10^{10}\,\text{m}^{-1}$$

We have used $1\,\text{J} = 1\,\text{kg m}^2\,\text{s}^{-2}$. It follows that

$$\kappa L = (1.55\ldots\times10^{10}\,\text{m}^{-1})\times(100\times10^{-12}\,\text{m}) = 1.55\ldots$$

Equation 10.6 then yields

$$T = \left\{1 + \frac{(\text{e}^{1.55\ldots} - \text{e}^{-1.55\ldots})^2}{16\times0.9975\times(1-0.9975)}\right\}^{-1}$$
$$= 1.96\times10^{-3}$$

This value of T corresponds to a 0.2 per cent transmission probability; as indicated in Fig. 10.5, the larger the value of $L(2mV)^{1/2}/\hbar$ (here, 31) the smaller the value of T for energies close to, but below, the barrier height.

Self-test 10.1 Suppose that the junction between two semiconductors can be represented by a barrier of height 2.00 eV and length 100 pm. Calculate the probability that an electron of energy 1.95 eV can tunnel through the barrier.

Answer: $T = 0.881$

10.2 The Eckart potential energy barrier

The rectangular potential energy barrier has abrupt changes at the walls of the barrier (at $x = 0$ and L). A smoother, and more realistic, potential energy function is the **Eckart potential barrier**:

$$V(x) = \frac{4V_0\text{e}^{ax}}{(1+\text{e}^{ax})^2} \qquad (10.8)$$

Eckart potential barrier

where V_0 and a are constants with dimensions of energy and inverse length, respectively (Fig. 10.7). This potential function is often invoked in models of chemical reactivity because it bears a resemblance to the shape of the potential energy for a reaction as a function of the reaction coordinate (Topic 89), with reactants on the left of the barrier ($x \to -\infty$) and products on the right ($x \to +\infty$). The transmission probability for the Eckart barrier can provide insight into the nature of a chemical reaction that proceeds by tunnelling through a potential energy barrier, such as those involving the transfer of electrons or protons over short distances.

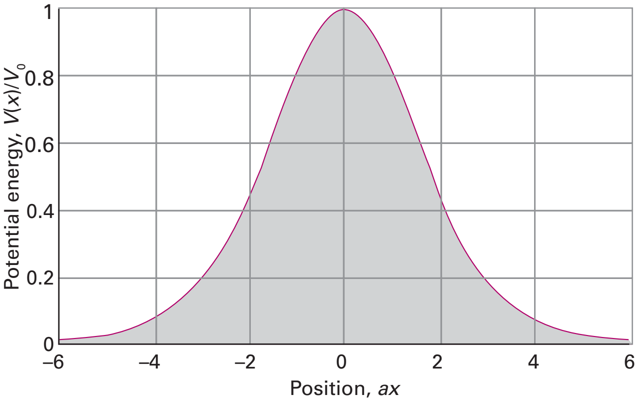


Figure 10.7 The Eckart potential barrier, as described in the text.

An analytical expression for the transmission probability for the Eckart potential function can be found by solving the Schrödinger equation, which in this case is

$$-\frac{\hbar^2}{2m}\frac{\text{d}^2\psi}{\text{d}x^2} + \frac{4V_0\text{e}^{ax}}{(1+\text{e}^{ax})^2}\psi = E\psi \qquad (10.9)$$

where m is the mass of the particle encountering the barrier. For studies of chemical reactivity, m is often identified with the reduced mass of the reactants; for example for the reaction of an atom A and a diatomic molecule BC, $1/m = 1/m_A + 1/(m_B + m_C)$.

The transmission probability, obtained from solution of eqn 10.9,[1] is given by:

$$T = \frac{\cosh x_1 - 1}{\cosh x_1 + \cosh x_2} \qquad (10.10a)$$

Eckart barrier Transmission probability

where

$$x_1 = 4\pi(2mE)^{1/2}/\hbar a \qquad (10.10b)$$

$$x_2 = 2\pi\left|8mV_0 - (\hbar a/2)^2\right|^{1/2}/\hbar a \qquad (10.10c)$$

and cosh x is the hyperbolic cosine function (see *The chemist's toolkit* 10.1).

---

[1] See C. Eckart, *Phys. Rev.* **35**, 1303 (1930). In this case, the solutions of the Schrödinger equation are the so-called hypergeometric functions.

The chemist's toolkit 10.1 Hyperbolic functions

The hyperbolic cosine (cosh) and hyperbolic sine (sinh) functions are defined as

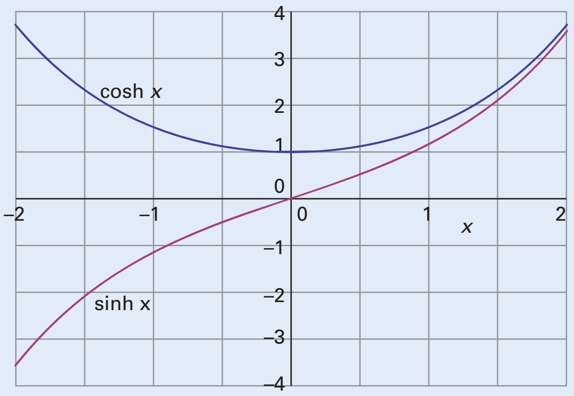
$$\cosh x = (e^{x} + e^{-x})/2 \qquad \sinh x = (e^{x} - e^{-x})/2$$

These functions, which are illustrated in Sketch 10.1 and available in most mathematical software packages, are related by

$$\cosh^2 x - \sinh^2 x = 1$$

At $x=0$, cosh $x=1$ and sinh $x=0$. The cosh function is even, $\cosh(-x)=\cosh x$, whereas the sinh function is odd, $\sinh(-x)=-\sinh x$. In the limits of $x\to\pm\infty$,

- as $x\to\infty$, $\cosh x\to\frac{1}{2}e^{x}$ and $\sinh x\to\frac{1}{2}e^{x}$
- as $x\to-\infty$, $\cosh x\to\frac{1}{2}e^{-x}$ and $\sinh x\to-\frac{1}{2}e^{-x}$



Sketch 10.1 The hyperbolic functions cosh *x* and sinh *x*.

Figure 10.8 shows the variation of the transmission probability with energy. Its behaviour is similar to that of the transmission probability for the rectangular potential barrier shown in Fig. 10.5 and discussed in Section 10.1. The primary difference is that there are no oscillations in the transmission probability at high energies for the Eckart barrier whereas there may be oscillations for the rectangular barrier (depending on the values of L, m, and V and due to the discontinuous nature of the potential energy at the barrier walls.)

Brief illustration 10.2 Transmission probabilities for an Eckart barrier

Suppose that the junction between two semiconductors can be represented by an Eckart barrier with $V_0=2.00$ eV (corresponding to 3.20×10^{-19} J) and $a=(100\ \text{pm})^{-1}$. The probability that an electron of energy 1.95 eV (corresponding to 3.12×10^{-19} J) can tunnel through the barrier is calculated using eqn 10.10:

$$x_1=\frac{4\pi(2mE)^{1/2}}{\hbar a}=\frac{4\pi\left\{2\times(9.109\times10^{-31}\,\text{kg})\times(3.12\ldots\times10^{-19}\,\text{J})\right\}^{1/2}}{(1.055\times10^{-34}\,\text{J s})\times(1.00\times10^{-10}\,\text{m})^{-1}}=8.98\ldots$$

$$\begin{aligned}x_2&=\frac{2\pi\left|8mV_0-(\hbar a/2)^2\right|^{1/2}}{\hbar a}\\&=\frac{2\pi\left|8\times(9.109\times10^{-31}\,\text{kg})\times(3.20\ldots\times10^{-19})-\left[(1.055\times10^{-34}\,\text{J s})\times(1.00\times10^{-10}\,\text{m})^{-1}/2\right]^2\right|^{1/2}}{(1.055\times10^{-34}\,\text{J s})\times(1.00\times10^{-10}\,\text{m})^{-1}}\\&=8.54\ldots\end{aligned}$$

$$T=\frac{\cosh x_1-1}{\cosh x_1+\cosh x_2}=\frac{\cosh(8.98\ldots)-1}{\cosh(8.98\ldots)+\cosh(8.54\ldots)}=0.609$$

This value of T is smaller than that of *Self-test* 10.1 because the Eckart potential effectively extends over a longer range than the rectangular potential barrier.

Self-test 10.2 Suppose that the removal of a proton which is hydrogen-bonded to the oxygen atom of a water molecule requires tunnelling through a potential barrier that can be represented by an Eckart function with $V_0=0.100$ eV and $a=(200\,\text{pm})^{-1}$. Calculate the probability that a proton with energy 0.095 eV can escape from the water molecule.

Answer: $T=0.012$

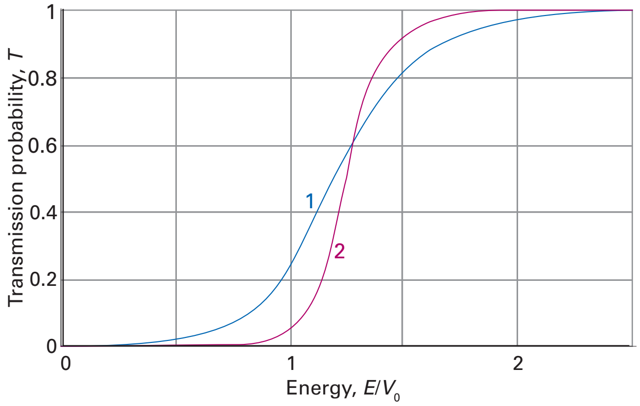


Figure 10.8 The transmission probability for an Eckart barrier and its variation with energy. The curves are labelled with the value of $(2mV_0)^{1/2}/a\hbar$.

10.3 The double-well potential

The **double-well potential** shown in Fig. 10.9 provides a useful model for a variety of processes which can occur as a result of tunnelling through a barrier. They include electron or proton transfer from donor to acceptor, electrical conductivity between two nanoparticles, and conformational change of a molecule. Here we focus on the last of these processes, and consider conformational changes in a trigonal pyramidal AB_3 molecule (such as NH_3). We shall represent the potential energy of the conformation AB_3 by the left-hand well, and the potential energy of the inverted (B_3A) molecule by the right-hand well. The potential energy when the pyramidal molecule has been flattened is represented by the barrier between wells. If the barrier is high, inversion is difficult (as for a well-made umbrella); if the barrier is low, inversion by tunnelling readily occurs.

When the potential barrier is infinitely high (in practice, very high), the two conformations AB_3 and B_3A cannot interconvert. We denote the ground-state wavefunction of AB_3 by ψ_L and that of B_3A by ψ_R; the two wavefunctions have the same energy. When the barrier is lower, tunnelling can occur (recall Fig. 10.2) and the wavefunction ψ_L seeps through the barrier and has nonzero amplitude where ψ_R (which has also seeped through the barrier) is nonzero (Fig. 10.10a). The conformations AB_3 and B_3A can now interconvert and we seek a new wavefunction to describe the composite system; the wavefunction must be delocalized over both of the potential energy wells of the double-well potential. One such (unnormalized) wavefunction is the linear combination $\psi_L+\psi_R$; the coefficients of ψ_L and ψ_R in the linear combination are equal because there is equal probability of finding the molecule in either the AB_3 or B_3A conformation (recall Postulate V of Topic 7).

The functions ψ_L and ψ_R can also be used to form another linear combination capable of describing the composite system, namely the (unnormalized) wavefunction $\psi_L-\psi_R$; again, there is equal probability of finding the molecule in either potential well. The wavefunctions $\psi_L+\psi_R$ and $\psi_L-\psi_R$ are depicted in Fig. 10.10b; they have different probability amplitudes, especially in the vicinity of the potential barrier ($\psi_L-\psi_R$ has a node in the middle of the barrier) and as a result these two linear combinations have different energies. The state described by the linear combination $\psi_L+\psi_R$ is lower in energy, its actual value depending on the height of the barrier. The occurrence of tunnelling through the finite potential energy barrier has resulted in two states delocalized over both of the potential energy wells and having different energies, a phenomenon known as **inversion doubling.**

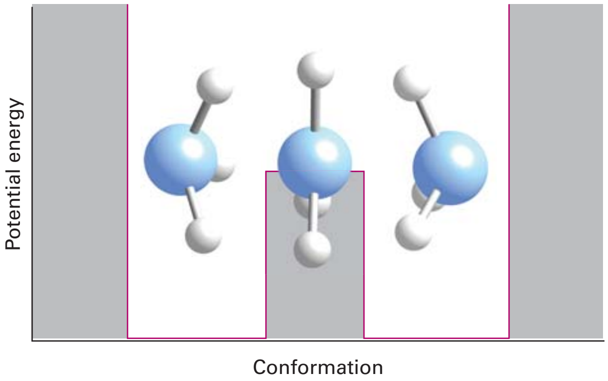


Figure 10.9 The double-well potential, a model of the potential energy curve for a molecule that undergoes inversion.

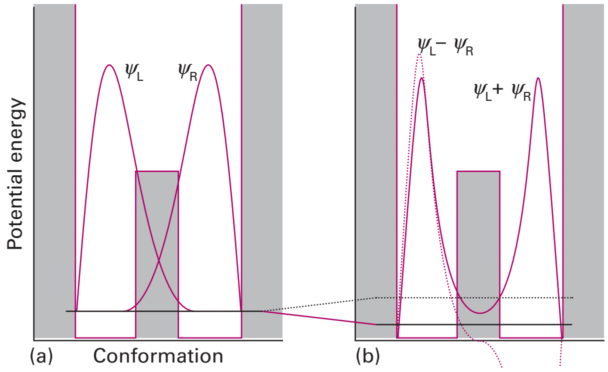


Figure 10.10 (a) To a first approximation, the molecule oscillates like a particle in a box in either of the two potential wells: the wavefunctions shown correspond to the ground state of the particle in a box with the allowance for seepage into the barrier due to tunnelling. (b) When inversion is allowed, the wavefunctions of the molecule can be modelled as the linear combinations shown. The horizontal lines indicate the energies, which differ for the two linear combinations shown in (b).

Brief illustration 10.3 The inversion frequency in the ammonia molecule

In the case of ammonia, the states represented by the wavefunctions $\psi_L + \psi_R$ and $\psi_L - \psi_R$ differ in energy by 1.6×10^{-23} J. The spectroscopic transition between the two states occurs in the microwave region of the electromagnetic spectrum at $0.79\,\mathrm{cm}^{-1}$, corresponding to a wavelength of 13 mm and a frequency of 24 GHz; the frequency, obtained from the Bohr frequency condition (eqn 4.4 of Topic 4), is called the 'inversion frequency'. The transition in NH_3 is the most intense microwave transition known for any molecule and is the basis of 'maser action', the early forerunner of the laser.

Self-test 10.3 The phenomenon of inversion doubling observed in NH_3 is not likely to be observed in its deuterated analogue ND_3. Explain why.

Answer: D heavier than H; tunnelling unlikely to occur

Checklist of concepts

☐ **1.** Penetration into or through a classically forbidden region is called **tunnelling**.

☐ **2.** The probability of tunnelling decreases with an increase in the height and width of the potential barrier.

☐ **3.** Light particles are more able to tunnel through barriers than heavy ones.

☐ **4.** The **Eckart potential** is a useful model to describe potential energy barriers in chemical reactions.

☐ **5.** Tunnelling through a finite barrier separating two potential wells results in states delocalized over both wells and having different energies, a phenomenon known as **inversion doubling**.

Checklist of equations

Property	Equation	Comment	Equation number
Transmission probability	$T=\left\{1+(e^{\kappa L}-e^{-\kappa L})^2/16\varepsilon(1-\varepsilon)\right\}^{-1}$	Rectangular potential barrier	10.6
	$T=16\varepsilon(1-\varepsilon)e^{-2\kappa L}$	High, wide rectangular barrier	10.7
Eckart potential barrier	$V(x)=4V_0e^{ax}/(1+e^{ax})^2$		10.8

TOPIC 11

Translational motion in several dimensions

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➤ Why do you need to know this material?

Because electrons in atoms, molecules, and nanostructures move in three-dimensional space, you need to know how to use the concepts of quantum theory to treat the translation of particles in several dimensions.

➤ What is the key idea?

The solutions of the Schrödinger equation for translational motion in two and three dimensions are generalizations to multiple dimensions of the one-dimensional solution.

➤ What do you need to know already?

You should be familiar with the solutions of the Schrödinger equation for a particle in a one-dimensional box (Topic 9).

Topic 9 presents translational motion in one dimension. In this Topic, we discuss the energies and wavefunctions for particles free to move in several dimensions. We work our way up from one dimension to three in two steps: first, we consider a two-dimensional system, and then generalize it to three. The technique presented here is also relevant to other three-dimensional systems, such as atoms, and we encounter it again in Topic 17. Moreover, in this Topic we also encounter the phenomenon of 'degeneracy', in which different wavefunctions correspond to the same energy. That is another property that plays an important role in the description of the structures of atoms and molecules.

11.1 Motion in two dimensions

Consider a rectangular two-dimensional region of a surface with length L_1 in the x-direction and L_2 in the y-direction; the potential energy is zero everywhere except at the walls, where it is infinite (Fig. 11.1). As a result, the particle is never found at the walls and its wavefunction is zero there and everywhere outside the two-dimensional region. Between the walls, because the particle has contributions to its kinetic energy from its motion in both the x and y directions, the Schrödinger equation has two kinetic energy terms, one for each axis. For a particle of mass m the equation is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right)=E\psi \qquad (11.1)$$

This is a *partial* differential equation (see *Mathematical background* 2), a differential equation in more than one variable, and the resulting wavefunctions are functions of both x and y, denoted $\psi(x, y)$. This dependence means that the wavefunction

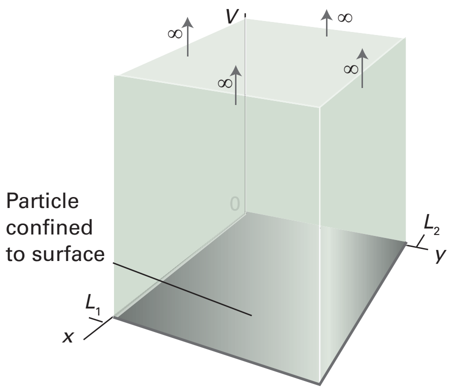

Figure 11.1 A two-dimensional square well. The particle is confined to the plane bounded by impenetrable walls. As soon as it touches the walls, its potential energy rises to infinity.

and the corresponding probability density depend on the location in the plane, with each position specified by the coordinates x and y.

(a) Separation of variables

A partial differential equation of the form of eqn 11.1 can be simplified by the **separation of variables technique**, which divides the equation into two or more ordinary differential equations, one for each variable. We show in the *Justification* below using this technique that the wavefunction can be written as a product of functions, one depending only on x and the other only on y:

$$\psi(x,y)=X(x)Y(y) \tag{11.2a}$$

and that the total energy is given by

$$E=E_X+E_Y \tag{11.2b}$$

where E_X is the energy associated with the motion of the particle parallel to the x-axis, and likewise for E_Y and motion parallel to the y-axis.

Justification 11.1 The separation of variables

The first step to confirm that the Schrödinger equation is separable and the wavefunction can be factored into the product of two functions X and Y is to note that, because X is independent of y and Y is independent of x, we can write

$$\frac{\partial^2\psi}{\partial x^2}=\frac{\partial^2 XY}{\partial x^2}=Y\frac{\mathrm{d}^2X}{\mathrm{d}x^2} \qquad \frac{\partial^2\psi}{\partial y^2}=\frac{\partial^2 XY}{\partial y^2}=X\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}$$

Note the replacement of the partial derivatives by ordinary derivatives in each case. Then eqn 11.1 becomes

$$-\frac{\hbar^2}{2m}\left(Y\frac{\mathrm{d}^2X}{\mathrm{d}x^2}+X\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}\right)=EXY$$

Next, we divide both sides by XY, and rearrange the resulting equation into

$$\frac{1}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2}+\frac{1}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}=-\frac{2mE}{\hbar^2}$$

The first term on the left is independent of y, so if y is varied only the second term of the two on the left can change. But the sum of these two terms is a constant given by the right-hand side of the equation. Therefore, if the second term did change, then the right-hand side could not be constant. Consequently, even the second term cannot change when y is changed. In other words, the second term is a constant, which we write $-2mE_Y/\hbar^2$. By a similar argument, the first term is a constant when x changes, and we write it $-2mE_X/\hbar^2$, with $E=E_X+E_Y$. Therefore, we can write

$$\frac{1}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2}=-\frac{2mE_X}{\hbar^2} \qquad \frac{1}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}=-\frac{2mE_Y}{\hbar^2}$$

These expressions rearrange into the two ordinary (that is, single-variable) differential equations

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2X}{\mathrm{d}x^2}=E_XX \tag{11.3a}$$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}=E_YY \tag{11.3b}$$

Each of the two ordinary differential equations in eqn 11.3 is the same as the one-dimensional particle-in-a-box Schrödinger equation (Topic 9). The boundary conditions are also the same, apart from the detail of requiring $X(x)$ to be zero at $x=0$ and L_1, and $Y(y)$ to be zero at $y=0$ and L_2. We can therefore adapt the results obtained in Topic 9 without further calculation (see eqn 9.8):

$$X_{n_1}(x)=\left(\frac{2}{L_1}\right)^{1/2}\sin\left(\frac{n_1\pi x}{L_1}\right) \quad \text{for } 0\le x\le L_1$$

$$Y_{n_2}(y)=\left(\frac{2}{L_2}\right)^{1/2}\sin\left(\frac{n_2\pi y}{L_2}\right) \quad \text{for } 0\le y\le L_2$$

Then, because $\psi=XY$,

Two-dimensional box Wavefunctions

$$\begin{aligned}\psi_{n_1,n_2}(x,y)&=\frac{2}{(L_1L_2)^{1/2}}\sin\left(\frac{n_1\pi x}{L_1}\right)\sin\left(\frac{n_2\pi y}{L_2}\right)\\ &\text{for } 0\le x\le L_1,\ 0\le y\le L_2\\ \psi_{n_1,n_2}(x,y)&=0 \qquad \text{outside box}\end{aligned} \tag{11.4a}$$

Similarly, because $E=E_X+E_Y$, the energy of the particle is limited to the values

$$E_{n_1,n_2}=\left(\frac{n_1^2}{L_1^2}+\frac{n_2^2}{L_2^2}\right)\frac{h^2}{8m} \qquad (11.4b)$$

Two-dimensional box Energy levels

with the two quantum numbers taking the values $n_1=1,2,\ldots$ and $n_2=1,2,\ldots$ independently. The state of lowest energy is $(n_1=1, n_2=1)$ and $E_{1,1}$ is the zero-point energy.

Brief illustration 11.1 The zero-point energy of a particle in a two-dimensional box

An electron trapped in a cavity of dimensions $L_1=1.0\,\text{nm}$ and $L_2=2.0\,\text{nm}$ can be described by a particle-in-a-box wavefunction. The zero-point energy of the electron is given by eqn 11.4b with $n_1=1$ and $n_2=1$:

$$E_{1,1}=\left\{\frac{1^2}{(1.0\times10^{-9}\,\text{m})^2}+\frac{1^2}{(2.0\times10^{-9}\,\text{m})^2}\right\}\frac{(6.626\times10^{-34}\,\text{J s})^2}{8\times(9.109\times10^{-31}\,\text{kg})}$$
$$=7.5\times10^{-20}\,\text{J}$$

Self-test 11.1 Calculate the energy separation between the levels $n_1=n_2=2$ and $n_1=n_2=1$ of an electron trapped in a square cavity with sides of length 1.0 nm.

Answer: 3.6×10^{-19} J

Some of the wavefunctions are plotted as contours in Fig. 11.2. They are the two-dimensional versions of the wavefunctions shown in Fig. 9.4. Whereas in one dimension the wavefunctions resemble states of a vibrating string with ends fixed, in two dimensions the wavefunctions correspond to vibrations of a rectangular plate with fixed edges.

Brief illustration 11.2 The distribution of a particle in a two-dimensional box

Consider an electron confined to a square cavity of length L, and in the state with quantum numbers $n_1=1$, $n_2=2$. Because the probability density is

$$\psi_{1,2}^2(x,y)=\frac{4}{L^2}\sin^2\left(\frac{\pi x}{L}\right)\sin^2\left(\frac{2\pi y}{L}\right)$$

the most probable locations correspond to $\sin^2(\pi x/L)=1$ and $\sin^2(2\pi y/L)=1$, or $(x, y)=(L/2,L/4)$ and $(L/2,3L/4)$. The least probable locations (the nodes, where the wavefunction passes through zero) correspond to zeroes in the probability density within the box, which occur along the line $y=L/2$.

Self-test 11.2 Determine the most probable locations of an electron in a square cavity of length L when it is in the state with quantum numbers $n_1=2$, $n_2=3$.

Answer: points ($x=L/4$ and $3L/4$, $y=L/6$, $L/2$ and $5L/6$)

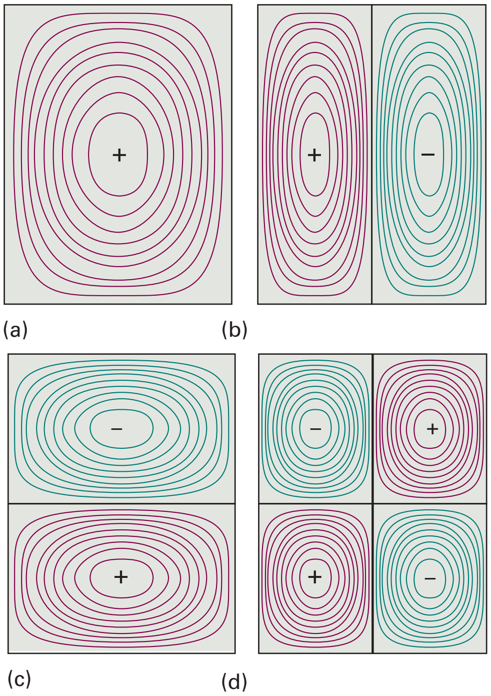

Figure 11.2 The wavefunctions for a particle confined to a rectangular surface depicted as contours of equal amplitude. (a) $n_1=1$, $n_2=1$, the state of lowest energy; (b) $n_1=1$, $n_2=2$; (c) $n_1=2$, $n_2=1$; (d) $n_1=2$, $n_2=2$.

(b) Degeneracy

A special feature of the solutions arises when the box is not merely rectangular but square, with $L_1=L_2=L$. Then the wavefunctions and their energies are

$$\psi_{n_1,n_2}(x,y)=\frac{2}{L}\sin\left(\frac{n_1\pi x}{L}\right)\sin\left(\frac{n_2\pi y}{L}\right) \quad \text{for } 0\le x\le L,\ 0\le y\le L$$
$$\psi_{n_1,n_2}(x,y)=0 \qquad \text{outside box} \qquad (11.5a)$$

Two-dimensional square box Wavefunctions

$$E_{n_1,n_2}=(n_1^2+n_2^2)\frac{h^2}{8mL^2} \qquad (11.5b)$$

Two-dimensional square box Energy levels

Consider the cases $n_1=1$, $n_2=2$ and $n_1=2$, $n_2=1$:

$$\psi_{1,2}=\frac{2}{L}\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi y}{L}\right) \qquad E_{1,2}=\frac{5h^2}{8mL^2}$$
$$\psi_{2,1}=\frac{2}{L}\sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right) \qquad E_{2,1}=\frac{5h^2}{8mL^2}$$

Although the wavefunctions are different, they have the same energy. The technical term for different wavefunctions corresponding to the same energy is **degeneracy**, and in this case we say that the state with energy $5h^2/8mL^2$ is 'doubly degenerate'.

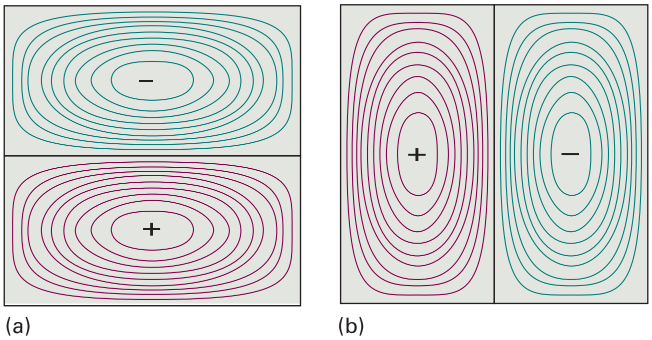

Figure 11.3 The wavefunctions for a particle confined to a square well. Note that one wavefunction can be converted into the other by rotation of the box by 90°. The two functions correspond to the same energy. True degeneracy is a consequence of symmetry.

The occurrence of degeneracy is related to the symmetry of the system. Figure 11.3 shows contour diagrams of the two degenerate functions $\psi_{1,2}$ and $\psi_{2,1}$. Because the box is square, one wavefunction can be converted into the other simply by rotating the plane by 90°. Interconversion by rotation through 90° is not possible when the plane is not square, and $\psi_{1,2}$ and $\psi_{2,1}$ are then not degenerate. Other examples of degeneracy occur in quantum mechanical systems (for instance, in the hydrogen atom, Topic 17), and all of them can be traced to the symmetry properties of the system.

Brief illustration 11.3 Degeneracies in a two-dimensional box

The energy of a particle in a two-dimensional square box of length L in the state with $n_1=1$, $n_2=7$ is

$$E_{1,7}=(1^2+7^2)\frac{h^2}{8mL^2}=\frac{50h^2}{8mL^2}$$

This state is degenerate with the state with $n_1=7$ and $n_2=1$. Thus, at first sight the energy level $50h^2/8mL^2$ is doubly degenerate. However, in certain systems there may be states that are not apparently related by symmetry but are 'accidentally' degenerate. Such is the case here, for the state with $n_1=5$ and $n_2=5$ also has energy $50h^2/8mL^2$ (Fig. 11.4). Accidental degeneracy can often be traced to a symmetry that is not immediately obvious; it is also encountered in the hydrogen atom (Topic 17).

Self-test 11.3 Find a state (n_1, n_2) for a particle in a rectangular box with sides of length $L_1=L$ and $L_2=2L$ that is accidentally degenerate with the state (4,4).

Answer: $(n_1=2, n_2=8)$

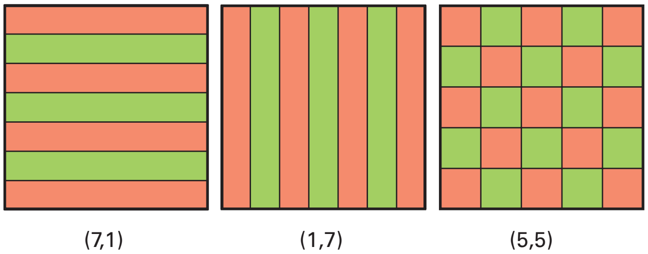

Figure 11.4 Accidental degeneracy is a consequence of hidden symmetry. These three states are degenerate but only the first two, (7,1) and (1,7), are interrelated by symmetry. The third state, (5,5), is not obviously related by any symmetry transformation of the square region. Only the location of the nodes is shown in each case.

11.2 Motion in three dimensions

We are now ready to take the final step, to three dimensions. The system consists of a particle of mass m confined to a box of length L_1 in the x-direction, L_2 in the y-direction, and L_3 in the z-direction. Inside the box, the potential energy is zero and inside the walls it is infinite. This system could be a model for a quantum mechanical system of a gas in a container of macroscopic dimensions or for an electron confined to a small cavity in a solid.

The step is easy to take, for it should be obvious (and can be proved by the method of separation of variables) that the wavefunction simply has another factor:

$$\psi_{n_1,n_2,n_3}(x,y,z)=\left(\frac{8}{L_1L_2L_3}\right)^{1/2}\sin\frac{n_1\pi x}{L_1}\sin\frac{n_2\pi y}{L_2}\sin\frac{n_3\pi z}{L_3}$$
$$\text{for } 0\le x\le L_1, 0\le y\le L_2, 0\le z\le L_3 \qquad (11.6a)$$

Three-dimensional box Wave-functions

Outside the box, because the potential is infinite the wavefunction is zero. Likewise, the energy has a third contribution from motion in the z-direction:

$$E_{n_1,n_2,n_3}=\left(\frac{n_1^2}{L_1^2}+\frac{n_2^2}{L_2^2}+\frac{n_3^2}{L_3^2}\right)\frac{h^2}{8m} \qquad (11.6b)$$

Three-dimensional box Energy levels

The quantum numbers n_1, n_2, and n_3 are all positive integers 1, 2, … that can be varied independently. The system has a zero-point energy ($E_{1,1,1}=3h^2/8mL^2$ for a cubic box) and, as for the two-dimensional system, there can be both true and accidental degeneracies.

Example 11.1 Analysing transitions in a cubic box

Solutions of alkali metals in liquid ammonia are widely used as reducing agents in organic synthesis. For example, the addition of sodium to liquid ammonia generates a solvated electron which is effectively trapped in a cavity 0.30 nm in diameter formed by ammonia molecules. Suppose the solvated electron can be modelled as a particle moving freely inside a cubic box. If the length of the box is taken to be 0.30 nm, what energy is required for the electron to undergo a transition from its lowest energy state to the state which is next-higher in energy?

Method The quantized energies are given in eqn 11.6b. The lowest energy state has $n_1=1$, $n_2=1$, and $n_3=1$. The electron makes a transition to the state with $n_1=2$, $n_2=1$, and $n_3=1$ which has the next-higher energy. (The same answer results if we choose the states (1,2,1) or (1,1,2).) Compute $\Delta E=E_{2,1,1}-E_{1,1,1}$.

Answer Using eqn 11.6b with $L_1=L_2=L_3=L=0.30\times10^{-9}$ m, we find

$$\begin{aligned}\Delta E&=E_{2,1,1}-E_{1,1,1}=(2^2+1^2+1^2)\frac{h^2}{8mL^2}-(1^2+1^2+1^2)\frac{h^2}{8mL^2}\\&=\frac{3h^2}{8mL^2}=\frac{3\times(6.626\times10^{-34}\,\mathrm{J\,s})^2}{8\times(9.109\times10^{-31}\,\mathrm{kg})\times(0.30\times10^{-9}\,\mathrm{m})^2}\\&=2.0\times10^{-18}\,\mathrm{J}\end{aligned}$$

or 2.0 aJ. If this transition were caused by radiation, it would follow from the Bohr frequency condition (eqn 4.4 of Topic 4) that the transition frequency would be $\nu=\Delta E/h=3.0\times10^{15}$ Hz, corresponding to a wavelength of 100 nm.

Self-test 11.4 In dilute solutions of sodium in ammonia, there is an absorption of 1.5 μm radiation by the solvated electrons which accounts for the blue colour of the solution. In the particle-in-a-three-dimensional-box model of the solvated electron, what box length L would account for an absorption of this wavelength?

Answer: $L=1.2$ nm

Checklist of concepts

☐ 1. The wavefunction for a particle in a two- or three-dimensional box is the product of wavefunctions for the particle in a one-dimensional box.

☐ 2. The energy of a particle in a two- or three-dimensional box is the sum of energies for the particle in two or three one-dimensional boxes.

☐ 3. The zero-point energy for a particle in a two-dimensional box corresponds to the state with quantum numbers ($n_1=1$, $n_2=1$); for three dimensions, ($n_1=1$, $n_2=1$, $n_3=1$).

☐ 4. **Degeneracy** occurs when different wavefunctions correspond to the same energy.

☐ 5. The occurrence of degeneracy is a consequence of the symmetry of the system.

Checklist of equations

Property	Equation	Comment	Equation number
Wavefunction for a particle in a two-dimensional box	$\psi_{n_1,n_2}(x,y)$ $=(2/(L_1L_2)^{1/2})\sin(n_1\pi x/L_1)\sin(n_2\pi y/L_2)$ $0\le x\le L_1,\ 0\le y\le L_2$ $\psi_{n_1,n_2}(x,y)=0$ outside box	$n_1, n_2=1, 2, \ldots$	11.4a
Energy for a particle in a two-dimensional box	$E_{n_1,n_2}=(n_1^2/L_1^2+n_2^2/L_2^2)h^2/8m$	$n_1, n_2=1, 2, \ldots$	11.4b
Wavefunction for a particle in a three-dimensional box	$\psi_{n_1,n_2,n_3}(x,y,z)=(8/(L_1L_2L_3))^{1/2}\times$ $\sin(n_1\pi x/L_1)\ \sin(n_2\pi y/L_2)\ \sin(n_3\pi z/L_3)$ for $0\le x\le L_1,\ 0\le y\le L_2,\ 0\le z\le L_3$ $\psi_{n_1,n_2,n_3}(x,y,z)=0$ outside box	$n_1, n_2, n_3=1, 2, \ldots$	11.6a
Energy for a particle in a three-dimensional box	$E_{n_1,n_2,n_3}=(n_1^2/L_1^2+n_2^2/L_2^2+n_3^2/L_3^2)h^2/8m$	$n_1, n_2, n_3=1, 2, \ldots$	11.6b

TOPIC 12

Vibrational motion

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➤ Why do you need to know this material?

The detection and interpretation of vibrational frequencies is the basis of infrared spectroscopy (Topic 43), and you also need to understand molecular vibration in order to interpret thermodynamic properties, such as heat capacities (Topic 58). Molecular vibration plays a role in the rates of chemical reactions, so you need this material to be ready for a discussion of the quantum mechanical aspects of chemical kinetics (Topic 89).

➤ What is the key idea?

The energy levels of a harmonic oscillator form an evenly spaced ladder with the lowest rung corresponding to the zero-point energy. The wavefunctions are products of a polynomial and a Gaussian (bell-shaped) function.

➤ What do you need to know already?

You should know how to formulate the Schrödinger equation given a potential energy function (Topic 6). You should also be familiar with the concepts of tunnelling (Topic 10) and the expectation value of an observable (Topic 7). For the closing section, you need to be familiar with the concepts of rate constant and activation energy (Topic 85).

Atoms in molecules and solids vibrate around their mean positions as bonds stretch, compress, and bend. This Topic considers one particular type of vibrational motion, that of 'harmonic motion' in one dimension. A particle undergoes **harmonic motion** if it experiences a restoring force proportional to its displacement:

$$F=-k_\mathrm{f}x \qquad \textit{Harmonic motion} \qquad \text{Restoring force} \qquad (12.1)$$

where k_f is the **force constant**: the stiffer the 'spring', the greater the value of k_f. Because force is related to potential energy by $F=-\mathrm{d}V/\mathrm{d}x$ (see Topic 2), the force in eqn 12.1 corresponds to the particle having a potential energy

$$V(x)=\tfrac{1}{2}k_\mathrm{f}x^2 \qquad \text{Parabolic potential energy} \qquad (12.2)$$

when it is displaced through a distance x from its equilibrium position. This expression, which is the equation of a parabola (Fig. 12.1), is the origin of the term 'parabolic potential energy' for the potential energy characteristic of a harmonic oscillator. The Schrödinger equation for the particle of mass m is therefore

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}+\tfrac{1}{2}k_\mathrm{f}x^2\psi(x)=E\psi(x) \qquad \textit{Harmonic oscillator} \qquad \text{Schrödinger equation} \qquad (12.3)$$

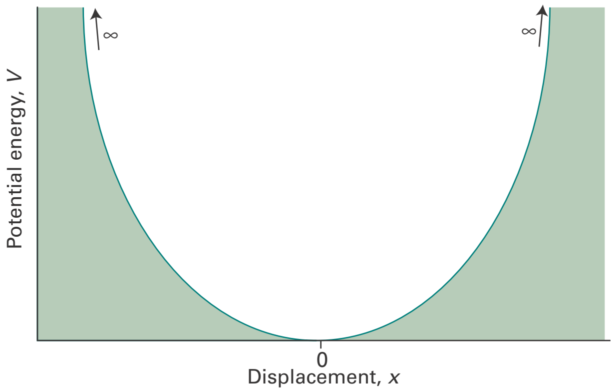

Figure 12.1 The parabolic potential energy $V=\frac{1}{2}k_f x^2$ of a harmonic oscillator, where x is the displacement from equilibrium. The narrowness of the curve depends on the force constant k_f: the larger the value of k_f, the narrower the well.

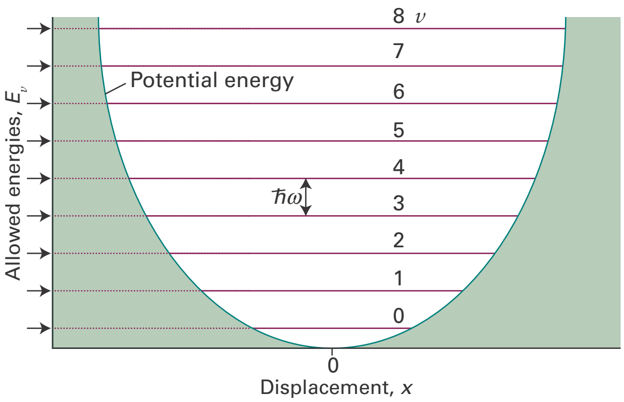

Figure 12.2 The energy levels of a harmonic oscillator are evenly spaced with separation $\hbar\omega$, with $\omega=(k_f/m)^{1/2}$. Even in its lowest energy state, an oscillator has an energy greater than zero.

We can anticipate that the energy of an oscillator will be quantized because the wavefunction has to satisfy boundary conditions (as in Topic 9 for a particle in a box): it will not be found with very large extensions because its potential energy rises to infinity there. That is, when we impose the boundary conditions $\psi=0$ at $x=\pm\infty$, we can expect to find that only certain wavefunctions and their corresponding energies are possible.

12.1 The energy levels

Equation 12.3 is a standard equation in the theory of differential equations and its solutions are well known to mathematicians.[1] The permitted energy levels are

$$E_v=(v+\tfrac{1}{2})\hbar\omega \qquad \omega=(k_f/m)^{1/2} \qquad v=0,\ 1,\ 2,\ \ldots \tag{12.4}$$

Harmonic oscillator Energy levels

where v is the **vibrational quantum number**. Note that ω (omega) is large when the force constant is large and the mass small. It follows that the separation between adjacent levels is

$$E_{v+1}-E_v=\hbar\omega \tag{12.5}$$

which is the same for all v. Therefore, the energy levels form a uniform ladder of spacing $\hbar\omega$ (Fig. 12.2). The energy separation $\hbar\omega$ is negligibly small for macroscopic objects (with large mass) for which classical mechanics is adequate for describing vibrational motion; however, the energy separation is of great importance for objects with mass similar to that of atoms.

Because the smallest permitted value of v is 0, it follows from eqn 12.4 that a harmonic oscillator has a zero-point energy

$$E_0=\tfrac{1}{2}\hbar\omega \tag{12.6}$$

Harmonic oscillator Zero-point energy

The mathematical reason for the zero-point energy is that v cannot take negative values, for if it did the wavefunction would not obey the boundary conditions. The physical reason is the same as for the particle in a box (Topic 9): the particle is confined, its position is not completely uncertain, and therefore its momentum, and hence its kinetic energy, cannot be exactly zero. We can picture this zero-point state as one in which the particle fluctuates incessantly around its equilibrium position; classical mechanics would allow the particle to be perfectly still.

Atoms vibrate relative to one another in molecules, with the bond acting like a spring. The question then arises as to what mass to use to predict the frequency of the vibration. In general, the relevant mass is a complicated combination of the masses of all the atoms that move, with each contribution weighted by the amplitude of the atom's motion. That amplitude depends on the mode of motion, such as whether the vibration is a bending motion or a stretching motion, so each mode of vibration has a characteristic 'effective mass'. For a diatomic molecule AB, however, for which there is only one mode of vibration, corresponding to the stretching and compression of the bond, the **effective mass**, μ, has a very simple form:

$$\mu=\frac{m_A m_B}{m_A+m_B} \tag{12.7}$$

Diatomic molecule Effective mass

When A is much heavier than B, m_B can be neglected in the denominator and the effective mass is $\mu\approx m_B$, the mass of the lighter atom. This result is plausible, for in the limit of the heavy

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[1] For details, see our *Molecular quantum mechanics*, Oxford University Press (2011).

atom being like a brick wall, only the lighter atom moves and hence determines the vibrational frequency.

Brief illustration 12.1 The vibrational energy separation in a diatomic molecule

The effective mass of $^1H^{35}Cl$ is

$$\mu=\frac{m_{\rm H}m_{\rm Cl}}{m_{\rm H}+m_{\rm Cl}}=\frac{(1.0078m_{\rm u})\times(34.9688m_{\rm u})}{(1.0078m_{\rm u})+(34.9688m_{\rm u})}=0.9796m_{\rm u}$$

which is close to the mass of the proton. The force constant of the bond is $k_{\rm f}=516.3\,{\rm N\,m^{-1}}$. It follows from eqn 12.4, with μ in place of m, that

$$\omega=\left(\frac{k_{\rm f}}{\mu}\right)^{1/2}=\left(\frac{516.3\,{\rm N\,m^{-1}}}{0.9796\times(1.66054\times10^{-27}\,{\rm kg})}\right)^{1/2}=5.634\times10^{14}\,{\rm s^{-1}}$$

(We have used $1\,{\rm N}=1\,{\rm kg\ m\ s^{-2}}$.) Therefore the separation of adjacent levels is (eqn 12.5)

$$E_{v+1}-E_v=(1.05457\times10^{-34}\,{\rm J\,s})\times(5.634\times10^{14}\,{\rm s^{-1}})=5.941\times10^{-20}\,{\rm J}$$

or 59.41 zJ, about 0.37 eV. This energy separation corresponds to 36 kJ mol^{-1}, which is chemically significant. The zero-point energy, eqn 12.6, of this molecular oscillator is 29.71 zJ, which corresponds to 0.19 eV, or 18 kJ mol^{-1}.

Self-test 12.1 Suppose a hydrogen atom is adsorbed on the surface of a gold nanoparticle by a bond of force constant 855 N m^{-1}. Calculate its zero-point vibrational energy.

Answer: 37.7 zJ, 22.7 kJ mol^{-1}, 0.24 eV

The result in *Brief illustration* 12.1 implies that excitation requires radiation of frequency $\nu=\Delta E/h=90\,{\rm THz}$ and wavelength $\lambda=c/\nu=3.3\,\mu{\rm m}$. It follows that transitions between adjacent vibrational energy levels of molecules are stimulated by or emit infrared radiation (Topic 43).

12.2 The wavefunctions

Like the particle in a box (Topic 9), a particle undergoing harmonic motion is trapped in a symmetrical well in which the potential energy rises to large values (and ultimately to infinity) for sufficiently large displacements (compare Figs 9.1 and 12.1). However, there are two important differences:

- Because the potential energy climbs towards infinity only as x^2 and not abruptly, the wavefunction approaches zero more slowly at large displacements than for the particle in a box.
- As the kinetic energy of the oscillator depends on the displacement in a more complex way (on account of the variation of the potential energy), the curvature of the wavefunction also varies in a more complex way.

The detailed solution of eqn 12.3 confirms these points and shows that the wavefunctions for a harmonic oscillator have the form

$$\psi(x)=N\times(\text{polynomial in }x)\times(\text{bell-shaped Gaussian function})$$

where N is a normalization constant. A Gaussian function is a bell-shaped function of the form e^{-x^2} (Fig. 12.3). The precise form of the wavefunctions is

$$\psi_v(x)=N_vH_v(y)e^{-y^2/2}\qquad y=\frac{x}{\alpha}\quad\alpha=\left(\frac{\hbar^2}{mk_{\rm f}}\right)^{1/4}\qquad \textit{Harmonic oscillator}\quad \text{Wavefunctions}\qquad(12.8)$$

The factor $H_v(y)$ is a **Hermite polynomial;** their form and some of their properties are listed in Table 12.1. Hermite polynomials, which are members of a class of functions called 'orthogonal polynomials', have a wide range of important properties which allow a number of quantum mechanical calculations to be done with relative ease. Note that the first few Hermite polynomials are very simple: for instance, $H_0(y)=1$ and $H_1(y)=2y$.

Because $H_0(y)=1$, the wavefunction for the ground state (the lowest energy state, with $v=0$) of the harmonic oscillator is

$$\psi_0(x)=N_0e^{-y^2/2}=N_0e^{-x^2/2\alpha^2}\qquad \textit{Harmonic oscillator}\quad \text{Ground-state wavefunction}\qquad(12.9a)$$

and the corresponding probability density is

$$\psi_0^2(x)=N_0^2e^{-y^2}=N_0^2e^{-x^2/\alpha^2}\qquad \textit{Harmonic oscillator}\quad \text{Ground-state probability density}\qquad(12.9b)$$

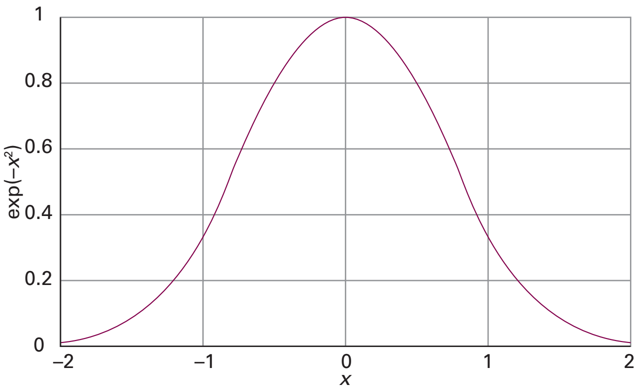


Figure 12.3 The graph of the Gaussian function, $f(x)=e^{-x^2}$.

Table 12.1 The Hermite polynomials $H_v(y)$

v	$H_v(y)$
0	1
1	$2y$
2	$4y^2-2$
3	$8y^3-12y$
4	$16y^4-48y^2+12$
5	$32y^5-160y^3+120y$
6	$64y^6-480y^4+720y^2-120$

The Hermite polynomials are solutions of the differential equation

$$H_v''-2yH_v'+2vH_v=0$$

where primes denote differentiation. They satisfy the recursion relation

$$H_{v+1}-2yH_v+2vH_{v-1}=0 \qquad \frac{\mathrm{d}H_v}{\mathrm{d}y}=2vyH_{v-1}$$

An important integral is

$$\int_{-\infty}^{\infty} H_{v'}H_v\mathrm{e}^{-y^2}\,\mathrm{d}y=\begin{cases}0 & \text{if } v'\neq v\\ \pi^{1/2}2^v v! & \text{if } v'=v\end{cases}$$

The wavefunction and the probability density are shown in Fig. 12.4. Both curves have their largest values at zero displacement (at $x=0$), so they capture the classical picture of the zero-point energy as arising from the ceaseless fluctuation of the particle about its equilibrium position.

Example 12.1 Confirming that a wavefunction is a solution of the Schrödinger equation

Confirm that the ground-state wavefunction (eqn 12.9a) is a solution of the Schrödinger equation 12.3.

Method Substitute the wavefunction given in eqn 12.9a into eqn 12.3. Use the definition of α given in eqn 12.8 to determine the energy on the right-hand side of eqn 12.3 and confirm that it matches the zero-point energy given in eqn 12.6.

Answer We need to evaluate the second derivative of the ground-state wavefunction:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}x}N_0\mathrm{e}^{-x^2/2\alpha^2}&=-N_0\left(\frac{x}{\alpha^2}\right)\mathrm{e}^{-x^2/2\alpha^2}\\ \frac{\mathrm{d}^2}{\mathrm{d}x^2}N_0\mathrm{e}^{-x^2/2\alpha^2}&=\frac{\mathrm{d}}{\mathrm{d}x}\left\{-N_0\left(\frac{x}{\alpha^2}\right)\mathrm{e}^{-x^2/2\alpha^2}\right\}\\ &=-\frac{N_0}{\alpha^2}\mathrm{e}^{-x^2/2\alpha^2}+N_0\left(\frac{x}{\alpha^2}\right)^2\mathrm{e}^{-x^2/2\alpha^2}\\ &=-(1/\alpha^2)\psi_0+(x^2/\alpha^4)\psi_0\end{aligned}$$

Substituting ψ_0 into eqn 12.3 and using the definition of α (eqn 12.8), we obtain

$$\frac{\hbar^2}{2m}\left(\frac{mk_\mathrm{f}}{\hbar^2}\right)^{1/2}\psi_0-\frac{\hbar^2}{2m}\left(\frac{mk_\mathrm{f}}{\hbar^2}\right)x^2\psi_0+\tfrac{1}{2}k_\mathrm{f}x^2\psi_0=E\psi_0$$

The second and third terms on the left-hand side cancel and we obtain $E=\frac{1}{2}\hbar(k_\mathrm{f}/m)^{1/2}$ in accord with eqn 12.6 for the zero-point energy.

Self-test 12.2 Confirm that the wavefunction in eqn 12.10 is a solution of eqn 12.3.

Answer: $E=\frac{3}{2}\hbar\omega$

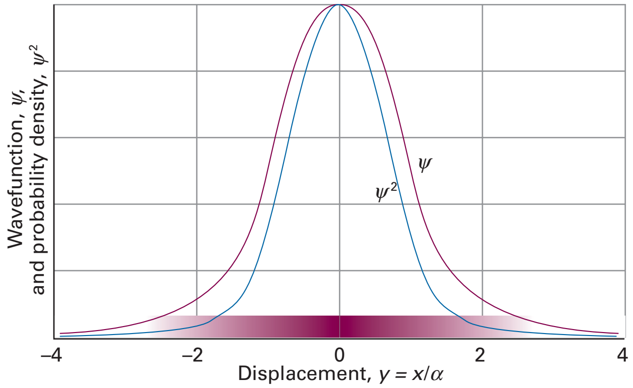


Figure 12.4 The normalized wavefunction and probability density (shown also by shading) for the lowest energy state of a harmonic oscillator.

The wavefunction for the first excited state of the oscillator, the state with $v=1$, is

$$\psi_1(x)=N_1 2y\mathrm{e}^{-y^2/2}=N_1\left(\frac{2}{\alpha}\right)x\mathrm{e}^{-x^2/2\alpha^2} \tag{12.10}$$

Harmonic oscillator

First excited-state wavefunction

This function has a node at zero displacement ($x=0$), and the probability density has maxima at $x=\pm\alpha$ (Fig. 12.5).

The shapes of several wavefunctions are shown in Fig. 12.6 and the corresponding probability densities are shown in Fig. 12.7. At high quantum numbers, harmonic oscillator wavefunctions have their largest amplitudes near the turning points

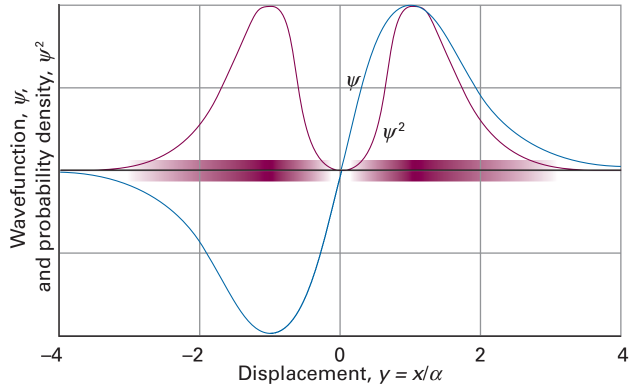


Figure 12.5 The normalized wavefunction and probability density (shown also by shading) for the first excited state of a harmonic oscillator.

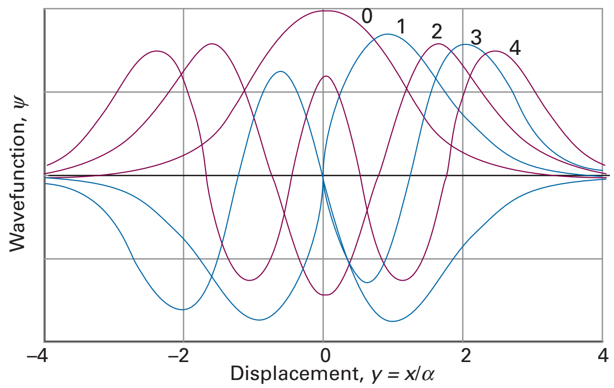


Figure 12.6 The normalized wavefunctions for the first five states of a harmonic oscillator. Note that the number of nodes is equal to v and that alternate wavefunctions are symmetrical or asymmetrical about $y=0$ (zero displacement).

of the classical motion (the locations at which $V=E$, so the kinetic energy is zero). We see classical properties emerging in the correspondence principle limit of high quantum numbers (Topic 9), for a classical particle is most likely to be found at the turning points (where it travels most slowly) and is least likely to be found at zero displacement (where it travels most rapidly).

Note the following features of the wavefunctions:

- The Gaussian function goes very strongly to zero as the displacement increases (in either direction), so all the wavefunctions approach zero at large displacements.
- The exponent y^2 is proportional to $x^2 \times (mk_f)^{1/2}$, so the wavefunctions decay more rapidly for large masses and stiff springs.
- As v increases, the Hermite polynomials become larger at large displacements (as x^v), so the wavefunctions grow large before the Gaussian function damps them down to zero: as a result, the wavefunctions spread over a wider range as v increases (Fig. 12.7).

Physical interpretation

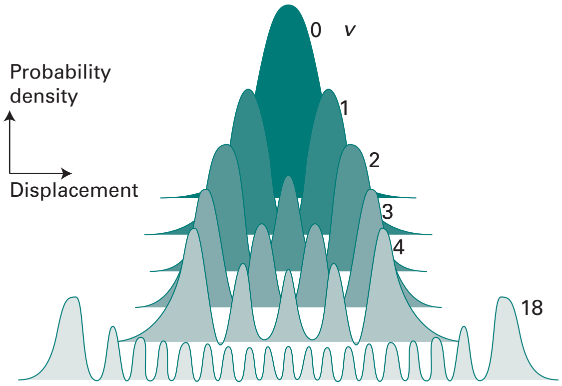


Figure 12.7 The probability densities for the first five states of a harmonic oscillator and the state with $v=18$. Note how the regions of highest probability density move towards the turning points of the classical motion as v increases.

Example 12.2 Normalizing a harmonic oscillator wavefunction

Find the normalization constant for the harmonic oscillator wavefunctions.

Method Normalization is carried out by evaluating the integral of $|\psi|^2$ over all space and then finding the normalization factor from eqn 5.2. The normalized wavefunction is then equal to $N\psi$. In this one-dimensional problem, the volume element is $\mathrm{d}x$ and the integration is from $-\infty$ to $+\infty$. The wavefunctions are expressed in terms of the dimensionless variable $y=x/\alpha$, so begin by expressing the integral in terms of y by using $\mathrm{d}x=\alpha\mathrm{d}y$. The integrals required are given in Table 12.1.

Answer The unnormalized wavefunction is

$$\psi_v(x) = H_v(y)\mathrm{e}^{-y^2/2}$$

It follows from the integrals given in Table 12.1 that

$$\int_{-\infty}^{\infty} \psi_v^* \psi_v \mathrm{d}x = \alpha \int_{-\infty}^{\infty} \psi_v^* \psi_v \mathrm{d}y = \alpha \int_{-\infty}^{\infty} H_v^2(y)\mathrm{e}^{-y^2}\mathrm{d}y$$
$$= \alpha\pi^{1/2}2^v v!$$

where $v! = v(v-1)(v-2)\ldots1$. Therefore,

$$N_v = \left(\frac{1}{\alpha\pi^{1/2}2^v v!}\right)^{1/2}$$

Note that, unlike the normalization constant for a particle in a box, for a harmonic oscillator N_v is different for each value of v.

Self-test 12.3 Confirm, by explicit evaluation of the integral, that ψ_0 and ψ_1 are orthogonal.

Answer: Evaluate the integral $\int_{-\infty}^{\infty} \psi_0^* \psi_1 \mathrm{d}x$ by using the information in Table 12.1

Example 12.3 Locating the nodes of a harmonic oscillator

Consider the H—Cl chemical bond of *Brief illustration* 12.1. If the molecule is undergoing harmonic motion with $v=2$, determine the H—Cl bond distances at which there is zero probability density of finding the molecule. The equilibrium bond length is 120 pm.

Method The distances at which there is zero probability density of finding the bond distance are the nodes of the $v=2$ harmonic oscillator wavefunction. Since the Gaussian function does not pass through zero, the nodes will be those values of x at which the Hermite polynomial passes though zero. Recall that x represents the displacement from equilibrium.

Answer Because $H_2(y)=4y^2-2$, we need to solve $4y^2-2=0$, which has solutions at $y=\pm1/2^{1/2}$. The nodes are therefore at $x=\pm\alpha/2^{1/2}$. Using μ in place of m in eqn 12.8, we find

$$x = \pm\frac{\alpha}{2^{1/2}} = \pm\left(\frac{\hbar^2}{4\mu k_\mathrm{f}}\right)^{1/4}$$

$$= \pm\left(\frac{(1.055\times10^{-34}\,\mathrm{J\,s})^2}{4\times0.9796\times(1.661\times10^{-27}\,\mathrm{kg})\times(516.3\,\mathrm{N\,m^{-1}})}\right)^{1/4}$$

$$= \pm 7.59\,\mathrm{pm}$$

Because x is the displacement from equilibrium, these displacements correspond to H—Cl bond distances of 112 pm and 128 pm. For higher values of v, it is best and often necessary to use numerical methods (for example, a root-extraction procedure of a mathematics package) to locate zeroes.

Self-test 12.4 Suppose the molecule is vibrationally excited to the state $v=3$. At what bond distances will the molecule not be found?

Answer: $x = 0, \pm\alpha(3/2)^{1/2}$; 120 pm, 107 pm, 133 pm

12.3 The properties of oscillators

The average value of a property is calculated by evaluating the expectation value of the corresponding operator (eqn 7.2a). Now that we know the wavefunctions of the harmonic oscillator, we can start to explore its properties by evaluating integrals of the type

$$\langle \Omega \rangle = \int_{-\infty}^{\infty} \psi_v^* \hat{\Omega} \psi_v \,\mathrm{d}x \tag{12.11}$$

(Here and henceforth, the wavefunctions are all taken to be normalized to 1.) When the explicit wavefunctions are substituted, the integrals look fearsome, but the Hermite polynomials have many simplifying features.

(a) Mean values

We show in the following example that the mean displacement, $\langle x\rangle$, and the mean square displacement, $\langle x^2\rangle$, of the oscillator when it is in the state with quantum number v are

$$\langle x\rangle = 0 \tag{12.12a}$$

Harmonic oscillator Mean displacement

$$\langle x^2\rangle = \left(v+\tfrac{1}{2}\right)\frac{\hbar}{(mk_\mathrm{f})^{1/2}} \tag{12.12b}$$

Harmonic oscillator Mean square displacement

The result for $\langle x\rangle$ shows that the oscillator is equally likely to be found on either side of $x=0$ (like a classical oscillator). The result for $\langle x^2\rangle$ shows that the mean square displacement increases with v. This increase is apparent from the probability densities in Fig. 12.7, and corresponds to the classical amplitude of swing increasing as the oscillator becomes more highly excited.

Example 12.4 Calculating properties of a harmonic oscillator

Consider the harmonic oscillator motion of the H—Cl molecule in *Brief illustration* 12.1. Calculate the mean displacement of the oscillator when it is in a state with quantum number v.

Method Normalized wavefunctions must be used to calculate the expectation value. The operator for position along x is multiplication by the value of x (Topic 6). The resulting integral can be evaluated either

- by inspection (the integrand is the product of an odd and an even function), or
- by explicit evaluation using the formulas in Table 12.1.

The former procedure makes use of the definitions that an even function is one for which $f(-x)=f(x)$ and an odd function is one for which $f(-x)=-f(x)$. Therefore, the product of an odd and even function is itself odd, and the integral of an odd function over a symmetrical range about $x=0$ is zero. The latter procedure using explicit integration is illustrated here to give practice in the calculation of expectation values. We shall need the relation $x=\alpha y$, which implies that $\mathrm{d}x=\alpha\mathrm{d}y$.

Answer The integral we require is

$$\langle x\rangle = \int_{-\infty}^{\infty}\psi_v^* x \psi_v \,\mathrm{d}x = N_v^2\int_{-\infty}^{\infty}(H_v\mathrm{e}^{-y^2/2})x(H_v\mathrm{e}^{-y^2/2})\,\mathrm{d}x$$

$$= \alpha^2 N_v^2\int_{-\infty}^{\infty}(H_v\mathrm{e}^{-y^2/2})y(H_v\mathrm{e}^{-y^2/2})\,\mathrm{d}y$$

$$= \alpha^2 N_v^2\int_{-\infty}^{\infty}H_v y H_v\mathrm{e}^{-y^2}\,\mathrm{d}y$$

Now use the recursion relation (Table 12.1) to form

$$yH_v = vH_{v-1} + \tfrac{1}{2}H_{v+1}$$

which turns the integral into

$$\int_{-\infty}^{\infty}H_v y H_v \mathrm{e}^{-y^2}\,\mathrm{d}y = v\int_{-\infty}^{\infty}H_v H_{v-1}\mathrm{e}^{-y^2}\,\mathrm{d}y + \frac{1}{2}\int_{-\infty}^{\infty}H_v H_{v+1}\mathrm{e}^{-y^2}\,\mathrm{d}y$$

Both integrals are zero (See Table 12.1), so $\langle x\rangle=0$. The mean displacement is zero because the displacement occurs equally on either side of the equilibrium position.

Self-test 12.5 Calculate the mean square displacement $\langle x^2\rangle$ of the H—Cl bond distance from its equilibrium position by using the recursion relation in Table 12.1 twice.

Answer: $\left(v+\tfrac{1}{2}\right)\times 115\,\mathrm{pm}^2$; eqn 12.12b, with μ in place of m

The mean potential energy of an oscillator, the expectation value of $V=\frac{1}{2}k_f x^2$, can now be calculated very easily:

$$\langle V\rangle = \tfrac{1}{2}\langle k_f x^2\rangle = \tfrac{1}{2}k_f\langle x^2\rangle = \frac{1}{2}(v+\tfrac{1}{2})\hbar\left(\frac{k_f}{m}\right)^{1/2}$$

or

$$\langle V\rangle = \frac{1}{2}(v+\tfrac{1}{2})\hbar\omega \tag{12.13a}$$

Harmonic oscillator Mean potential energy

Because the total energy in the state with quantum number v is $(v+\frac{1}{2})\hbar\omega$, it follows that

$$\langle V\rangle = \frac{1}{2}E_v \tag{12.13b}$$

Harmonic oscillator Mean potential energy

The total energy is the sum of the potential and kinetic energies, so it follows at once that the mean kinetic energy of the oscillator is (as could also be shown using the kinetic energy operator)

$$\langle E_k\rangle = \tfrac{1}{2}E_v \tag{12.13c}$$

Harmonic oscillator Mean kinetic energy

The result that the mean potential and kinetic energies of a harmonic oscillator are equal (and therefore that both are equal to half the total energy) is a special case of the **virial theorem**:

> If the potential energy of a particle has the form $V=ax^b$, then its mean potential and kinetic energies are related by

$$2\langle E_k\rangle = b\langle V\rangle \tag{12.14}$$

Virial theorem

For a harmonic oscillator $b=2$, so $\langle E_k\rangle=\langle V\rangle$, as we have found. The virial theorem is a shortcut to the establishment of a number of useful results, and we shall use it again.

(b) Tunnelling

An oscillator may be found at extensions with $V>E$ that are forbidden by classical physics, for they correspond to negative kinetic energy; this is an example of the phenomenon of tunnelling (Topic 10). As shown in Example 12.5, for the lowest energy state of the harmonic oscillator, there is about an 8 per cent chance of finding the oscillator stretched beyond its classical limit and an 8 per cent chance of finding it with a classically forbidden compression. These tunnelling probabilities are independent of the force constant and mass of the oscillator.

Example 12.5 Calculating the tunnelling probability for the harmonic oscillator

Calculate the probability that the ground-state harmonic oscillator will be found in a classically forbidden region.

Method Find the expression for the classical turning point, x_{tp}, where the kinetic energy vanishes, by equating the potential energy to the total energy E of the harmonic oscillator. Proceed to calculate the probability of finding the oscillator stretched beyond the classical turning point using eqn 5.5 (Topic 5):

$$P=\int_{x_{tp}}^{\infty}\psi_v^2\mathrm{d}x$$

The variable of integration is best expressed in terms of $y=x/\alpha$ and the integral to be evaluated is a special case of the *error function*, erf z, defined as (see Integral G.6 of the *Resource section*)

$$\mathrm{erf}\,z = 1-\frac{2}{\pi^{1/2}}\int_z^{\infty}\mathrm{e}^{-y^2}\mathrm{d}y$$

and evaluated for some values of z in Table 12.2 (this function is commonly available in mathematical software packages). By symmetry, the probability of being found stretched into a classically forbidden region is the same as that of being found compressed into a classically forbidden region.

Answer According to classical mechanics, the turning point, x_{tp}, of an oscillator occurs when its kinetic energy is zero, which is when its potential energy $\frac{1}{2}k_f x^2$ is equal to its total energy E. This equality occurs when

$$x_{tp}^2=\frac{2E}{k_f} \quad \text{or} \quad x_{tp}=\pm\left(\frac{2E}{k_f}\right)^{1/2}$$

with E given by eqn 12.4. The probability of finding the oscillator stretched beyond a displacement x_{tp} is the sum of the probabilities $\psi^2\mathrm{d}x$ of finding it in any of the intervals $\mathrm{d}x$ lying between x_{tp} and infinity:

Table 12.2 The error function

z	erf z
0	0
0.01	0.0113
0.05	0.0564
0.10	0.1125
0.50	0.5205
1.00	0.8427
1.50	0.9661
2.00	0.9953

$$P=\int_{x_\mathrm{tp}}^{\infty}\psi_v^2\mathrm{d}x$$

The variable of integration is best expressed in terms of $y=x/\alpha$ with $\alpha=(\hbar^2/mk_\mathrm{f})^{1/4}$, and then the turning point on the right lies at

$$y_\mathrm{tp}=\frac{x_\mathrm{tp}}{\alpha}=\left\{\frac{2(v+\frac{1}{2})\hbar\omega}{\alpha^2k_\mathrm{f}}\right\}^{1/2}\overset{\omega=(k_\mathrm{f}/m)^{1/2}}{=}(2v+1)^{1/2}$$

For the state of lowest energy ($v=0$), $y_\mathrm{tp}=1$ and the probability is

$$P=\int_{x_\mathrm{tp}}^{\infty}\psi_0^2\mathrm{d}x=\alpha N_0^2\int_1^{\infty}\mathrm{e}^{-y^2}\mathrm{d}y$$

The integral is a special case of the error function, erf z, given above. In the present case (see Example 12.1 for N_0 and use $0!=1$)

$$P=\tfrac{1}{2}(1-\mathrm{erf}\,1)=\tfrac{1}{2}(1-0.843)=0.079$$

It follows that in 7.9 per cent of a large number of observations, any oscillator in the state $v=0$ will be found stretched to a classically forbidden extent. There is the same probability of finding the oscillator with a classically forbidden compression. The total probability of finding the oscillator tunnelled into a classically forbidden region (stretched or compressed) is about 16 per cent.

Self-test 12.6 Calculate the probability that a harmonic oscillator in the state $v=1$ will be found at a classically forbidden extension. (Follow the argument given in Example 12.5 and use the method of integration by parts (see *Mathematical background* 1) to obtain an integral which can be expressed in terms of the error function.)

Answer: $P=0.056$

The tunnelling of the harmonic oscillator has effects on the types of processes described in Topic 10. For example, a more realistic model of the potential energy describing conformational changes of the AB_3 molecule uses two harmonic oscillator (parabolic) wells separated by a barrier (Fig. 12.8) rather than the double-potential well (Topic 10). The tunnelling of the $v=0$ wavefunction through the potential barrier is responsible for inversion doubling.

The probability of finding the oscillator in classically forbidden regions decreases quickly with increasing v, and vanishes entirely as v approaches infinity, as we would expect from the correspondence principle. Macroscopic oscillators (such as pendulums) are in states with very high quantum numbers, so the tunnelling probability is wholly negligible. Molecules, however, are normally in their vibrational ground states, and for them the probability is very significant.

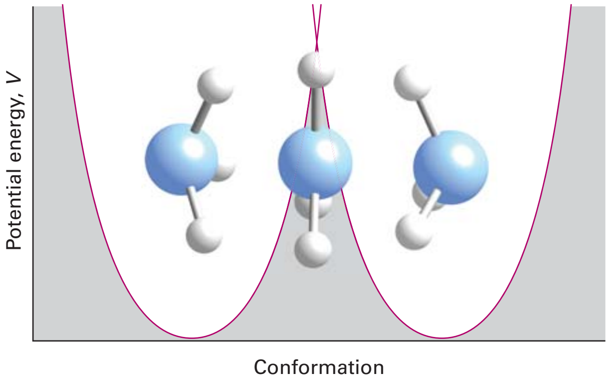


Figure 12.8 A model potential energy to describe conformational changes of the AB_3 molecule. Two harmonic oscillator (parabolic) wells are separated by a barrier. (Compare Fig. 10.9.)

12.4 Applications of the harmonic oscillator model in chemistry

The harmonic oscillator is a powerful model that can help chemists understand a number of phenomena. We have seen (Section 12.1) that the existence of quantized vibrational motion in diatomic molecules—and molecules in general—can be explained by considering the chemical bond as a harmonic oscillator. In turn, this insight leads to the interpretation of molecular infrared spectra. Topics 43 and 44 explore vibrational spectroscopy in more detail. Here we provide two examples to illustrate the power of the harmonic oscillator model to provide insight into the dynamics of molecules and the mechanisms of chemical reactions.

(a) Molecular dynamics

Molecules are dynamic, in the sense that their atoms move in relation to each other. One example of such motion is the stretching and compression of a bond. Other forms of motion are bond bending, during which a bond angle opens and closes, and bond torsion, the internal rotation, or twisting, of one bond relative to another. These three modes of motion can be regarded as harmonic motion. For example, if the equilibrium bond angle is θ_e, the potential energy is

$$V_\mathrm{bend}=\tfrac{1}{2}k_\mathrm{f,bend}(\theta-\theta_\mathrm{e})^2 \qquad (12.15)$$

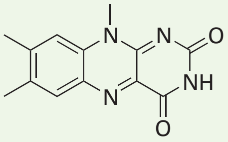
where $k_\mathrm{f,bend}$ is the bending force constant, a measure of how difficult it is to change the bond angle. This equation bears a striking resemblance to eqn 12.2, which we have used to describe bond stretching.

Brief illustration 12.2 The energy of bond angle bending

Theoretical studies have estimated that the lumiflavin isoalloazine ring system (**1**) has an energy minimum at the bending angle of 15°, but that it requires only 1.41×10^{-20} J or 8.50 kJ mol^{-1} to increase the angle to 30°. The force constant for lumiflavin bending is therefore

$$k_{\mathrm{f,bend}}=\frac{2V_{\mathrm{bend}}}{(\theta-\theta_{\mathrm{e}})^2}=\frac{2\times(1.41\times10^{-20}\,\mathrm{J})}{(30^\circ-15^\circ)^2}=1.3\times10^{-22}\,\mathrm{J\,deg^{-2}}$$

corresponding to 75 J deg^{-2} mol^{-1}.

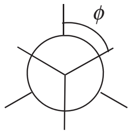


1 Lumiflavin

Self-test 12.7 It takes 0.90 aJ to bend a C—C—C bond by 2.0° from its equilibrium bond angle. What is the force constant for this bending motion?

Answer: 4.5×10^{-19} J deg^{-2}, 2.7×10^{5} J deg^{-2} mol^{-1}

To explore bond torsion, consider rotation around the C—C bond in ethane, which can be described in terms of the angle ϕ shown in (**2**). For small variations of ϕ, the torsional motion around the C—C bond can be expected to be that of a harmonic oscillator, and the energy separation between adjacent energy levels of the oscillator is given by $\Delta E=\hbar\omega$, where ω is the torsional frequency.



2

(b) The kinetic isotope effect

The postulation of a plausible reaction mechanism requires careful analysis of many experiments designed to determine the fate of atoms during the formation of products. Observation of the **kinetic isotope effect**, a decrease in the rate of a chemical reaction upon replacement of one atom in a reactant by a heavier isotope, facilitates the identification of bond-breaking events in the rate-determining step. A **primary kinetic isotope effect** is observed when the rate-determining step requires the scission of a bond involving the isotope. A **secondary kinetic isotope effect** is the reduction in reaction rate even though the bond involving the isotope is not broken to form product. In both cases, the effect arises from the change in activation energy (Topic 85) that accompanies the replacement of an atom by a heavier isotope on account of changes in the zero-point vibrational energies. We now explore the primary kinetic isotope effect in some detail.

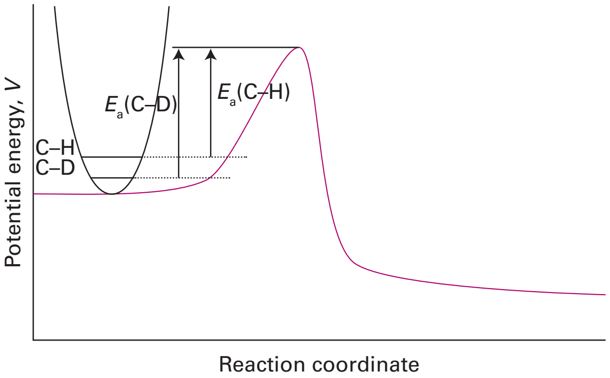


Figure 12.9 Changes in the reaction profile when a C—H bond undergoing cleavage is deuterated. In this figure the C—H and C—D bonds are modelled as harmonic oscillators. The only significant change is in the zero-point energy of the reactants, which is lower for C—D than for C—H. As a result, the activation energy is greater for C—D cleavage than for C—H cleavage.

Consider a reaction in which a C—H bond is cleaved. If scission of this bond is the rate-determining step (Topic 86), then the reaction coordinate corresponds to the stretching of the C—H bond and the potential energy profile is shown in Fig. 12.9. On deuteration, the dominant change is the reduction of the zero-point energy of the bond (because the deuterium atom is heavier). The whole reaction profile is not lowered, however, because the relevant vibration in the activated complex has a very low force constant, so there is little zero-point energy associated with the reaction coordinate in either form of the activated complex. We show in the following *Justification* that, as a consequence of this reduction, the activation energy change upon deuteration is

$$E_a(\mathrm{C{-}D})-E_a(\mathrm{C{-}H})=\tfrac{1}{2}N_{\mathrm{A}}\hbar\omega(\mathrm{C{-}H})\left\{1-\left(\frac{\mu_{\mathrm{CH}}}{\mu_{\mathrm{CD}}}\right)^{1/2}\right\} \qquad (12.16)$$

where ω is the relevant vibrational frequency (in radians per second), μ is the relevant effective mass, and

$$\frac{k_{\mathrm{r}}(\mathrm{C{-}D})}{k_{\mathrm{r}}(\mathrm{C{-}H})}=\mathrm{e}^{-\zeta}\quad\text{with}\quad\zeta=\frac{\hbar\omega(\mathrm{C{-}H})}{2kT}\left\{1-\left(\frac{\mu_{\mathrm{CH}}}{\mu_{\mathrm{CD}}}\right)^{1/2}\right\} \qquad (12.17)$$

Note that $\zeta>0$ (ζ is zeta) because $\mu_{\mathrm{CD}}>\mu_{\mathrm{CH}}$ and that $k_{\mathrm{r}}(\mathrm{C{-}D})/k_{\mathrm{r}}(\mathrm{C{-}H})<1$, meaning that, as expected from Fig. 12.9, the rate constant decreases upon deuteration. We also conclude that $k_{\mathrm{r}}(\mathrm{C{-}D})/k_{\mathrm{r}}(\mathrm{C{-}H})$ decreases with decreasing temperature.

Justification 12.1 The primary kinetic isotope effect

We assume that, to a good approximation, a change in the activation energy arises only from the change in zero-point energy of the stretching vibration, so, from Fig. 12.9,

$$E_a(\text{C–D})-E_a(\text{C–H})=N_A\left\{\frac{1}{2}\hbar\omega(\text{C–H})-\frac{1}{2}\hbar\omega(\text{C–D})\right\}$$
$$=\frac{1}{2}N_A\hbar\{\omega(\text{C–H})-\omega(\text{C–D})\}$$

where ω is the relevant vibrational frequency. From eqn 12.4, we know that $\omega(\text{C—D})=(\mu_{\text{CH}}/\mu_{\text{CD}})^{1/2}\,\omega(\text{C—H})$, where μ is the relevant effective mass. Making this substitution in the equation above gives eqn 12.16.

If we assume further that the pre-exponential factor does not change upon deuteration, then the rate constants for the two species should be in the ratio

$$\frac{k_r(\text{C−D})}{k_r(\text{C−H})}=\mathrm{e}^{-\{E_a(\text{C–D})-E_a(\text{C–H})\}/RT}=\mathrm{e}^{-\{E_a(\text{C–D})-E_a(\text{C–H})\}/N_AkT}$$

where we have used $R=N_Ak$. Equation 12.17 follows after using eqn 12.16 for $E_a(\text{C–D})-E_a(\text{C–H})$ in this expression.

Brief illustration 12.3 The primary kinetic isotope effect

From infrared spectra, the fundamental vibrational wavenumber $\tilde{\nu}$ for stretching of a C—H bond is about 3000 cm^{-1}. To convert this wavenumber to an angular frequency, $\omega=2\pi\tilde{\nu}$, we use $\omega=2\pi c\tilde{\nu}$, and it follows that

$$\omega=2\pi\times(2.998\times10^{10}\,\text{cm s}^{-1})\times(3000\,\text{cm}^{-1})$$
$$=5.65\times10^{14}\,\text{s}^{-1}$$

The ratio of effective masses is

$$\frac{\mu_{\text{CH}}}{\mu_{\text{CD}}}=\left(\frac{m_Cm_H}{m_C+m_H}\right)\times\left(\frac{m_C+m_D}{m_Cm_D}\right)=\left(\frac{12.01\times1.0078}{12.01+1.0078}\right)$$
$$\times\left(\frac{12.01+2.0140}{12.01\times2.0140}\right)=0.539\ldots$$

Now we can use eqn 12.17 to calculate

$$\zeta=\frac{(1.055\times10^{-34}\,\text{Js})\times(5.65\ldots\times10^{14}\,\text{s}^{-1})}{2\times(1.381\times10^{-23}\,\text{J K}^{-1})\times(298\,\text{K})}\times(1-0.539\ldots^{1/2})$$
$$=1.92\ldots$$

and

$$\frac{k_r(\text{C−D})}{k_r(\text{C−H})}=\mathrm{e}^{-1.92\ldots}=0.146$$

We conclude that at room temperature C—H cleavage should be about 7 times faster than C—D cleavage, other conditions being equal. However, experimental values of $k_r(\text{C—D})/k_r(\text{C—H})$ can differ significantly from those predicted by eqn 12.17 on account of the severity of the assumptions in the model.

Self-test 12.8 The bromination of a deuterated hydrocarbon at 298 K proceeds 6.4 times more slowly than the bromination of the undeuterated material. What value of the force constant for the cleaved bond can account for this difference?

Answer: $k_f=450\,\text{N m}^{-1}$, which is consistent with $k_f(\text{C—H})$

Checklist of concepts

☐ 1. A particle undergoing **harmonic motion** experiences a restoring force proportional to its displacement; its potential energy is parabolic.

☐ 2. The energy levels of a harmonic oscillator form an evenly spaced ladder.

☐ 3. The wavefunctions of a harmonic oscillator are products of a Hermite polynomial and a Gaussian (bell-shaped) function.

☐ 4. There is a zero-point vibrational energy, which is consistent with, and can be interpreted in terms of, the uncertainty principle.

☐ 5. The probability of finding the harmonic oscillator in classically forbidden regions is significant for the ground vibrational state ($v=0$) but decreases quickly with increasing vibrational quantum number v.

☐ 6. The **kinetic isotope effect** is the decrease in the rate constant of a chemical reaction upon replacement of one atom in a reactant by a heavier isotope.

Checklist of equations

Property	Equation	Comment	Equation number
Energy of harmonic oscillator	$E_v=(v+\tfrac{1}{2})\hbar\omega \quad \omega=(k_f/m)^{1/2}$	$v=1, 2, \ldots$	12.4
Zero-point energy of harmonic oscillator	$E_0=\tfrac{1}{2}\hbar\omega$		12.6
Wavefunction of harmonic oscillator	$\psi_v(x)=N_vH_v(y)\mathrm{e}^{-y^2/2}$ $y=x/\alpha \quad \alpha=(\hbar^2/mk_f)^{1/4}$ $N_v=(1/\alpha\pi^{1/2}2^v v!)^{1/2}$	$v=1, 2, \ldots$	12.8
Mean displacement of harmonic oscillator	$\langle x\rangle=0$		12.12a
Mean square displacement of harmonic oscillator	$\langle x^2\rangle=\left(v+\frac{1}{2}\right)\hbar/(mk_f)^{1/2}$		12.12b
Virial theorem	$2\langle E_k\rangle=b\langle V\rangle$	$V=ax^b$	12.14
Primary kinetic isotope effect	$k_r(\mathrm{C{-}D})/k_r(\mathrm{C{-}H})=\mathrm{e}^{-\zeta}$, $\zeta=(\hbar\omega(\mathrm{C{-}H})/2kT)\times\left\{1-\left(\mu_{\mathrm{C-H}}/\mu_{\mathrm{C-D}}\right)^{1/2}\right\}$	Cleavage of a C—H bond in the rate-determining step	12.17

TOPIC 13

Rotational motion in two dimensions

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➤ Why do you need to know this material?

Rotation is one of the modes of internal motion of molecules. Investigation of rotational motion introduces the concept of angular momentum, which is central to the quantum mechanical description of the electronic structure of atoms and molecules, and the interpretation of details observed in molecular spectra.

➤ What is the key idea?

The energy and the angular momentum of a particle rotating in two dimensions are quantized.

➤ What do you need to know already?

You should know the postulates of quantum mechanics (Topics 5–7), and be familiar with the concept of angular momentum in classical physics (*Foundations,* Topic 2).

Rotation is an important aspect of motion, and is encountered in the discussion of the electronic structure of atoms and molecules (Topics 17 and 23), the spectroscopy of molecules (particularly but not only microwave spectroscopy, Topic 42), and of various aspects of electrons trapped in cavities in solids. This Topic provides an initial introduction by focusing on rotation in two dimensions, or rotation in a plane; although the applicability of two-dimensional rotation as a model for real (three-dimensional) systems is limited, many of the characteristics encountered in two dimensions apply to the more general case of rotation in three dimensions (Topic 14).

13.1 A particle on a ring

Just as *linear* momentum is a central concept for the discussion of linear motion (Topic 9), *angular* momentum is central to the discussion of rotational motion. For a particle moving on a circle of radius r in the xy-plane and having a linear momentum of magnitude p at some instant, the angular momentum around the perpendicular z-axis is

$$J_z = \pm pr \qquad \textit{Particle on a ring, classical expression} \qquad \text{Angular momentum} \qquad (13.1)$$

A positive sign corresponds to clockwise motion (seen from below) and a negative sign corresponds to anticlockwise motion (Fig. 13.1). The kinetic energy of a particle of mass m and linear momentum p is $E_k = p^2/2m$. Therefore, if the particle is moving on a circle of radius r with angular momentum J_z, its kinetic energy is $E_k = (J_z/r)^2/2m = J_z^2/2mr^2$. Because its uniform potential energy may be taken to be zero, its total energy is

$$E = \frac{J_z^2}{2mr^2} \qquad \textit{Particle on a ring, classical expression} \qquad \text{Energy} \qquad (13.2a)$$

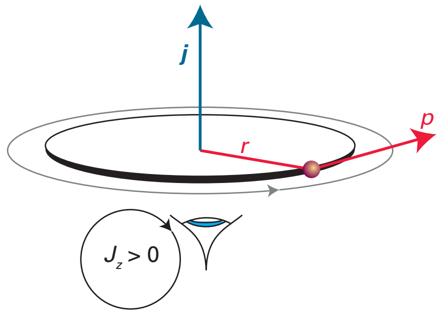


Figure 13.1 For a particle moving on a circle of radius *r* in the *xy*-plane and having a linear momentum of magnitude *p* at some instant, the classical angular momentum around the *z*-axis is $J_z = \pm pr$, where the positive (negative) sign corresponds to clockwise (anticlockwise) motion, as seen from below.

The moment of inertia, I, of the particle around the centre of rotation is mr^2, so this energy may also be written as

$$E=\frac{J_z^2}{2I} \qquad \textit{Particle on a ring, classical expression} \qquad \text{Energy} \qquad (13.2\text{b})$$

Equation 13.2b applies to any body of moment of inertia I rotating in a plane, not just a point mass on a circle. For instance, it applies to a circular disc of mass m and radius R, with $I=\frac{1}{2}mR^2$. It also applies to a diatomic molecule of bond length R composed of atoms of masses m_A and m_B, with the moment of inertia, as shown in the following *Justification*, interpreted as

$$I=\mu R^2 \quad \text{with} \quad \mu=\frac{m_A m_B}{m_A+m_B} \qquad \textit{Diatomic molecule} \qquad \text{Moment of inertia} \qquad (13.3)$$

Justification 13.1 The moment of inertia of a diatomic molecule

The moment of inertia about an axis is defined by

$$I=\sum_i m_i x_i^2$$

where x_i is the perpendicular distance of atom i of mass m_i from the axis (Fig. 13.2). For a diatomic molecule with bond length $R=x_B-x_A$ (taking $x_B>x_A$, and the origin at the centre of mass) and atoms of masses m_A and m_B, rotation proceeds around an axis passing through the centre of mass of the molecule, which is given by the condition (see Fig. 13.3)

$$m_B x_B=-m_A x_A \quad \text{or} \quad (\text{because } x_A=x_B-R) \; m_B x_B=m_A(R-x_B)$$

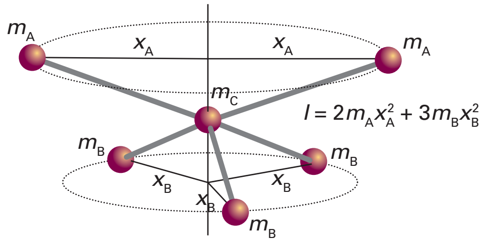


Figure 13.2 The definition of the moment of inertia about a selected axis in terms of the mass of a particle and its perpendicular distance from the axis.

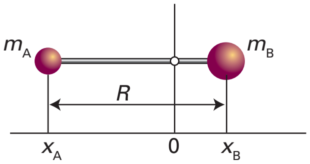


Figure 13.3 The moment of inertia of a diatomic molecule AB. x_A and x_B are the perpendicular distances from the atoms to the axis passing through the centre of mass of the molecule (taken to be the origin) and $R=x_B-x_A$.

It follows that $m_B x_B = m_A R - m_A x_B$ and therefore

$$x_B=\frac{m_A R}{m_A+m_B} \qquad x_A=x_B-R=-\frac{m_B R}{m_A+m_B}$$

The moment of inertia is therefore

$$\begin{aligned} I &= m_B x_B^2+m_A x_A^2 \\ &= m_B\left(\frac{m_A R}{m_A+m_B}\right)^2+m_A\left(-\frac{m_B R}{m_A+m_B}\right)^2 \\ &= \frac{m_B m_A^2+m_A m_B^2}{(m_B+m_A)^2}R^2=\frac{m_A m_B(m_A+m_B)}{(m_B+m_A)^2}R^2 \\ &= \frac{m_A m_B}{m_B+m_A}R^2=\mu R^2 \end{aligned}$$

in accord with eqn 13.3.

Brief illustration 13.1 The moment of inertia

For the diatomic molecule $^1H^{35}Cl$ of bond length 127.45 pm,

$$\mu=\frac{m_H m_{Cl}}{m_H+m_{Cl}}=\frac{(1.0078m_u)\times(34.9688m_u)}{(1.0078m_u)+(34.9688m_u)}=0.9796\ldots m_u$$

and the moment of inertia is

$$\begin{aligned} I &= (0.9796\ldots\times 1.66054\times 10^{-27}\,\text{kg})\times(127.45\times 10^{-12}\,\text{m})^2 \\ &= 2.6422\times 10^{-47}\,\text{kg}\,\text{m}^2 \end{aligned}$$

A note on good practice To calculate the moment of inertia of a molecule, the actual masses of the atoms must be used. It follows that isotopes of the atoms in the molecule must be specified.

Self-test 13.1 Repeat the calculation in *Brief illustration* 13.1 for $^2\text{H}^{35}\text{Cl}$ assuming the same bond length.

Answer: $\mu = 1.9043m_\text{u}$, $I = 5.1365\times10^{-47}\,\text{kg}\,\text{m}^2$

(a) The qualitative origin of quantized rotation

The linear momentum that appears in eqn 13.1 can be expressed as a wavelength of the orbiting particle by using the de Broglie relation $p = h/\lambda$ (Topic 4), which gives

$$J_z = \pm\frac{hr}{\lambda}$$

Likewise, the energy in eqn 13.2b becomes

$$E = \frac{h^2r^2}{2I\lambda^2}$$

Suppose for the moment that λ can take an arbitrary value. In that case, the wavefunction depends on the azimuthal angle ϕ, as shown in Fig. 13.4a. When ϕ increases beyond 2π, the wavefunction continues to change, but for an arbitrary wavelength it gives rise to a different value at a given point after each circuit, which is unacceptable because a wavefunction must be single-valued. An acceptable solution is obtained only if the wavefunction reproduces itself on successive circuits, as in Fig. 13.4b. Because only some wavefunctions have this property, it follows that only some angular momenta are acceptable, and therefore that only certain rotational energies are allowed. That is, the energy of the particle is quantized. Specifically, an integer number of wavelengths must fit the circumference of the ring (which is $2\pi r$):

$$n\lambda = 2\pi r \quad n = 0, 1, 2, \ldots \tag{13.4}$$

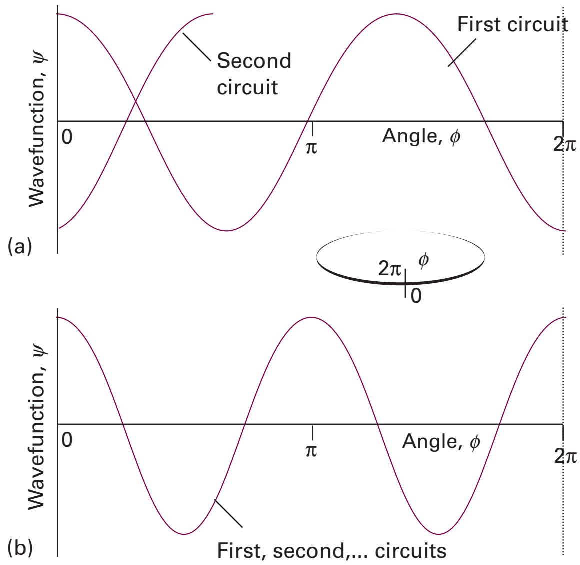


Figure 13.4 Two solutions of the Schrödinger equation for a particle on a ring. The circumference has been opened out into a straight line; the points at $\phi=0$ and 2π are identical. The solution in (a) is unacceptable because it is not single-valued. Moreover, on successive circuits it interferes destructively with itself, and does not survive. The solution in (b) is acceptable: it is single-valued, and on successive circuits it reproduces itself.

The value $n=0$ corresponds to $\lambda=\infty$; a 'wave' of infinite wavelength has a constant height at all values of ϕ. The angular momentum is therefore limited to the values

$$J_z = \pm\frac{hr}{\lambda} = \pm\frac{nhr}{2\pi r} = \pm\frac{nh}{2\pi} \quad n = 0, 1, 2, \ldots$$

The sign of J_z (which indicated the sense of the rotation) can be absorbed into the quantum number by replacing n by $m_l = 0, \pm1, \pm2, \ldots$ where we have allowed m_l (the conventional notation for this quantum number) to have positive and negative integer values. At the same time we recognize the presence of $h/2\pi = \hbar$ and obtain

$$J_z = m_l\hbar \quad m_l = 0, \pm1, \pm2, \ldots \tag{13.5}$$

Particle on a ring Angular momenta

Positive values of m_l correspond to rotation in a clockwise sense around the z-axis (as viewed in the direction of z, Fig. 13.5) and negative values of m_l correspond to anticlockwise rotation around z. It then follows from eqns 13.2b and 13.5 that the energy is limited to the values

$$E_{m_l} = \frac{m_l^2\hbar^2}{2I} \quad m_l = 0, \pm1, \pm2, \ldots \tag{13.6}$$

Particle on a ring Energy levels

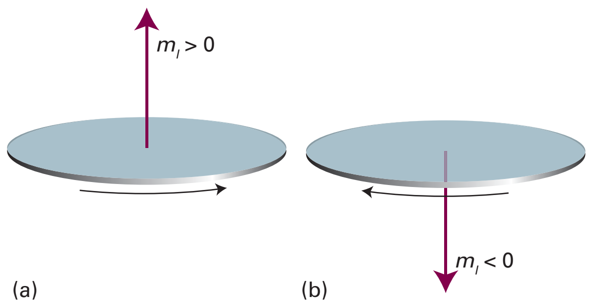


Figure 13.5 The angular momentum of a particle confined to a plane can be represented by a vector of length $|m_l|$ units along the z-axis and with an orientation that indicates the direction of motion of the particle. The direction is given by the right-hand screw rule, so (a) corresponds to $m_l > 0$, clockwise as seen from below, and (b) corresponds to $m_l < 0$, anticlockwise as seen from below.

We explore this result further by noting that:

- The energies, labelled by m_l, are quantized because m_l must be an integer.
- The occurrence of m_l as its square means that the energy of rotation is independent of the sense of rotation (the sign of m_l), as we expect physically. That is, states with a given nonzero value of $|m_l|$ are doubly degenerate.
- The state described by $m_l=0$ is non-degenerate, consistent with the interpretation that, when m_l is zero, the particle has an infinite wavelength and is 'stationary'; the question of the direction of rotation does not arise.
- There is no zero-point energy in this system: the lowest possible energy is $E_0=0$.

Physical interpretation

Brief illustration 13.2 The rotational energies

So that we can get a sense of the energies involved in rotation, suppose that we consider the case of a body with the same moment of inertia as an $^1H^{35}Cl$ molecule (see *Brief illustration* 13.1) that is confined to rotate in a plane. Then the energy of the doubly degenerate states with $m_l=\pm1$ is

$$E_{\pm1}=\frac{(\pm1)^2\hbar^2}{2I}=\frac{(1.055\times10^{-34}\,\mathrm{J\,s})^2}{2\times(2.642\times10^{-47}\,\mathrm{kg\,m^2})}=2.106\times10^{-22}\,\mathrm{J}$$

Because the lowest rotational state (with $m_l=0$) has zero energy, this value is the minimum energy needed to start the body rotating. After multiplication by Avogadro's constant, it corresponds to 0.1268 kJ mol^{-1}.

Self-test 13.2 Repeat the calculations in this *Brief illustration* for a body with the same moment of inertia as $^2H^{35}Cl$.

Answer: $E_{\pm1}=1.083\times10^{-22}$ J or 65.22 J mol^{-1}

(b) The solutions of the Schrödinger equation

We have arrived at a number of conclusions about rotational motion by combining some results from classical mechanics with the de Broglie relation. Such a procedure can be very useful for establishing the general form (and, as in this case, the exact energies and angular momenta) for a quantum mechanical system. However, to obtain the wavefunctions for the particle on a ring, to confirm that the correct energies have been obtained, and to obtain practice for more complex problems where this less formal approach is inadequate, we need to solve the Schrödinger equation explicitly. We show in the following *Justification* that the normalized wavefunctions and corresponding energies are given by

$$\psi_{m_l}(\phi)=\frac{e^{im_l\phi}}{(2\pi)^{1/2}}\quad m_l=0,\pm1,\pm2,\ldots\qquad \text{Particle on a ring}\quad \text{Wave-functions}\qquad (13.7a)$$

$$E_{m_l}=\frac{m_l^2\hbar^2}{2I}\qquad \text{Particle on a ring}\quad \text{Energy levels}\qquad (13.7b)$$

The wavefunction with $m_l=0$ is $\psi_0(\phi)=1/(2\pi)^{1/2}$, corresponding to uniform amplitude around the ring. That uniformity implies that the particle has zero kinetic energy. Because kinetic energy is the only source of energy, $E_0=0$ and there is no zero-point energy. This conclusion is consistent with the uncertainty principle, because the angular location of the particle is completely unknown, so the angular momentum (and hence the energy) can be specified exactly.

Justification 13.2 The solutions of the Schrödinger equation for a particle on a ring

The hamiltonian for a particle of mass m travelling on a circle in the xy-plane (with $V=0$) is the same as that for free motion in a plane (eqn 11.1 of Topic 11),

$$\hat{H}=-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\qquad \text{Hamiltonian}\qquad (13.8)$$

but with the constraint to a path of constant radius r. It is always a good idea to use coordinates that reflect the full symmetry of the system, so we introduce the coordinates r and ϕ (Fig. 13.6), where $x=r\cos\phi$ and $y=r\sin\phi$. As shown in *The chemist's toolkit* 13.1, we can write

$$\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}=\frac{\partial^2}{\partial r^2}+\frac{1}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}\qquad (13.9)$$

However, because the radius of the path is fixed, the derivatives with respect to r can be discarded. Only the last term in eqn 13.9 then survives and the hamiltonian becomes simply

$$\hat{H}=-\frac{\hbar^2}{2mr^2}\frac{d^2}{d\phi^2}\qquad \text{Particle on a ring}\quad \text{Hamiltonian}\qquad (13.10a)$$

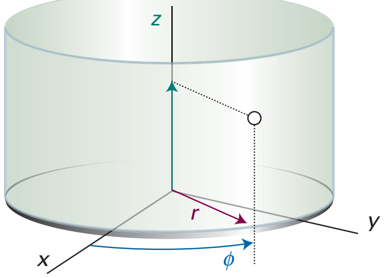


Figure 13.6 The cylindrical coordinates z, r, and ϕ for discussing systems with axial (cylindrical) symmetry. For a particle confined to the xy-plane, only r and ϕ can change.

The partial derivative has been replaced by a complete derivative because ϕ is now the only variable. The moment of inertia, $I=mr^2$ has appeared automatically so $\hat{H}$ may be written

$$\hat{H}=-\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}\qquad \textit{Particle on a ring}\quad \text{Hamiltonian}\qquad (13.10b)$$

and the Schrödinger equation is

$$-\frac{\hbar^2}{2I}\frac{d^2\psi}{d\phi^2}=E\psi\qquad \textit{Particle on a ring}\quad \text{Schrödinger equation}\qquad (13.11a)$$

We rewrite this equation as

$$\frac{d^2\psi}{d\phi^2}=-\frac{2IE}{\hbar^2}\psi$$

For a given energy, $2IE/\hbar^2$ is a constant, which for convenience (and an eye on the future) we write as m_l^2. At this stage m_l is just a dimensionless number with no restrictions. Then the equation becomes

$$\frac{d^2\psi}{d\phi^2}=-m_l^2\psi\qquad (13.11b)$$

The (unnormalized) general solutions of this equation are

$$\psi_{m_l}(\phi)=e^{im_l\phi}\qquad (13.12)$$

as can be verified by substitution.

We now select the acceptable solutions from among these general solutions by imposing the condition that the wavefunction should be single-valued. That is, the wavefunction ψ must satisfy a **cyclic boundary condition**, and match at points separated by a complete revolution: $\psi(\phi+2\pi)=\psi(\phi)$. On substituting the general wavefunction into this condition, we find

$$\begin{aligned}\psi_{m_l}(\phi+2\pi)&=e^{im_l(\phi+2\pi)}=e^{im_l\phi}e^{2\pi im_l}=\psi_{m_l}(\phi)e^{2\pi im_l}\\&=\psi_{m_l}(\phi)(e^{\pi i})^{2m_l}\end{aligned}$$

As $e^{i\pi}=-1$ (Euler's formula, *Mathematical background* 3), this relation is equivalent to

$$\psi_{m_l}(\phi+2\pi)=(-1)^{2m_l}\psi_{m_l}(\phi)$$

Because cyclic boundary conditions require $(-1)^{2m_l}=1, 2m_l$ must be a positive or a negative even integer (including 0), and therefore m_l must be an integer: $m_l=0, \pm1, \pm2, \ldots$.

We now normalize the wavefunction by finding the normalization constant N given by eqn 5.2 (with dx replaced by $d\phi$) :

$$N=\frac{1}{\left(\int_0^{2\pi}\psi^*\psi\,d\phi\right)^{1/2}}=\frac{1}{\left(\underbrace{\int_0^{2\pi}e^{-im_l\phi}e^{im_l\phi}d\phi}_{\int_0^{2\pi}d\phi}\right)^{1/2}}=\frac{1}{(2\pi)^{1/2}}\qquad (13.13)$$

and the normalized wavefunctions for a particle on a ring are those given by eqn 13.7a. The expression for the energies of the states (eqn 13.7b) is obtained by rearranging the relation $m_l^2=2IE/\hbar^2$ into $E=m_l^2\hbar/2I$.

The chemist's toolkit 13.1 Cylindrical coordinates

The natural coordinates to use in a system with cylindrical symmetry are **cylindrical coordinates**, with r the radius, ϕ the azimuth, and z the location along the axis (Sketch 13.1). The relation between cylindrical and Cartesian coordinates is

$$x=r\cos\phi\quad y=r\sin\phi\quad z$$

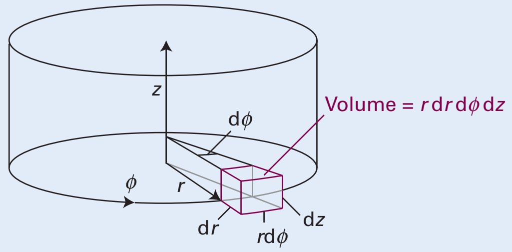
For a system confined to a plane, z may be set equal to 0. The volume element in cylindrical coordinates (see Sketch 13.1) is

$$d\tau=r\,dr\,d\phi\,dz$$

For a two-dimensional system, z is ignored: the 'volume' element is simply $rdrd\phi$ and the first and second derivatives with respect to the remaining variable coordinates are

$$x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}=\frac{\partial}{\partial\phi}$$

$$\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}=\frac{\partial^2}{\partial r^2}+\frac{1}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}$$



Sketch 13.1 The cylindrical coordinates used for discussing a system with cylindrical symmetry. The volume element is also shown.

Example 13.1 Using the particle-on-a-ring model

The particle-on-a-ring is a crude but illustrative model of cyclic, conjugated molecular systems. Treat the π electrons in benzene as particles freely moving over a circular ring of carbon atoms and calculate the minimum energy required for the excitation of a π electron. The carbon–carbon bond length in benzene is 140 pm.

Method For reasons that will be familiar from introductory chemistry, each carbon atom contributes one p electron to the π orbitals and each energy level can be occupied by two electrons. Therefore, six electrons in the conjugated system move along the perimeter of the ring, and since each state is occupied by two electrons, only the $m_l=0, +1$, and -1 states are occupied (with the last two being degenerate). The minimum energy required for excitation corresponds to a transition of an electron from the $m_l=+1$ (or -1) state to the $m_l=+2$ (or -2) state. Use eqn 13.7b, and the mass of the electron, to calculate the energies of the states; take the radius of the ring to be the carbon–carbon bond length.

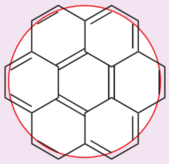
Answer From eqn 13.7b, the energy separation between the $m_l=+1$ and the $m_l=+2$ states is

$$\Delta E = E_{+2} - E_{+1} = (4-1) \times \frac{(1.055\times10^{-34}\,\text{J s})^2}{2\times(9.109\times10^{-31}\,\text{kg})\times(1.40\times10^{-10}\,\text{m})^2}$$
$$= 9.35\times10^{-19}\,\text{J}$$

Therefore the minimum energy required to excite an electron is 9.35×10^{-19} J or 563 kJ mol^{-1}. This energy separation corresponds to an absorption frequency of 1.41 PHz (1 PHz $=10^{15}$ Hz) and a wavelength of 213 nm; the experimental value for a transition of this kind is 260 nm. That such a primitive model gives relatively good agreement is encouraging. In addition, even though the model is primitive, it gives insight into the origin of the quantized π electron energy levels in cyclic conjugated systems (Topic 26).

A note on good practice Note that, when quoting the value of m_l, it is good practice always to give the sign, even if m_l is positive. Thus, we write $m_l=+1$, not $m_l=1$.

Self-test 13.3 Using the particle on a ring model, calculate the minimum energy required for the excitation of a π electron in coronene, $C_{24}H_{12}$ (1). Assume that the radius of the ring is three times the carbon–carbon bond length in benzene and that the electrons are confined to the periphery of the molecule. Ignore the central 'benzene' ring and count only 18 π electrons.



1 Coronene
(model ring in red)

Answer: For transition from $m_l=+4$ to $m_l=+5$: $\Delta E=3.12\times10^{-19}$ J or 188 kJ mol^{-1}

13.2 Quantization of angular momentum

We have seen that the angular momentum around the z-axis is quantized and confined to the values given in eqn 13.5 ($J_z=m_l\hbar$). The wavefunction for the particle on a ring is given by eqn 13.7a:

$$\psi_{m_l}(\phi) = \frac{e^{im_l\phi}}{(2\pi)^{1/2}} = \frac{1}{(2\pi)^{1/2}}(\cos m_l\phi + i\sin m_l\phi)$$

Therefore, as $|m_l|$ increases, the increasing angular momentum is associated with:

- an increase in the number of nodes in the real ($\cos m_l\phi$) and imaginary ($\sin m_l\phi$) parts of the wavefunction (the complex function does not have nodes but its real and imaginary components each do);
- a decrease in the wavelength and, by the de Broglie relation, an increase in the linear momentum with which the particle travels round the ring (Fig. 13.7).

Physical interpretation

Brief illustration 13.3 Nodes in the wavefunction

Whereas the $m_l=0$ ground-state wavefunction has no nodes, the $m_l=+1$ wavefunction

$$\psi_{+1}(\phi) = \frac{e^{i\phi}}{(2\pi)^{1/2}} = \frac{1}{(2\pi)^{1/2}}(\cos\phi + i\sin\phi)$$

has nodes at $\phi=\pi/2$ and $3\pi/2$ in its real part and at $\phi=0$ and π in its imaginary part. An increase in the number of nodes results in greater curvature of the (real and imaginary parts of the) wavefunction, consistent with an increase in kinetic and, in this case, total energy.

Self-test 13.4 Determine the number of nodes in the real and imaginary parts of the wavefunction for a state of general m_l.

Answer: $2m_l$ nodes each in real and imaginary part

We can come to the same conclusion about quantization of the z-component of angular momentum more formally by using the argument about the relation between eigenvalues and the values of observables established in Topic 6 by Postulate IV.

In classical mechanics the angular momentum l_z about the z-axis, as shown in the *Justification* below, is given by

$$l_z = xp_y - yp_x \qquad \textit{z-Component of angular momentum} \qquad (13.14)$$

where p_x is the component of linear momentum parallel to the x-axis and p_y is the component parallel to the y-axis.

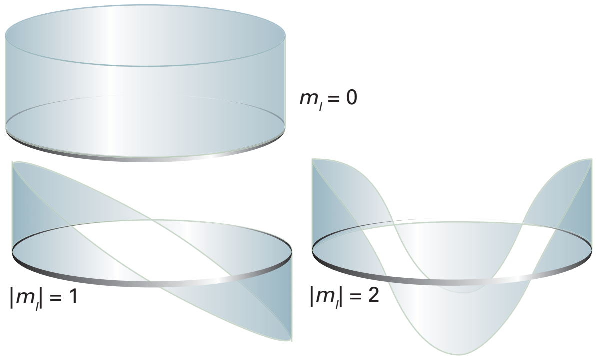


Figure 13.7 The real parts of the wavefunctions of a particle on a ring. As shorter wavelengths are achieved, the magnitude of the angular momentum around the z-axis grows in steps of $\hbar$.

Justification 13.3 The angular momentum in classical mechanics

In classical mechanics, the angular momentum $\boldsymbol{l}$ of a particle with position $\boldsymbol{r}$ and linear momentum $\boldsymbol{p}$ is given by the vector product $\boldsymbol{l}=\boldsymbol{r}\times\boldsymbol{p}$ (see *The chemist's toolkit* 13.2 for a reminder about vector products). For motion restricted to two dimensions, with $\boldsymbol{i}$ and $\boldsymbol{j}$ denoting unit vectors (vectors of length 1) pointing along the positive directions on the x- and y-axes, respectively,

$$\boldsymbol{r}=x\boldsymbol{i}+y\boldsymbol{j} \quad \boldsymbol{p}=p_x\boldsymbol{i}+p_y\boldsymbol{j}$$

where p_x is the component of linear momentum parallel to the x-axis and p_y is the component parallel to the y-axis. Therefore,

$$\boldsymbol{l}=\boldsymbol{r}\times\boldsymbol{p}=(x\boldsymbol{i}+y\boldsymbol{j})\times(p_x\boldsymbol{i}+p_y\boldsymbol{j})=(xp_y-yp_x)\boldsymbol{k}$$

where $\boldsymbol{k}$ is the unit vector pointing along the positive z-axis. For a particle rotating in the xy-plane, the angular momentum vector lies entirely along the z-axis with a magnitude given by $|xp_y-yp_x|$ (Fig. 13.8).

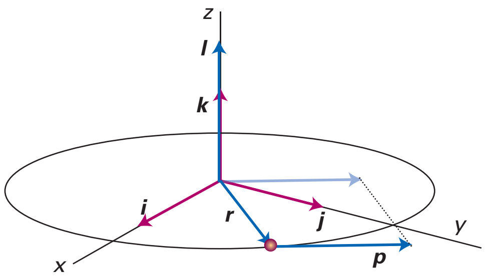


Figure 13.8 The classical angular momentum $\boldsymbol{l}$ of a particle with position $\boldsymbol{r}$ and linear momentum $\boldsymbol{p}$ is given by the vector product $\boldsymbol{l}=\boldsymbol{r}\times\boldsymbol{p}$. For the motion restricted to the xy-plane as depicted here, $\boldsymbol{r}=x\boldsymbol{i}+y\boldsymbol{j}$, $\boldsymbol{p}=p_x\boldsymbol{i}+p_y\boldsymbol{j}$, and $\boldsymbol{l}=(xp_y-yp_x)\boldsymbol{k}$, with $\boldsymbol{i}$, $\boldsymbol{j}$, and $\boldsymbol{k}$ denoting unit vectors along the positive x-, y-, and z-axes.

The chemist's toolkit 13.2 Vector products

Given the vectors $\boldsymbol{a}$ and $\boldsymbol{b}$:

$$\boldsymbol{a}=a_x\boldsymbol{i}+a_y\boldsymbol{j}+a_z\boldsymbol{k} \quad \boldsymbol{b}=b_x\boldsymbol{i}+b_y\boldsymbol{j}+b_z\boldsymbol{k}$$

where $\boldsymbol{i}$, $\boldsymbol{j}$, and $\boldsymbol{k}$ are the unit vectors along the positive x-, y-, and z-axes and (a_x,a_y,a_z) and (b_x,b_y,b_z) are the components of $\boldsymbol{a}$ and $\boldsymbol{b}$ along the axes, the vector product between the two vectors is given by

$$\boldsymbol{a}\times\boldsymbol{b}=(a_yb_z-a_zb_y)\boldsymbol{i}+(a_zb_x-a_xb_z)\boldsymbol{j}+(a_xb_y-a_yb_x)\boldsymbol{k}$$

This quantity is a vector of magnitude $ab\sin\theta$, where θ is the angle between the vectors $\boldsymbol{a}$ and $\boldsymbol{b}$, with magnitudes a and b. Furthermore, $\boldsymbol{a}\times\boldsymbol{b}$ is a vector which is perpendicular to both $\boldsymbol{a}$ and $\boldsymbol{b}$.

The operators for the linear momentum components p_x and p_y are given in Topic 6, so the operator for angular momentum about the z-axis is

$$\hat{l}_z=\frac{\hbar}{i}\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right) \qquad (13.15a)$$

z-Component of the angular momentum operator

When expressed in terms of the cylindrical coordinates r and ϕ (*The chemist's toolkit* 13.1), this equation becomes

$$\hat{l}_z=\frac{\hbar}{i}\frac{\partial}{\partial\phi} \qquad (13.15b)$$

With the angular momentum operator available, we can test whether the wavefunction in eqn 13.7a is an eigenfunction. Because the wavefunction depends on only the coordinate ϕ, the partial derivative in eqn 13.15b can be replaced by a complete derivative and we find

$$\hat{l}_z\psi_{m_l}=\frac{\hbar}{i}\frac{d}{d\phi}\psi_{m_l}=\frac{\hbar}{i}\frac{d}{d\phi}\frac{e^{im_l\phi}}{(2\pi)^{1/2}}=im_l\frac{\hbar}{i}\frac{e^{im_l\phi}}{(2\pi)^{1/2}}=m_l\hbar\psi_{m_l} \qquad (13.16)$$

That is, ψ_{m_l} is an eigenfunction of $\hat{l}_z$, and corresponds to an angular momentum $m_l\hbar$, in accord with eqn 13.5. When m_l is positive, the angular momentum is positive (clockwise rotation when seen from below); when m_l is negative, the angular momentum is negative (anticlockwise when seen from below).

These features are the origin of the **vector representation** of angular momentum, in which the magnitude is represented by the length of a vector and the direction of motion by its orientation (Fig. 13.9). This vector representation of angular momentum is also useful in classical physics but there is one crucial difference: in quantum mechanics the length of the vector is restricted to discrete values (corresponding to permitted values of m_l) whereas in classical physics the length is continuously variable.

Brief illustration 13.4 The vector representation of angular momentum

Suppose that the particle on a ring is in a state with $m_l=+3$. The magnitude of its angular momentum is $3\hbar$ (or 3.165×10^{-34} J s), so the angular momentum itself is represented by a vector of length 3 (in units of $\hbar$) pointing along the positive z-axis. The wheel (of mass 2 kg and radius 0.3 m) of a bicycle moving forward at 20 km h^{-1} has an angular momentum of about 3 J s, corresponding to $|m_l|=3\times10^{34}$. If the z-axis runs from left to right through the axle of the wheel, we would write $m_l=+3\times10^{34}$.

Self-test 13.5 Repeat for a particle in a state with $m_l=-2$.

Answer: Vector of length 2 (in units of $\hbar$) pointing along the negative z-axis

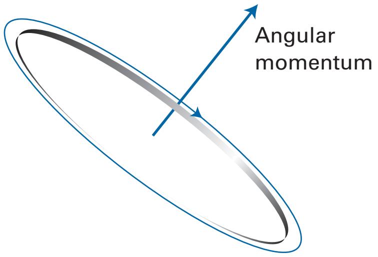


Figure 13.9 The basic ideas of the vector representation of angular momentum: the magnitude of the angular momentum is represented by the length of the vector, and the orientation of the motion in space is represented by the orientation of the vector (using the right-hand screw rule).

When the particle is in a state of precisely known angular momentum $m_l\hbar$ its location around the ring is completely unknown because the probability density is uniform:

$$\psi_{m_l}^{*}\psi_{m_l}=\left(\frac{e^{im_l\phi}}{(2\pi)^{1/2}}\right)^{*}\left(\frac{e^{im_l\phi}}{(2\pi)^{1/2}}\right)=\left(\frac{e^{-im_l\phi}}{(2\pi)^{1/2}}\right)\left(\frac{e^{im_l\phi}}{(2\pi)^{1/2}}\right)=\frac{1}{2\pi}$$

Angular momentum and angular position are a pair of complementary observables (in the sense defined in Topic 8; see Problem 13.9), and the inability to specify them simultaneously with arbitrary precision is another example of the uncertainty principle.

Checklist of concepts

☐ **1.** The **energy and angular momentum** for a particle rotating in two dimensions are quantized; quantization results from the requirement that the wavefunction satisfy a cyclic boundary condition.

☐ **2.** All energy levels of a particle rotating in two dimensions are doubly degenerate except for the lowest level ($m_l=0$).

☐ **3.** There is no zero-point energy for a particle rotating in a plane.

☐ **4.** In the **vector representation** of angular momentum, the magnitude is represented by the length of a vector and the direction of motion by its orientation. The length of the vector is restricted to discrete values (corresponding to permitted values of m_l).

☐ **5.** It is impossible to specify the angular momentum and location of the particle rotating in two dimensions simultaneously with arbitrary precision.

☐ **6.** The angular momentum and angular position are a pair of complementary observables.

Checklist of equations

Property	Equation	Comment	Equation number
z-Component of angular momentum of particle on ring	$l_z=m_l\hbar$	$m_l=0,\pm1,\pm2,\ldots$	13.5
Wavefunction of particle on ring	$\psi_{m_l}(\phi)=e^{im_l\phi}/(2\pi)^{1/2}$	$m_l=0,\pm1,\pm2,\ldots$	13.7a
Energy of particle on ring	$E_{m_l}=m_l^2\hbar^2/2I$	$m_l=0,\pm1,\pm2,\ldots$	13.7b
Angular momentum operator	$l_z=(\hbar/i)\partial/\partial\phi$	*z*-component	13.15b

TOPIC 14

Rotational motion in three dimensions

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➤ Why do you need to know this material?

The discussion of rotation in three dimensions introduces the concept of orbital angular momentum, which is central to the description of the electronic structure of atoms and underlies the description of the rotation of molecules and molecular spectroscopy.

➤ What is the key idea?

The energy and the angular momentum of a particle rotating in three dimensions are quantized.

➤ What do you need to know already?

You should be familiar with the postulates of quantum mechanics (Topics 5–7). This topic extends the description of rotational motion in two dimensions (Topic 13).

The properties of a body able to rotate in three dimensions can be developed like the corresponding problem in two dimensions (Topic 13), but with the body able to rotate with respect to a third axis. Another way of expressing the transition from two dimensions to three is that the particle that in Topic 13 is confined to moving on a ring in a plane is now free to migrate over the surface of a sphere. The 'particle' may be an electron confined to a spherical surface or it might be a point in a solid body, such as a molecule, that represents the overall motion of the body about a centre of rotation. Thus, if the solutions are expressed in terms of the moment of inertia $I=mr^2$, then they can be used to describe the three-dimensional rotation of any body of that moment of inertia, such as a solid ball (which, if its mass is M and its radius is R, has $I=\frac{2}{5}MR^2$) or a molecule, such as CH_4 (which, if the C—H bond length is R, has $I=\frac{8}{3}m_H R^2$).

14.1 A particle on a sphere

We consider a particle of mass m that is free to move anywhere on the surface of a sphere of radius r. The sphere can be thought of as a three-dimensional stack of rings of differing radii with the freedom for the particle to migrate from one ring to another. The cyclic boundary condition for the particle on each ring leads to the quantum number m_l that is encountered for motion on an individual ring. The

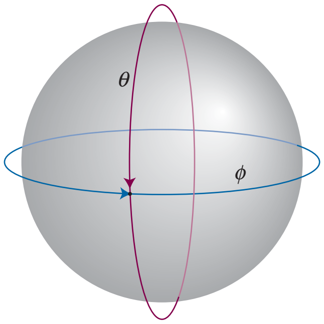


Figure 14.1 The wavefunction of a particle on the surface of a sphere must satisfy two cyclic boundary conditions. This requirement leads to two quantum numbers for its state of angular momentum.

requirement that the wavefunction must match as a path is traced over the poles as well as round the equator of the sphere surrounding the central point introduces a second cyclic boundary condition and therefore a second quantum number (Fig. 14.1).

(a) The wavefunctions

The hamiltonian operator for motion in three dimensions (Table 6.1) is

$$\hat{H}=-\frac{\hbar^2}{2m}\nabla^2+V \quad \textit{Three dimensions} \quad \text{Hamiltonian operator} \tag{14.1a}$$

$$\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2} \quad \textit{Three dimensions} \quad \text{Laplacian} \tag{14.1b}$$

The laplacian, ∇^2 (read 'del squared'), is a convenient abbreviation for the sum of the three second derivatives. For the particle confined to a spherical surface, $V=0$ wherever it is free to travel and r is a constant. To take advantage of the symmetry of the problem and the fact that r is constant for a particle on a sphere, we use **spherical polar coordinates** (*The chemist's toolkit* 14.1). The wavefunction is therefore a function of the colatitude, θ, and the azimuth, ϕ, and we write it $\psi(\theta,\phi)$. The Schrödinger equation is therefore

$$-\frac{\hbar^2}{2m}\nabla^2\psi=E\psi \quad \textit{Particle on a sphere} \quad \text{Schrödinger equation} \tag{14.2}$$

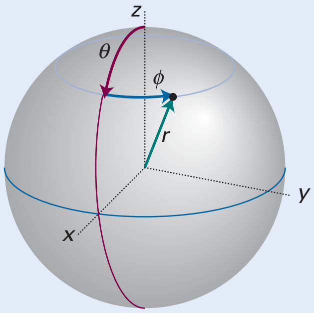
The Schrödinger equation in eqn 14.2 is solved by using the technique of separation of variables (see *Mathematical background* 2), which confirms that, as shown in the following *Justification*, the wavefunction can be written as a product of functions

$$\psi(\theta,\phi)=\Theta(\theta)\Phi(\phi) \tag{14.3}$$

The chemist's toolkit 14.1 Spherical polar coordinates

The natural coordinates to use in a system with spherical symmetry are spherical polar coordinates, with r the **radius**, θ the **colatitude**, and ϕ the **azimuth** (Sketch 14.1). As can be inferred from Sketch 14.1, the relation between spherical polar and Cartesian coordinates is

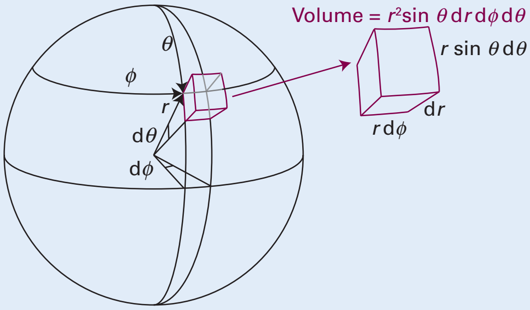
$$x=r\sin\theta\cos\phi \qquad y=r\sin\theta\sin\phi \qquad z=r\cos\theta$$



Sketch 14.1 The spherical polar coordinates used for discussing a system with spherical symmetry.

The volume element in spherical polar coordinates (Sketch 14.2) is

$$\mathrm{d}\tau=r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\phi\,\mathrm{d}\theta$$



Sketch 14.2 The volume element in spherical polar coordinates.

Similarly, the laplacian in spherical polar coordinates is (Table 6.1)

$$\nabla^2=\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\Lambda^2$$

and the legendrian, Λ^2, is

$$\Lambda^2=\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$$

where Θ is a function only of θ and Φ is a function only of ϕ. As confirmed in the *Justification*, the Φ are the solutions for a particle on a ring (Topic 13) and the overall solutions are specified by the **orbital angular momentum quantum number** l and the **magnetic quantum number** m_l. These quantum numbers are restricted to the values

$$l=0,1,2,\ldots \qquad m_l=l,l-1,\ldots,-l$$

The quantum number l is non-negative and, for a given value of l, there are $2l+1$ permitted values of m_l.

Justification 14.1 The solutions of the Schrödinger equation for a particle on a sphere

Because r is constant, we can discard the part of the laplacian that involves differentiation with respect to r, and so write the Schrödinger equation as

$$-\frac{\hbar^2}{2mr^2}\Lambda^2\psi=E\psi$$

The moment of inertia, $I=mr^2$, has appeared. This expression can be rearranged into

$$\Lambda^2\psi=-\varepsilon\psi \qquad \varepsilon=\frac{2IE}{\hbar^2}$$

To verify that this expression is separable, we try the substitution $\psi=\Theta\Phi$ and use the form of the legendrian in *The chemist's toolkit* 14.1:

$$\Lambda^2\Theta\Phi=\frac{1}{\sin^2\theta}\frac{\partial^2(\Theta\Phi)}{\partial\phi^2}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial(\Theta\Phi)}{\partial\theta}=-\varepsilon\Theta\Phi$$

We now use the fact that Θ and Φ are each functions of one variable, so the partial derivatives become complete derivatives:

$$\frac{\Theta}{\sin^2\theta}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2}+\frac{\Phi}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}=-\varepsilon\Theta\Phi$$

Division through by $\Theta\Phi$ and multiplication by $\sin^2\theta$ gives

$$\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2}+\frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}=-\varepsilon\sin^2\theta$$

and, after minor rearrangement,

$$\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2}+\frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}+\varepsilon\sin^2\theta=0$$

The first term on the left depends only on ϕ and the remaining two terms depend only on θ. By the argument presented in *Mathematical background* 2, each term is equal to a constant. Thus, if we set the first term equal to the constant $-m_l^2$ (using a notation chosen with an eye to the future), the separated equations are

$$\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2}=-m_l^2 \qquad \frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}+\varepsilon\sin^2\theta=m_l^2$$

The first of these two equations is the same as that encountered for the particle on a ring (Topic 13) and has the same solutions:

$$\Phi=\frac{1}{(2\pi)^{1/2}}\mathrm{e}^{\mathrm{i}m_l\phi} \qquad m_l=0,\pm1,\pm2,\ldots$$

(Shortly we shall see that m_l is in fact bounded for a three-dimensional system, unlike the two-dimensional system.) The second equation is new, but its solutions are well known to mathematicians as 'associated Legendre functions'. The cyclic boundary condition for the matching of the wavefunction at $\phi=0$ and 2π restricts m_l to positive and negative integer values (including 0), as for a particle on a ring. The additional requirement that the wavefunctions also match on a journey over the poles (as in Fig. 14.1) results in the introduction of the second quantum number, l, with non-negative integer values. However, the presence of the quantum number m_l in the second equation implies that the ranges of the two quantum numbers are linked, and it turns out that for a given value of l, m_l ranges in integer steps from $-l$ to $+l$, as quoted in the text.

The normalized wavefunctions $\psi(\theta,\phi)$ for a given l and m_l are usually denoted $Y_{lm_l}(\theta,\phi)$ and are called the **spherical harmonics** (Table 14.1 and Fig. 14.2). They are as fundamental to the description of waves on spherical surfaces as the harmonic (sine and cosine) functions are to the description of waves on lines and planes. These important functions satisfy the equation[1]

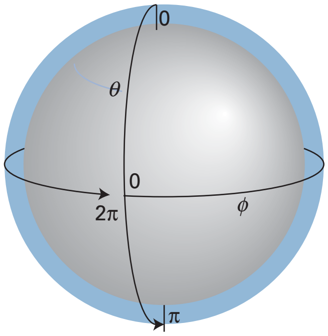


Figure 14.2 The surface of a sphere is covered by allowing θ to range from 0 to π, and then sweeping that arc around a complete circle by allowing ϕ to range from 0 to 2π.

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[1] For a full account of the solution, see our *Molecular quantum mechanics*, Oxford University Press (2011).

Table 14.1 The spherical harmonics

l	m_l	$Y_{lm_l}(\theta,\phi)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
	±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{\pm i\phi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
	±1	$\mp\left(\frac{15}{8\pi}\right)^{1/2}\cos\theta\sin\theta\, e^{\pm i\phi}$
	±2	$\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta-3\cos\theta)$
	±1	$\mp\left(\frac{21}{64\pi}\right)^{1/2}(5\cos^2\theta-1)\sin\theta\, e^{\pm i\phi}$
	±2	$\left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
	±3	$\mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta\, e^{\pm 3i\phi}$

$$\Lambda^2 Y_{lm_l}(\theta,\phi)=-l(l+1)Y_{lm_l}(\theta,\phi) \tag{14.4}$$

Figure 14.3 shows a representation of the spherical harmonics for $l=0$ to 4 and $m_l=0$; the use of the dark and light shading, which correspond to different signs of the wavefunction, emphasizes the location of the angular nodes (the positions at which the wavefunction passes through zero). Note that:

- There are no angular nodes around the z-axis for functions with $m_l=0$. The spherical harmonic with $l=0$, $m_l=0$ has no nodes at all: it is a 'wave' of constant height at all positions of the surface.
- The spherical harmonic with $l=1$, $m_l=0$ has a single angular node at $\theta=\pi/2$; therefore, the equatorial plane is a nodal plane.
- The spherical harmonic with $l=2$, $m_l=0$ has two angular nodes.

Physical interpretation

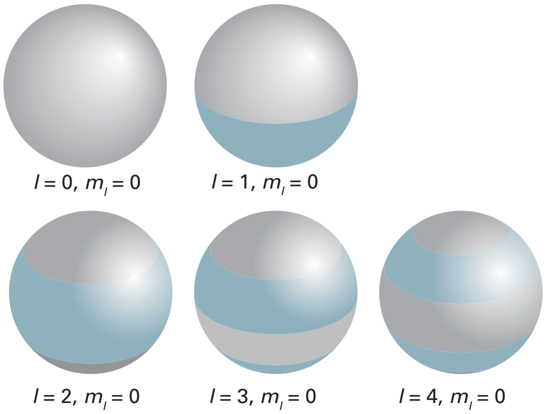


Figure 14.3 A representation of the wavefunctions of a particle on the surface of a sphere that emphasizes the location of angular nodes: grey and blue shading correspond to different signs of the wavefunction. Note that the number of nodes increases as the value of l increases. All these wavefunctions correspond to $m_l=0$; a path round the vertical z-axis of the sphere does not cut through any nodes.

Brief illustration 14.1 The angular nodes of the spherical harmonics

For the spherical harmonic with $l=2$, $m_l=0$, the angular nodes correspond to angles where (see Table 14.1) $3\cos^2\theta-1=0$, or $\cos\theta=\pm(1/3)^{1/2}$. The angular nodes are therefore at 54.7° and 125.3° (close to the latitudes of Los Angeles and Buenos Aires on an actual globe).

Self-test 14.1 Find the angular nodes for the spherical harmonic $l=3$, $m_l=0$.

Answer: $\theta=39.2°, 90°, 140.8°$

(b) The energies

In general, the number of angular nodes is equal to l. As the number of nodes increases, the wavefunctions become more buckled, and with this increasing curvature we can anticipate that the kinetic energy of the particle (and therefore its total energy, because the potential energy is zero) increases.

It is established in *Justification* 14.1 that the Schrödinger equation for a particle for which only the angular coordinates are variable is

$$-\frac{\hbar^2}{2mr^2}\Lambda^2\psi=E\psi$$

with $mr^2=I$. However, we have also seen that the wavefunctions ψ, which we now know are the spherical harmonics Y, satisfy eqn 14.4. Therefore, this equation becomes

$$-\frac{\hbar^2}{\underbrace{2mr^2}_{I}}\overbrace{\Lambda^2 Y_{lm_l}}^{-l(l+1)Y_{lm_l}} = E\psi, \quad \text{or} \quad l(l+1)\frac{\hbar^2}{2I}Y_{lm_l} = E_{lm_l}Y_{lm_l}$$

where we have allowed for the possibility that the energies depend on the two quantum numbers. We can conclude that the allowed energies of the particle are

$$E_{lm_l} = l(l+1)\frac{\hbar^2}{2I} \qquad \text{(14.5)}$$

Particle on a sphere Energy levels

According to this equation

- The energies are quantized because $l=0, 1, 2, \ldots$.
- The energies are independent of the value of m_l for a given value of l, and henceforth we shall denote them simply as E_l.
- Because there are $2l+1$ different wavefunctions (one for each value of m_l) that correspond to the same energy, it follows that a level with quantum number l is $(2l+1)$-fold degenerate.
- There is no zero-point energy, and $E_0=0$.

Physical interpretation

Example 14.1 Using the rotational energy levels

Determine the energies and degeneracies of the lowest four energy levels of an $^1H^{35}Cl$ molecule freely rotating in three dimensions. What is the frequency of the transition between the lowest two rotational levels? The moment of inertia of an $^1H^{35}Cl$ molecule is $2.6422\times10^{-47}\,\mathrm{kg\,m^2}$.

Method The rotational energies are given in eqn 14.5; but, for reasons that are developed in Topic 41, the angular momentum quantum number of rotating molecules is denoted J in place of l, and we use that symbol here. The degeneracy of a level with quantum number J is $2J+1$, the analogue of $2l+1$. A transition between two rotational levels can be brought about by the emission or absorption of a photon with a frequency given by the Bohr frequency condition (Topic 4, $h\nu=\Delta E$).

Answer First, note that

$$\frac{\hbar^2}{2I}=\frac{(1.055\times10^{-34}\,\mathrm{J\,s})^2}{2\times(2.6422\times10^{-47}\,\mathrm{kg\,m^2})}=2.106\ldots\times10^{-22}\,\mathrm{J}$$

or 0.2106… zJ. We now draw up the following table, where the molar energies are obtained by multiplying the individual energies by Avogadro's constant:

J	E/zJ	E/(J mol^{-1})	Degeneracy
0	0	0	1
1	0.4212	253.6	3
2	1.264	760.9	5
3	2.527	1522	7

The energy separation between the two lowest rotational energy levels ($J=0$ and 1) is 4.212×10^{-22} J, which corresponds to a photon frequency of

$$\nu=\frac{\Delta E}{h}=\frac{4.212\times10^{-22}\,\mathrm{J}}{6.626\times10^{-34}\,\mathrm{J\,s}}=6.357\times10^{11}\,\overbrace{\mathrm{s^{-1}}}^{\mathrm{Hz}}=635.7\,\mathrm{GHz}$$

Radiation with this frequency belongs to the microwave region of the electromagnetic spectrum, so microwave spectroscopy is used to study molecular rotations (Topic 42). Because the transition energies depend on the moment of inertia, microwave spectroscopy is a very accurate technique for the determination of bond lengths.

Self-test 14.2 What is the frequency of the transition between the lowest two rotational levels in $^2H^{35}Cl$? (Its moment of inertia is 5.1365×10^{-47} kg m^2.)

Answer: 327.0 GHz

14.2 Angular momentum

Just as important as the quantization of energy is the quantization of the particle's angular momentum. In classical mechanics (*Justification* 13.3 of Topic 13) the angular momentum is represented by the vector $\boldsymbol{l}=\boldsymbol{r}\times\boldsymbol{p}$ ($\boldsymbol{r}$ and $\boldsymbol{p}$ being the position and linear momentum vectors, respectively) with components l_x, l_y, and l_z along the x-, y-, and z-axes. In quantum mechanics, the angular momentum is discussed in terms of the corresponding angular momentum operators.

(a) The angular momentum operators

The operator for the z-component of the angular momentum is given in Topic 13 as $\hat{l}_z=(\hbar/\mathrm{i})(\partial/\partial y - y\partial/\partial x)$ and equivalently $\hat{l}_z=(\hbar/\mathrm{i})(\partial/\partial\phi)$. Similar expressions hold for the operators for the x- and y-components.

$$\begin{aligned}\hat{l}_x&=\frac{\hbar}{\mathrm{i}}\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)\\ \hat{l}_y&=\frac{\hbar}{\mathrm{i}}\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)\\ \hat{l}_z&=\frac{\hbar}{\mathrm{i}}\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)=\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial\phi}\end{aligned} \qquad \text{(14.6)}$$

Angular momentum operators

The commutation relations among the three operators, which you are invited to derive in Problem 14.9, are

$$[\hat{l}_x,\hat{l}_y]=\mathrm{i}\hbar\hat{l}_z \quad [\hat{l}_y,\hat{l}_z]=\mathrm{i}\hbar\hat{l}_x \quad [\hat{l}_z,\hat{l}_x]=\mathrm{i}\hbar\hat{l}_y \qquad \text{(14.7)}$$

Angular momentum commutators

Because these operators do not commute, the observables they represent are complementary (Topic 8) and more than one of them cannot be specified simultaneously.

The operator corresponding to the magnitude of the angular momentum is obtained by noting that

$$\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2 \qquad (14.8)$$

Operator for square of magnitude of angular momentum

This operator commutes with all three components (see Problem 14.11):

$$[\hat{l}^2, \hat{l}_q^2] = 0 \qquad q = x, y, \text{ and } z \qquad (14.9)$$

Commutators of angular momentum operators

Because these operators commute, they do not correspond to complementary observables. In other words, if the square of the magnitude of the angular momentum is known, and therefore the magnitude itself is known, it is possible to specify any one of its components (but not more than one, by the consequences of eqn 14.7).

(b) Space quantization

The magnitude of the angular momentum can be determined from the properties of the operator in eqn 14.8. However, it is much simpler to find the magnitude by noting that the energy of the particle is related classically to its angular momentum l by $E = l^2/2I$ (see Topic 13). Therefore, by comparing this equation with eqn 14.5, we can deduce that the square of the magnitude of the angular momentum is given by $l(l+1)\hbar^2$ and therefore that the magnitude is itself confined to the values

$$\text{Magnitude of angular momentum} = \{l(l+1)\}^{1/2}\hbar \qquad l = 0, 1, 2, \ldots \qquad (14.10)$$

Furthermore, as shown in the *Justification* below by using the operator $\hat{l}_z$, the angular momentum about the z-axis is also quantized and, for a given value of l, it has the values

$$z\text{-Component of angular momentum} = m_l\hbar \qquad m_l = +l, l-1, \ldots, -l \qquad (14.11)$$

A note on good practice When quoting the value of m_l, always give the sign, even if m_l is positive. Thus, write $m_l = +2$, not $m_l = 2$.

Justification 14.2 The z-component of angular momentum for a particle on a sphere

The operator for the z-component of the angular momentum in polar coordinates is given in eqn 14.6:

$$\hat{l}_z = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial\phi}$$

With this operator available, we can test if the wavefunction in eqn 14.3 is an eigenfunction:

$$\hat{l}_z\psi = \hat{l}_z\Theta\Phi = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial\phi}\Theta\Phi = \Theta\frac{\hbar}{\mathrm{i}}\overbrace{\frac{\mathrm{d}}{\mathrm{d}\phi}\Phi}^{\mathrm{i}m_l\Phi} = \Theta\times m_l\hbar\Phi = m_l\hbar\psi$$

The partial derivative has been replaced above by a full derivative because Θ is independent of ϕ and we have used the result, as given in *Justification* 14.1, that $\Phi \propto \mathrm{e}^{\mathrm{i}m_l\phi}$. Therefore, the wavefunctions are eigenfunctions of $\hat{l}_z$, and correspond to an angular momentum around the z-axis of $m_l\hbar$, in accord with eqn 14.11.

Brief illustration 14.2 The magnitude of the angular momentum

The lowest four rotational energy levels of the $^1H^{35}Cl$ molecule of Example 14.1 correspond to $J = 0, 1, 2, 3$. Using eqns 14.10 and 14.11, we can draw up the following table:

J	Magnitude of angular momentum/$\hbar$	Degeneracy	z-Component of angular momentum/$\hbar$
0	0	1	0
1	$2^{1/2}$	3	+1, 0, −1
2	$6^{1/2}$	5	+2, +1, 0, −1, −2
3	$12^{1/2}$	7	+3, +2, +1, 0, −1, −2, −3

Self-test 14.3 What is the degeneracy and magnitude of the angular momentum for $J = 5$?

Answer: 11, $30^{1/2}\hbar$

The result that m_l is confined to the values $l, l-1, \ldots, -l$ for a given value of l means that the component of angular momentum about the z-axis—the contribution to the total angular momentum of rotation around that axis—may take only $2l+1$ values. If we represent the angular momentum by a vector of length $\{l(l+1)\}^{1/2}$, then it follows that this vector must be oriented so that its projection on the z-axis is m_l and that it can have only $2l+1$ orientations rather than the continuous range of orientations of a rotating classical body (Fig. 14.4). The remarkable implication is that *the orientation of a rotating body is quantized.*

Example 14.2 Calculating the angle of orientation of the angular momentum vector

Consider the two lowest energy levels of a $^1H^{35}Cl$ molecule freely rotating in three dimensions. What are the angles that the angular momentum vectors can make to the z-axis?

Method For the two lowest rotational energy levels, identify the values of the angular momentum quantum number J and its z-component, which is denoted M_J. Use eqns 14.10 and 14.11 (replacing l and m_l by J and M_J) and trigonometry to deduce the angle θ that the angular momentum vector makes to the z-axis.

Answer The angle that the angular momentum vector makes to the z-axis is given by

$$\cos\theta = \frac{M_J\hbar}{\{J(J+1)\}^{1/2}\hbar} = \frac{M_J}{\{J(J+1)\}^{1/2}}$$

We draw up the following table:

J	M_J	$\cos\theta$	θ
0	0	0	90°
1	+1	$\left(\frac{1}{2}\right)^{1/2}$	45°
1	0	0	90°
1	−1	$-\left(\frac{1}{2}\right)^{1/2}$	135°

Self-test 14.4 What angle does the angular momentum vector make to the z-axis for a particle described by the wavefunction $Y_{2,-1}$?

Answer: $\theta = 114.1°$

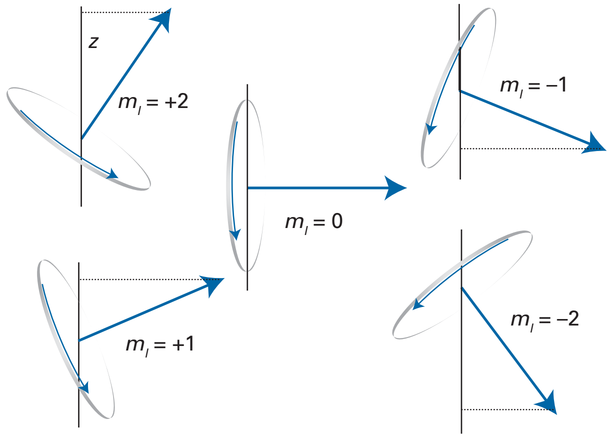


Figure 14.4 The permitted orientations of angular momentum when $l = 2$. We shall see soon that this representation is too specific because the azimuthal orientation of the vector (its angle around z) is indeterminate.

The quantum mechanical result that a rotating body may not take up an arbitrary orientation with respect to some specified axis (for example, an axis defined by the direction of an externally applied electric or magnetic field) is called **space quantization**. It was confirmed by an experiment first performed by Otto Stern and Walther Gerlach in 1921, who shot a beam of silver atoms through an inhomogeneous magnetic field (Fig. 14.5). The idea behind the experiment was that a silver atom behaves like a magnet and interacts with the applied field (a point explored in more detail in the discussion of 'spin' in Topic 19.). According to classical mechanics, because the orientation of the angular momentum can take any value, the associated magnet can take any orientation. Because the direction in which the magnet is driven by the inhomogeneous field depends on the magnet's orientation, it follows that a broad band of atoms is expected to emerge from the region where the magnetic field acts. According to quantum mechanics, however, because the orientation of the angular momentum is quantized, the associated magnet lies in a number of discrete orientations, so several sharp bands of atoms are expected.

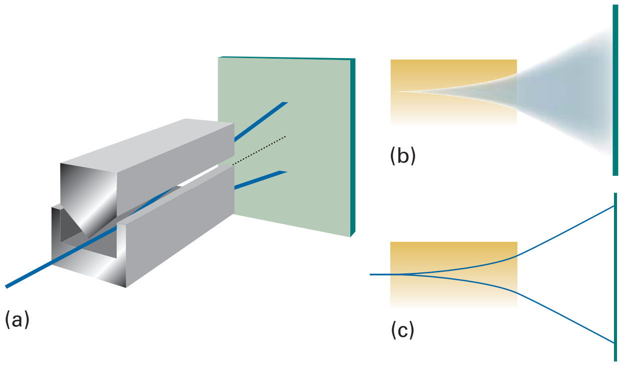


Figure 14.5 (a) The experimental arrangement for the Stern–Gerlach experiment: the magnet provides an inhomogeneous field. (b) The classically expected result. (c) The observed outcome using silver atoms.

In their first experiment, Stern and Gerlach appeared to confirm the classical prediction. However, the experiment is difficult because collisions between the atoms in the beam blur the bands. When the experiment was repeated with a beam of very low intensity (so that collisions were less frequent), they observed discrete bands, and so confirmed the quantum prediction.

(c) The vector model

So far, we have discussed the magnitude of the angular momentum and its z-component. In classical physics, we would be able to specify the components about the x- and y-axes too and be able to represent the angular momentum by a vector with a definite orientation. According to quantum mechanics, we *already* have as complete a description of the angular momentum of a rotating object as it is possible to have, and can say nothing further about the orientation of the vector.

The reason for this restriction is that, as described above, the components of angular momentum are mutually complementary and therefore if one is specified (the z-component, typically), then the other two components cannot be specified. (The single exception to this statement is the trivial case $l=0$, for which all three components are zero.) On the other hand, the operator for the square of the magnitude of the angular momentum commutes with all three components (eqn 14.9). Therefore, we may specify precisely and simultaneously the magnitude of the angular momentum and any *one* of the components of the angular momentum. It follows that the illustration in Fig. 14.4, which is summarized in Fig.14.6a, gives a false impression of the state of the system, because it suggests definite values for the *x*- and *y*-components. A more accurate picture must reflect the impossibility of specifying l_x and l_y if l_z is known.

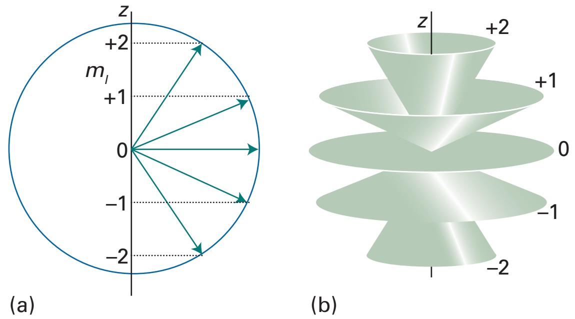


Figure 14.6 (a) A summary of Fig. 14.4. However, because the azimuthal angle of the vector around the *z*-axis is indeterminate, a better representation is as in (b), where each vector lies at an unspecified azimuthal angle on its cone.

The **vector model** of angular momentum uses pictures like that in Fig. 14.6b. The cones are drawn with sides of length $\{l(l+1)\}^{1/2}$, and represent the magnitude of the angular momentum (in units of $\hbar$). Each cone has a definite projection (of m_l) on the *z*-axis, representing the system's precise value of l_z. The l_x and l_y projections, however, are indefinite. The vector representing the state of angular momentum can be thought of as lying with its tip on any point on the mouth of the cone. At this stage it should not be thought of as sweeping round the cone; that aspect of the model will be added later when we allow the picture to convey more information.

Brief illustration 14.3 The vector model of the angular momentum

If the wavefunction of a rotating molecule is given by the spherical harmonic $Y_{3,+2}$ then the angular momentum can be represented by a cone

- with a side of length $12^{1/2}$ (representing the magnitude of $12^{1/2}\hbar$); and
- with a projection of +2 on the *z*-axis (representing the *z*-component of $+2\hbar$).

Additionally, by the equation in Example 14.2, the side of the cone makes an angle of 54.7° to the *z*-axis.

Self-test 14.5 Analyse the vector model of angular momentum if the wavefunction is given by the spherical harmonic $Y_{3,-1}$.

Answer: length is $12^{1/2}$, projection is −1, angle of 106.8°

Checklist of concepts

☐ 1. For a particle rotating in three dimensions, the cyclic boundary conditions imply that the magnitude and *z*-component of the angular momentum are quantized.

☐ 2. Because the energy of a rotating body is related to the magnitude of the angular momentum, the rotational energy is quantized.

☐ 3. Because the components of angular momentum do not commute, only the magnitude of the angular momentum and one of its components can be specified precisely and simultaneously.

☐ 4. The wavefunctions for the rotation of a body in three dimensions (as represented by a particle moving on the surface of a sphere) are the spherical harmonics.

☐ 5. **Space quantization** refers to the quantum mechanical result that a rotating body may not take up an arbitrary orientation with respect to some specified axis.

☐ 6. In the **vector model** of angular momentum, the angular momentum is represented by a cone with a side of length $\{l(l+1)\}^{1/2}$ and a projection of m_l on the *z*-axis. The vector can be thought of as lying with its tip on an indeterminate point on the mouth of the cone.

Checklist of equations

Property	Equation	Comment	Equation number
Energy of particle on sphere	$E_l = l(l+1)\hbar^2/2I$	$l = 0, 1, 2, \ldots$	14.5
Angular momentum commutators	$[\hat{l}_x, \hat{l}_y] = i\hbar\hat{l}_z$ $[\hat{l}_y, \hat{l}_z] = i\hbar\hat{l}_x$ $[\hat{l}_z, \hat{l}_x] = i\hbar\hat{l}_y$ $[\hat{l}^2, \hat{l}_q] = 0, \quad q = x, y$, and z	Note cyclic symmetry of *xyz*	14.7 14.9
Magnitude of angular momentum	$\{l(l+1)\}^{1/2}\hbar$	$l = 0, 1, 2, \ldots$	14.10
z-Component of angular momentum	$m_l\hbar$	$m_l = +l, l-1, \ldots, -l$	14.11

Focus 3 on The quantum mechanics of motion

Topic 9 Translational motion in one dimension

Discussion question

9.1 Discuss the physical origin of quantization of energy for a particle confined to motion inside a one-dimensional box.

Exercises

9.1(a) Determine the linear momentum and kinetic energy of a free electron described by the wavefunction e^{ikx} with $k = 3\,m^{-1}$.
9.1(b) Determine the linear momentum and kinetic energy of a free proton described by the wavefunction e^{-ikx} with $k = 5\,m^{-1}$.

9.2(a) Write the wavefunction for a particle of mass 2.0 g travelling to the left with a kinetic energy of 20 J.
9.2(b) Write the wavefunction for a particle of mass 1.0 g travelling to the right at $10\,m\,s^{-1}$.

9.3(a) Calculate the energy separations in joules, kilojoules per mole, and electronvolts, and as a wavenumber, between the levels (a) $n = 2$ and $n = 1$, (b) $n = 6$ and $n = 5$ of an electron in a one-dimensional nanoparticle modelled by a box of length 1.0 nm.
9.3(b) Calculate the energy separations in joules, kilojoules per mole, and electronvolts, and as a wavenumber, between the levels (a) $n = 3$ and $n = 1$, (b) $n = 7$ and $n = 6$ of an electron in a one-dimensional nanoparticle modelled by a box of length 1.5 nm.

9.4(a) A conjugated polyene can be modelled by a particle in a one-dimensional box. Calculate the probability that an electron will be found between $0.49L$ and $0.51L$ in a box of length L when it has (a) $n = 1$, (b) $n = 2$. Take the wavefunction to be a constant in this narrow range.
9.4(b) A conjugated polyene can be modelled by a particle in a one-dimensional box. Calculate the probability that a particle will be found between $0.65L$ and $0.67L$ in a box of length L when it has (a) $n = 1$, (b) $n = 2$. Take the wavefunction to be a constant in this narrow range.

9.5(a) Calculate the expectation values of $\hat{p}$ and $\hat{p}^2$ for a particle in the state $n = 1$ in a square-well potential used to model a one-dimensional nanoparticle.
9.5(b) Calculate the expectation values of $\hat{p}$ and $\hat{p}^2$ for a particle in the state $n = 2$ in a square-well potential used to model a one-dimensional nanoparticle.

9.6(a) An electron is squeezed between two confining walls, one of which can be moved inwards. At what separation of the walls will the zero-point energy of the electron be equal to its rest mass energy, m_ec^2? Express your answer in terms of the parameter $\lambda_C = h/m_ec$, the 'Compton wavelength' of the electron.
9.6(b) Now replace the electron in Exercise 9.6(a) by a proton. At what separation of the walls will the zero-point energy of the proton be equal to its rest mass energy, m_pc^2?

9.7(a) What are the most likely locations of a particle in a box of length L in the state $n = 5$?
9.7(b) What are the most likely locations of a particle in a box of length L in the state $n = 4$?

Problems

9.1 Calculate the separation between the two lowest translational energy levels of an O_2 molecule in a one-dimensional container of length 5.0 cm. At what value of n does the energy of the molecule reach $\frac{1}{2}kT$ at 300 K, and what is the separation of this level from the one immediately below?

9.2 Suppose the state of an electron in a certain one-dimensional cavity of length 1.0 nm in a semiconductor is described by the normalized wavefunction $\psi(x) = \frac{1}{2}\psi_1(x) + \left(\frac{1}{2}\mathrm{i}\right)\psi_2(x) - \left(\frac{1}{2}\right)^{1/2}\psi_4(x)$, where $\psi_n(x)$ is given by eqn 9.8a. When the energy of the electron is measured, what is the outcome? What is the expectation value of the energy?

9.3 An electron confined to a metallic nanoparticle is modelled as a particle in a one-dimensional box of length L. If the electron is in the state $n = 1$, calculate the probability of finding it in the following regions: (a) $0 \le x \le \frac{1}{2}L$, (b) $0 \le x \le \frac{1}{4}L$, (c) $\frac{1}{2}L - \delta x \le x \le \frac{1}{2}L + \delta x$.

9.4 Repeat Problem 9.3 for a general value of n.

9.5 The wavefunction for a free particle e^{ikx} is not square-integrable and therefore cannot be normalized in a box of infinite length. However, to circumvent this problem, we suppose that the particle is in a region of finite length L, normalize the wavefunction, and then allow L to become infinite at the end of the calculations that use the wavefunction. Find the normalization constant for the wavefunction e^{ikx}, assuming that a free particle is in a region of length L.

9.6 Consider two different particles moving in one dimension x, one (particle 1) described by the (unnormalized) wavefunction $\psi_1(x) = e^{\mathrm{i}(x/\mathrm{m})}$ and the second (particle 2) described by the (unnormalized) wavefunction $\psi_2(x) = \frac{1}{2}(e^{2\mathrm{i}(x/\mathrm{m})} + e^{3\mathrm{i}(x/\mathrm{m})} + e^{-2\mathrm{i}(x/\mathrm{m})} + e^{-3\mathrm{i}(x/\mathrm{m})})$. If the positions of the particles were measured, which would be found to be more localized in space (that is, which has a position known more precisely)? Explain your answer with a diagram.

9.7 Show for a particle in a box that Δx approaches its classical value as $n \to \infty$. *Hint*: In the classical case the distribution is uniform across the box, and so in effect $\psi(x) = 1/L^{1/2}$.

9.8 When β-carotene is oxidized *in vivo*, it forms two molecules of retinal (vitamin A), a precursor to the pigment in the retina responsible for vision. The conjugated system of retinal consists of 11 C atoms and one O atom. In the ground state of retinal, each level up to $n = 6$ is occupied by two electrons. Assuming an average internuclear distance of 140 pm, calculate (a) the separation in energy between the ground state and the first excited state in which one electron occupies the state with $n = 7$, and (b) the frequency and wavelength of the radiation required to produce a transition between these two states. (c) Using your results, choose between the words in parentheses in the following sentence to generate a rule for the prediction of frequency shifts in the absorption spectra of linear polyenes:

The absorption spectrum of a linear polyene shifts to (higher/lower) frequency as the number of conjugated atoms (increases/decreases).

Topic 10 Tunnelling

Discussion questions

10.1 Discuss the physical origins of quantum mechanical tunnelling. Identify chemical systems where tunnelling might play a role.

10.2 Describe the features that stem from nanometre-scale dimensions that are not found in macroscopic objects.

Exercises

10.1(a) Suppose that the junction between two semiconductors can be represented by a barrier of height 2.0 eV and length 100 pm. Calculate the transmission probability of an electron with energy 1.5 eV.

10.1(b) Suppose that a proton of an acidic hydrogen atom is confined to an acid that can be represented by a barrier of height 2.0 eV and length 100 pm. Calculate the probability that a proton with energy 1.5 eV can escape from the acid.

Problems

10.1 Derive eqn 10.6, the expression for the transmission probability and show that it reduces to eqn 10.7 when $\kappa L \gg 1$.

10.2 Repeat the analysis of this Topic to determine the transmission coefficient T and the reflection probability, R, the probability that a particle incident on the left of the barrier will reflect from the barrier and be found moving to the left away from the barrier, for $E > V$. Suggest a physical reason for the variation of T as depicted in Fig. 10.5.

10.3 An electron inside a one-dimensional nanoparticle has a potential energy different from its potential energy once it has escaped through the confining barrier. Consider a particle moving in one dimension with $V = 0$ for $-\infty < x \leq 0$, $V = V_2$ for $0 < x \leq L$, and $V = V_3$ for $L \leq x < \infty$ and incident from the left. The energy of the particle lies in the range $V_2 > E > V_3$. (a) Calculate the transmission coefficient, T. (b) Show that the general equation for T reduces to eqn 10.6 when $V_3 = 0$.

10.4 The wavefunction inside a long barrier of height V is $\psi = N\mathrm{e}^{-\kappa x}$. Calculate (a) the probability that the particle is inside the barrier and (b) the average penetration depth of the particle into the barrier.

10.5 Many biological electron transfer reactions, such as those associated with biological energy conversion, may be visualized as arising from electron tunnelling between protein-bound cofactors, such as cytochromes, quinones, flavins, and chlorophylls. This tunnelling occurs over distances that are often greater than 1.0 nm, with sections of protein separating electron donor from acceptor. For a specific combination of donor and acceptor, the rate of electron tunnelling is proportional to the transmission probability, with $\kappa \approx 7\,\mathrm{nm}^{-1}$ (eqn 10.7). By what factor does the rate of electron tunnelling between two cofactors increase as the distance between them changes from 2.0 nm to 1.0 nm?

10.6 The ability of a proton to tunnel through a barrier contributes to the rapidity of proton transfer reactions in solution and therefore to the properties of acids and bases. Estimate the relative probabilities that a proton and a deuteron ($m_\mathrm{D} = 3.342 \times 10^{-27}$ kg) can tunnel through the same barrier of height 1.0 eV (1.6×10^{-19} J) and length 100 pm when their energy is 0.90 eV. Comment on your result.

Topic 11 Translational motion in several dimensions

Discussion questions

11.1 Describe the features of the solution of the particle in a one-dimensional box that appear in the solutions of the particle in two- and three-dimensional boxes. What concept applies to the latter but not to a one-dimensional box?

11.2 Discuss the occurrence of degeneracy in a rectangular two-dimensional box in which one side is three times the length of the second side: consider hidden symmetry.

Exercises

11.1(a) Some nanostructures can be modelled as an electron confined to a two-dimensional region. Calculate the energy separations in joules, kilojoules per mole, and electronvolts between the levels (a) $n_1 = n_2 = 2$ and $n_1 = n_2 = 1$, (b) $n_1 = n_2 = 6$ and $n_1 = n_2 = 5$ of an electron in a square box with sides of length 1.0 nm. Go on to express the separations as a wavenumber.

11.1(b) Some nanostructures can be modelled as an electron confined to a three-dimensional region. Calculate the energy separations in joules, kilojoules per mole, and electronvolts between the levels (a) $n_1 = n_2 = n_3 = 2$ and $n_1 = n_2 = n_3 = 1$, (b) $n_1 = n_2 = n_3 = 6$ and $n_1 = n_2 = n_3 = 5$ of an electron in a cubic box with sides of length 1.0 nm. Go on to express the separations as a wavenumber.

11.2(a) Nanostructures commonly show physical properties that distinguish them from bulk materials. Calculate the wavelength and frequency of the radiation required to cause a transition between the levels in Exercise 11.1(a).
11.2(b) Nanostructures commonly show physical properties that distinguish them from bulk materials. Calculate the wavelength and frequency of the radiation required to cause a transition between the levels in Exercise 11.1(b).

11.3(a) Suppose a nanostructure is modelled by an electron confined to a rectangular region with sides of lengths $L_1 = 1.0\,\text{nm}$ and $L_2 = 2.0\,\text{nm}$ and is subjected to thermal motion with a typical energy equal to kT, where k is Boltzmann's constant. How low should the temperature be for the thermal energy to be comparable to (a) the zero-point energy, (b) the first excitation energy of the electron?
11.3(b) Suppose a nanostructure is modelled by an electron confined to a three-dimensional region with sides of lengths $L_1 = 1.0\,\text{nm}$, $L_2 = 2.0\,\text{nm}$, and $L_3 = 1.5\,\text{nm}$ and is subjected to thermal motion with a typical energy equal to $\frac{3}{2}kT$, where k is Boltzmann's constant. How low should the temperature be for the thermal energy to be comparable to (a) the zero-point energy, (b) the first excitation energy of the electron?

11.4(a) For quantum mechanical reasons, particles confined to nanostructures are not distributed uniformly through them. Calculate the probability that an electron confined to a square region with sides of length L will be found in the region $0.49L \le x \le 0.51L$ and $0.49L \le y \le 0.51L$ when it is in a state with (a) $n_1 = n_2 = 1$, (b) $n_1 = n_2 = 2$. Take the wavefunction to be a constant in this narrow range.
11.4(b) For quantum mechanical reasons, particles confined to nanostructures are not distributed uniformly through them. Calculate the probability that a hydrogen atom in a cubic cavity with sides of length L will be found in the region $0.49L \le x \le 0.51L$, $0.49L \le y \le 0.51L$ and $0.49L \le z \le 0.51L$ when it has (a) $n_1 = n_2 = n_3 = 1$, (b) $n_1 = n_2 = n_3 = 2$. Take the wavefunction to be a constant in this narrow range.

11.5(a) What are the most likely locations of an electron in a nanostructure modelled by a particle in a square box with sides of length L when it is in the state $n_1 = 4$, $n_2 = 5$?
11.5(b) What are the most likely locations of an electron in a nanostructure modelled by a particle in a cubic box with sides of length L when it is in the state $n_1 = 1$, $n_2 = 4$, $n_3 = 5$?

11.6(a) Locate the nodes of the wavefunction of an electron in a nanostructure modelled by a particle in a square region with sides of length L when it is in the state $n_1 = 2$, $n_2 = 3$.
11.6(b) Locate the nodes of the wavefunction of an electron in a nanostructure modelled by a particle in a cubic well with sides of length L when it is in the state $n_1 = 3$, $n_2 = 4$, $n_3 = 5$.

11.7(a) For quantum mechanical reasons, particles confined to nanostructures cannot be perfectly still even at $T = 0$. Calculate the expectation values of $\hat{p}$ and $\hat{p}^2$ for an electron in the ground state of a nanostructure modelled by a square box with sides of length L.
11.7(b) For quantum mechanical reasons, particles confined to nanostructures cannot be perfectly still even at $T = 0$. Calculate the expectation values of $\hat{p}$ and $\hat{p}^2$ for an electron in the ground state of a nanostructure modelled by a cubic box with sides of length L.

11.8(a) In Exercise 9.6(a) you were invited to explore whether compression could cause the zero-point energy of an electron to rise to equal its rest mass, m_ec^2, in one dimension. Repeat that calculation for a two-dimensional container. Express your answer in terms of the parameter $\lambda_C = h/m_ec$, the 'Compton wavelength' of the electron.
11.8(b) Repeat Exercise 11.8(a) for an electron squeezed inside a cubic box.

11.9(a) For a particle in a rectangular box with sides of length $L_1 = L$ and $L_2 = 2L$, find a state that is degenerate with the state $n_1 = n_2 = 2$. Degeneracy is normally associated with symmetry; why, then, are these two states degenerate?
11.9(b) For a particle in a rectangular box with sides of length $L_1 = L$ and $L_2 = 2L$, find a state that is degenerate with the state $n_1 = 2$, $n_2 = 8$. Degeneracy is normally associated with symmetry; why, then, are these two states degenerate?

11.10(a) Consider a particle in a cubic box. What is the degeneracy of the level that has an energy three times that of the lowest level?
11.10(b) Consider a particle in a cubic box. What is the degeneracy of the level that has an energy $\frac{14}{3}$ times that of the lowest level?

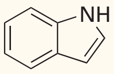
11.11(a) Calculate the percentage change in a given energy level of a particle in a cubic box when the length of the side of the cube is decreased by 10 per cent in each direction.
11.11(b) Calculate the percentage change in a given energy level of a particle in a square box when the length of the side of the square is decreased by 10 per cent in each direction.

11.12(a) Should a gas be treated quantum mechanically? An O_2 molecule is confined in a cubic box of volume $2.00\,\text{m}^3$. Assuming that the molecule has an energy equal to $\frac{3}{2}kT$ at $T = 300\,\text{K}$, what is the value of $n = (n_1^2 + n_2^2 + n_3^2)^{1/2}$, for this molecule? What is the energy separation between the levels n and $n+1$? What is its de Broglie wavelength? Would it be appropriate to describe this particle as behaving classically?
11.12(b) Should a gas be treated quantum mechanically? An N_2 molecule is confined in a cubic box of volume $1.00\,\text{m}^3$. Assuming that the molecule has an energy equal to $\frac{3}{2}kT$ at $T = 300\,\text{K}$, what is the value of $n = (n_1^2 + n_2^2 + n_3^2)^{1/2}$, for this molecule? What is the energy separation between the levels n and $n+1$? What is its de Broglie wavelength? Would it be appropriate to describe this particle as behaving classically?

Problems

11.1 Calculate the separation between the two lowest translational energy levels for an O_2 molecule in a cubic box with sides of length 5.0 cm. At what value of $n = n_1 = n_2 = n_3$ does the energy of the molecule reach $\frac{3}{2}kT$ at 300 K, and what is the separation of this level from one of the degenerate levels immediately below?

11.2 The particle in a two-dimensional box is a useful model for the motion of electrons around the indole rings (**1**), the conjugated cyclic compound found in the side chain of the amino acid tryptophan. As a first approximation, we can model indole as a rectangle with sides of length 280 pm and 450 pm, with 10 electrons in the conjugated system (the N atom provides two from its lone pair). Assume that in the ground state of the molecule each of the lowest available energy levels is occupied by two electrons. (a) Calculate the energy of an electron in the highest occupied level. (b) Calculate the wavelength of the radiation that can induce a transition between the highest occupied and lowest unoccupied levels.



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11.3 A very crude model of the buckminsterfullerene molecule (C_{60}) is to treat it as a collection of electrons in a cube with sides of length equal to the mean diameter of the molecule (0.7 nm). Suppose that only the π electrons of the carbon atoms contribute, and predict the wavelength of the first excitation of C_{60}. (The actual value is 730 nm.)

11.4 Now treat the buckminsterfullerene molecule as a sphere of radius $a = 0.35\,\text{nm}$, and predict the wavelength of the lowest energy transition of C_{60} resulting from excitation into an energy level not completely filled. You need to know that the energies are

$$E_{n,l}=\frac{F_{n,l}^2h^2}{8ma^2}$$

with the factors F and degeneracies g as follows:

n,l	1,0	1,1	1,2	2,0	1,3	2,1	1,4	2,2
$F_{n,l}$	1	1.430	1.835	2	2.224	2.459	2.605	2.895
$g_{n,l}$	1	3	5	1	7	3	9	5

11.5 When alkali metals dissolve in liquid ammonia, their atoms each lose an electron and give rise to a deep-blue solution that contains unpaired electrons occupying cavities in the solvent. These 'metal–ammonia solutions' have a maximum absorption at 1500 nm. Supposing that the absorption is due to the excitation of an electron in a spherical square well from its ground state to the next-higher state (see the preceding problem for information), what is the radius of the cavity?

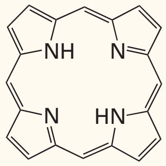
11.6 The detailed distribution of particles within nanostructures is of interest. Use mathematical software to draw contour maps of the wavefunctions and probability densities of a particle confined to a square surface with $n_1=4$ and $n_2=6$ (or other values of your choice). This problem is taken further in Problem 11.10. Go on—and this is a real challenge—to devise a way to depict the wavefunctions and probability densities of a cubic quantum dot (see *Impact* 3.1) in various states.

11.7 The energy levels of an electron in a nanoparticle and confined to a geometrically square region are proportional to $n^2=n_1^2+n_2^2$. This expression is an equation for a circle of radius n in (n_1,n_2)-space (with meaningful values in one quadrant). (a) Produce an argument that uses this relation to predict the degeneracy of a level with a high value of n. (b) Extend this argument to three dimensions.

11.8 Use the separation of variables method to derive the wavefunctions of eqn 11.6a.

11.9 Confirm by explicit differentiation that the wavefunction given in eqn 11.4a is a solution of the Schrödinger equation (eqn 11.1) for a particle in a two-dimensional box with energies given by eqn 11.4b.

11.10 In Problem 11.6 you were invited to plot contours showing the amplitude of the wavefunction and the probability density for various states of a particle confined to a plane. Develop that visualization in relation to the porphine ring (**2**), treating it as a square. Plot contours of the highest occupied wavefunction and the corresponding probability density superimposed on a drawing of the molecule. Does your map bear any relation to reality?



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11.11 Here we explore further the idea that quantum mechanical effects need to be invoked in the description of the electronic properties of metallic nanocrystals, here modelled as three-dimensional boxes. (a) Set up the Schrödinger equation for a particle of mass m in a three-dimensional rectangular box with sides L_1, L_2, and L_3. Show that the Schrödinger equation is separable. (b) Show that the wavefunction and the energy are defined by three quantum numbers. (c) Specialize the result from part (b) to an electron moving in a cubic box of side $L=5$ nm and draw an energy diagram showing the first 15 energy levels. Note that each energy level may consist of degenerate energy states. (d) Compare the energy level diagram from part (c) with the energy level diagram for an electron in a one-dimensional box of length $L=5$ nm. Are the energy levels becoming more or less sparsely distributed in the cubic box than in the one-dimensional box?

11.12 Can the location and momentum of an electron confined to two-dimensional motion in a nanostructure be determined precisely and simultaneously? Determine the values of $\Delta x=(\langle x^2\rangle-\langle x\rangle^2)^{1/2}$ and $\Delta p_x=(\langle p_x^2\rangle-\langle p_x\rangle^2)^{1/2}$ for a particle in a square box of length L in its lowest energy state. Go on to calculate $\Delta p_y=(\langle p_y^2\rangle-\langle p_y\rangle^2)^{1/2}$. Discuss these quantities with reference to the uncertainty principle.

Topic 12 Vibrational motion

Discussion questions

12.1 Describe the variation of the separation of the vibrational energy levels with the mass and force constant of the harmonic oscillator.

12.2 What is the physical reason for the existence of a zero-point vibrational energy?

12.3 Describe some applications of the harmonic oscillator model in chemistry.

Exercises

12.1(a) Calculate the zero-point energy of a harmonic oscillator consisting of a proton attached to a metal surface by a bond of force constant 155 N m^{-1}.

12.1(b) Calculate the zero-point energy of a harmonic oscillator consisting of a rigid CO molecule adsorbed to a metal surface by a bond of force constant 285 N m^{-1}.

12.2(a) For a harmonic oscillator of effective mass 1.33×10^{-25} kg, the difference in adjacent energy levels is 4.82 zJ. Calculate the force constant of the oscillator.

12.2(b) For a harmonic oscillator of effective mass 2.88×10^{-25} kg, the difference in adjacent energy levels is 3.17 zJ. Calculate the force constant of the oscillator.

12.3(a) Suppose a hydrogen atom is adsorbed on the surface of a gold nanoparticle by a bond of force constant 855 N m^{-1}. Calculate the wavelength of a photon needed to excite a transition between its neighbouring vibrational energy levels.

12.3(b) Suppose an oxygen atom ($m=15.9949m_u$) is adsorbed on the surface of a nickel nanoparticle by a bond of force constant 544 N m^{-1}. Calculate the wavelength of a photon needed to excite a transition between its neighbouring vibrational energy levels.

12.4(a) Refer to Exercise 12.3(a) and calculate the wavelength that would result from replacing hydrogen by deuterium.
12.4(b) Refer to Exercise 12.3(b) and calculate the wavelength that would result from replacing the oxygen atom by a rigid dioxygen molecule.

12.5(a) Locate the nodes of the harmonic oscillator wavefunction with $v=4$.
12.5(b) Locate the nodes of the harmonic oscillator wavefunction with $v=5$.

12.6(a) Calculate the normalization constant for an oscillator with $v=2$ and confirm that its wavefunction is orthogonal to the wavefunction for the state $v=4$.
12.6(b) Calculate the normalization constant for an oscillator with $v=3$ and confirm that its wavefunction is orthogonal to the wavefunction for the state $v=1$.

12.7(a) Assuming that the vibrations of a $^{35}Cl_2$ molecule are equivalent to those of a harmonic oscillator with a force constant $k_f=329\ \mathrm{N\ m^{-1}}$, what is the wavenumber of the radiation needed to excite the molecule vibrationally? The mass of a ^{35}Cl atom is $34.9688m_u$; the mass to use in the expression for the vibrational frequency of a diatomic molecule is the 'effective mass' $\mu=m_Am_B/(m_A+m_B)$, where m_A and m_B are the masses of the individual atoms.
12.7(b) Assuming that the vibrations of a $^{14}N_2$ molecule are equivalent to those of a harmonic oscillator with a force constant $k_f=2293.8\ \mathrm{N\ m^{-1}}$, what is the wavenumber of the radiation needed to excite the molecule vibrationally? The mass of a ^{14}N atom is $14.0031m_u$; see Exercise 12.7(a).

12.8(a) Calculate the probability that an O–H bond treated as a harmonic oscillator will be found at a classically forbidden extension when $v=1$.
12.8(b) Calculate the probability that an O–H bond treated as a harmonic oscillator will be found at a classically forbidden extension when $v=2$.

12.9(a) What is the relation between the mean kinetic and potential energies for a particle if the potential is proportional to x^3?
12.9(b) What is the relation between mean kinetic and potential energies of an electron in a hydrogen atom? *Hint*: The potential is Coulombic.

Problems

12.1 Give the symmetry (in terms of the function being even or odd) of the wavefunctions for the first four levels of a harmonic oscillator. How may this symmetry be expressed in terms of the quantum number v?

12.2 The mass to use in the expression for the vibrational frequency of a diatomic molecule is the effective mass $\mu=m_Am_B/(m_A+m_B)$, where m_A and m_B are the masses of the individual atoms. The following data on the infrared absorption wavenumbers ($\tilde{\nu}=1/\lambda=\nu/c$) of molecules is taken from G. Herzberg, *Spectra of diatomic molecules*, van Nostrand (1950):

	$H^{35}Cl$	$H^{81}Br$	HI	CO	NO
$\nu/\mathrm{cm^{-1}}$	2990	2650	2310	2170	1904

Calculate the force constants of the bonds and arrange them in order of increasing stiffness.

12.3 Confirm that a function of the form $e^{-\kappa x^2}$ is a solution of the Schrödinger equation for the ground state of a harmonic oscillator and find an expression for κ in terms of the mass and force constant of the oscillator.

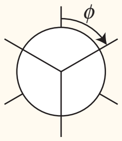
12.4 Calculate the mean kinetic energy of a harmonic oscillator by using the relations in Table 12.1.

12.5 Calculate the values of $\langle x^3\rangle$ and $\langle x^4\rangle$ for a harmonic oscillator by using the relations in Table 12.1.

12.6 We shall see in Topic 16 that the intensity of spectroscopic transitions between the vibrational states of a molecule is proportional to the square of the integral $\int \psi_{v'} x \psi_v\,\mathrm{d}x$ over all space. Use the relations between Hermite polynomials given in Table 12.1 to show that the only permitted transitions are those for which $v'=v\pm 1$ and evaluate the integral in these cases.

12.7 The potential energy of the rotation of one CH_3 group relative to its neighbour in ethane can be expressed as $V(\phi)=V_0\cos 3\phi$, where ϕ is the angle shown in **3**. (a) Show that for small displacements the motion of the group is harmonic and calculate the (molar) energy of excitation from $v=0$ to $v=1$. (b) What is the force constant for these small-amplitude oscillations? (c) The energy of impacts with any surrounding molecules is typically kT, where k is Boltzmann's constant. Should you expect the oscillations to be excited? (d) What do you expect to happen to the energy levels and wavefunctions as the excitation increases?

3



12.8 Carbon monoxide binds strongly to the Fe^{2+} ion of the haem group of the protein myoglobin. Estimate the vibrational frequency of CO bound to myoglobin by using the data in Problem 12.2 and by making the following assumptions: the atom that binds to the haem group is immobilized, the protein is infinitely more massive than either the C or O atom, the C atom binds to the Fe^{2+} ion, and binding of CO to the protein does not alter the force constant of the C≡O bond.

12.9 Of the four assumptions made in Problem 12.8, the last two are questionable. Suppose that the first two assumptions are still reasonable and that you have at your disposal a supply of myoglobin, a suitable buffer in which to suspend the protein, $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, $^{13}C^{18}O$, and an infrared spectrometer. Assuming that isotopic substitution does not affect the force constant of the C≡O bond, describe a set of experiments that (a) proves which atom, C or O, binds to the haem group of myoglobin, and (b) allows for the determination of the force constant of the C≡O bond for myoglobin-bound carbon monoxide.

12.10 In the study of macromolecules, such as synthetic polymers, proteins, and nucleic acids, one conformation commonly observed is that of a 'random coil'. For a one-dimensional random coil of N units, the restoring force at small displacements and at a temperature T is

$$F=-\frac{kT}{2l}\ln\left(\frac{N+n}{N-n}\right)$$

where l is the length of each monomer unit and nl is the distance between the ends of the chain. Show that for small extensions ($n\ll N$), the restoring force is proportional to n and therefore that the coil undergoes harmonic oscillation with force constant kT/Nl^2. Suppose that the mass to use for the vibrating chain is its total mass Nm, where m is the mass of one monomer unit, and deduce the root mean square separation of the ends of the chain due to quantum fluctuations in its vibrational ground state.

12.11 The 'most classical' linear combinations of harmonic oscillator wavefunctions are the so-called 'coherent states' which are described by the superposition

$$\psi_\alpha(x)=N\sum_{v=0}^{\infty}\frac{\alpha^v}{(v!)^{1/2}}\psi_v(x)$$

where α is a parameter. These states can be used to describe the radiation generated by lasers. (a) Show that the normalization constant is $N = e^{-|\alpha|^2/2}$. (b) Show that the wavefunctions ψ_α and ψ_β of two coherent states are not in general orthogonal. (c) Go on to show that a coherent state is the 'most classical' in the sense that the uncertainty relation for position and momentum for a particle it describes has its minimum value (that is, $\Delta x \Delta p = \frac{1}{2}\hbar$). *Hint*: Use a recursion relation in Table 12.1.

Topic 13 Rotational motion in two dimensions

Discussion question

13.1 Discuss the physical origin of quantization of energy for a particle confined to motion around a ring.

Exercises

13.1(a) Confirm that wavefunctions for a particle on a ring with different values of the quantum number m_l are mutually orthogonal.

13.1(b) Confirm that the wavefunction for a particle on a ring (eqn 13.7a) is normalized.

Problems

13.1 A synchrotron accelerates protons along a circular path of radius r. Suppose that the state of the proton is described by the unnormalized wavefunction $\psi(\phi) = \psi_{-1}(\phi) + 3^{1/2}\mathrm{i}\psi_{+1}(\phi)$. (a) Normalize this wavefunction. If measurements are made to determine (b) the total angular momentum and (c) the total energy of the proton, what will be the outcome? (d) What are the expectation values of these quantities?

13.2 Can the electronic structures of aromatic molecules be treated as electrons on a ring? Use such a model to predict the π electronic structure of benzene, allowing two electrons to occupy each state and supposing a radius of 133 pm. What is the wavelength of the first absorption band that you would predict on the basis of this model? (The actual value is 185 nm.)

13.3 The rotation of an $^1H^{127}I$ molecule can be pictured as the orbital motion of an H atom at a distance 160 pm from a stationary I atom. (This picture is quite good; to be precise, both atoms rotate around their common centre of mass, which in this case is very close to the I nucleus.) Suppose that the molecule rotates only in a plane (a restriction removed in Problem 14.1). (a) Calculate the wavelength of electromagnetic radiation needed to excite the molecule into rotation. (b) What, apart from 0, is the minimum angular momentum of the molecule?

13.4 A diatomic molecule with $\mu = 2.000 \times 10^{-26}$ kg and bond length 250.0 pm is rotating about its centre of mass in the xy-plane. The state of the molecule is described by the normalized wavefunction $\psi(\phi)$. When the total angular momentum of different molecules is measured, two possible results are obtained: a value of $3\hbar$ for 25 per cent of the time and a value of $-3\hbar$ for 75 per cent of the time. However, when the rotational energy of the molecules is measured, only a single result is obtained. (a) What is the expectation value of the angular momentum? (b) Write down an expression for the normalized wavefunction $\psi(\phi)$. (c) What is the result of measuring the energy?

13.5 What is the average angular position for a proton accelerated to a well-defined angular momentum in a synchrotron? Calculate $\langle\phi\rangle$, the mean value of ϕ, for a particle on a ring described by the wavefunction in eqn 13.7a. Explain your answer.

13.6 Evaluate the z-component of the angular momentum and the kinetic energy of a proton in a synchrotron of radius r in a state that is described by the (unnormalized) wavefunctions (a) $e^{\mathrm{i}\phi}$, (b) $e^{-2\mathrm{i}\phi}$, (c) $\cos\phi$, and (d) $(\cos\chi)\,e^{\mathrm{i}\phi} + (\sin\chi)\,e^{-\mathrm{i}\phi}$ with χ an arbitrary real parameter.

13.7 If a proton were accelerated on an elliptical ring rather than a circular ring, how would solution of the relevant Schrödinger equation proceed? In particular, is the Schrödinger equation for a particle on an elliptical ring of semi-major axes a and b separable? *Hint*: Although r varies with angle ϕ, the two are related by $r^2 = a^2\sin^2\phi + b^2\cos^2\phi$.

13.8 The particle on a ring is a useful model for the motion of electrons around the porphine ring (**2**), the conjugated macrocycle that forms the structural basis of the haem group and the chlorophylls. The group may be treated as a circular ring of radius 440 pm, with 22 electrons in the conjugated system moving along the perimeter. Assume that in the ground state of the molecule each level is occupied by two electrons. (a) Calculate the energy and angular momentum of an electron in the highest occupied level. (b) Calculate the frequency of radiation that can induce a transition between the highest occupied and lowest unoccupied levels.

13.9 The uncertainty principle takes on a different form for cyclic systems: $\Delta l_z \Delta\sin\phi \geq \frac{1}{2}\hbar|\langle\cos\phi\rangle|$, where $\Delta X = \{\langle X^2\rangle - \langle X\rangle^2\}^{1/2}$ in each case. Evaluate the quantities that appear in this expression for (a) a particle with angular momentum $+\hbar$, (b) a particle with wavefunction proportional to $\cos\phi$. Is the uncertainty principle satisfied in each case? Is there a difference between the two cases; if so, why?

Topic 14 Rotational motion in three dimensions

Discussion questions

14.1 Describe the features of the solution of the particle on a ring that appear in the solution of the particle on a sphere. What concept applies to the latter but not to the former?

14.2 Describe the vector model of angular momentum in quantum mechanics. What features does it capture? What is its status as a model?

Exercises

14.1(a) The rotation of a molecule can be represented by the motion of a point mass moving on the surface of a sphere. Calculate the magnitude of its angular momentum when $l=1$ and the possible components of the angular momentum on an arbitrary axis. Express your results as multiples of $\hbar$.

14.1(b) The rotation of a molecule can be represented by the motion of a point mass moving on the surface of a sphere with angular momentum quantum number $l=2$. Calculate the magnitude of its angular momentum and the possible components of the angular momentum on an arbitrary axis. Express your results as multiples of $\hbar$.

14.2(a) Draw scale vector diagrams to represent the states (a) $l=1$, $m_l=+1$, (b) $l=2$, $m_l=0$. What is the angle that the vector makes to the z-axis?

14.2(b) Draw scale vector diagrams for all the permitted rotational states of a body with $l=6$. What are the angles that the vectors make to the z-axis?

14.3(a) The number of states corresponding to a given energy plays a crucial role in atomic structure and thermodynamic properties. Determine the degeneracy of a body rotating with $l=3$.

14.3(b) The number of states corresponding to a given energy plays a crucial role in atomic structure and thermodynamic properties. Determine the degeneracy of a body rotating with $l=4$.

Problems

14.1 Modify Problem 13.3 so that the molecule is free to rotate in three dimensions, using for its moment of inertia $I=\mu R^2$, with $\mu=m_{\mathrm{H}}m_{\mathrm{I}}/(m_{\mathrm{H}}+m_{\mathrm{I}})$ and $R=160$ pm. Calculate the energies and degeneracies of the lowest four rotational levels, and predict the wavelength of electromagnetic radiation emitted in the $l=1\rightarrow 0$ transition. In which region of the electromagnetic spectrum does this wavelength appear?

14.2 The average moment of inertia of a benzene molecule is 1.5×10^{-45} kg m^2. What energy is needed to excite the molecule from its (three-dimensional) rotational ground state to the next-higher rotational level? What is the wavelength of electromagnetic radiation that would achieve that excitation? Where in the electromagnetic spectrum does that radiation lie?

14.3 A helium atom moving on the surface of a buckminsterfullerene molecule before it diffuses into the molecule's interior can be modelled as a free particle on the surface of a sphere of radius 0.35 nm. Suppose the state of the atom is described by a wavepacket of composition $\psi(\theta,\phi)=2^{1/2}Y_{2,+1}(\theta,\phi)+3\mathrm{i}Y_{2,+2}(\theta,\phi)+Y_{1,+1}(\theta,\phi)$. (a) Normalize this wavefunction. If (b) the total angular momentum, (c) the z-component of angular momentum, and (d) the total energy of the atom are measured, what results will be found? (e) What are the expectation values of these observables?

14.4 Use the properties of the spherical harmonics to identify the most probable angles a rotating linear molecule will make to an arbitrary axis when $l=1$, 2, and 3.

14.5 Use mathematical software to construct a wavepacket of the form

$$\Psi(\phi,t)=\sum_{m_l=0}^{m_{l,\max}} c_{m_l}\mathrm{e}^{\mathrm{i}(m_l\phi-E_{m_l}t/\hbar)} \qquad E_{m_l}=m_l^2\hbar^2/2I$$

with coefficients c of your choice (for example, all equal). Explore how the wavepacket migrates on the ring but spreads with time.

14.6 Confirm that the spherical harmonics (a) $Y_{0,0}$, (b) $Y_{2,-1}$, and (c) $Y_{3,+3}$ satisfy the Schrödinger equation for a particle free to rotate in three dimensions, and find its energy and angular momentum in each case.

14.7 Confirm by explicit integration that $Y_{1,+1}$ and $Y_{2,0}$ are orthogonal. (The integration required is over the surface of a sphere.)

14.8 Confirm that $Y_{3,+3}$ is normalized to 1. (The integration required is over the surface of a sphere.)

14.9 Derive (in Cartesian coordinates) the quantum mechanical operators for the three components of angular momentum starting from the classical definition of angular momentum, $\boldsymbol{l}=\boldsymbol{r}\times\boldsymbol{p}$. Show that any two of the components do not mutually commute, and find their commutator.

14.10 Starting from the operator $\hat{l}_z=\hat{x}\hat{p}_y-\hat{y}\hat{p}_x$, prove that in spherical polar coordinates $\hat{l}_z=-\mathrm{i}\hbar\partial/\partial\phi$.

14.11 Show that the commutator $[\hat{l}^2,\hat{l}_z]=0$, and then, without further calculation, justify the remark that $[\hat{l}^2,\hat{l}_q]=0$ for all $q=x$, y, and z.

14.12 A particle confined to within a spherical cavity is a reasonable starting point for the discussion of the electronic properties of spherical metal nanoparticles (*Impact* 3.1). Here, you are invited to show in a series of steps that the $l=0$ energy levels of an electron in a spherical cavity of radius R are quantized and given by

$$E_n=\frac{n^2h^2}{8m_{\mathrm{e}}R^2}$$

(a) The hamiltonian for a particle free to move inside a sphere of radius a is

$$\hat{H}=-\frac{\hbar^2}{2m}\nabla^2$$

Show that the Schrödinger equation is separable into radial and angular components. That is, begin by writing $\psi(r,\theta,\phi)=R(r)Y(\theta,\phi)$, where $R(r)$

depends only on the distance of the particle from the centre of the sphere, and $Y(\theta,\phi)$ is a spherical harmonic. Then show that the Schrödinger equation can be separated into two equations, one for $R(r)$, the radial equation, and the other for $Y(\theta,\phi)$, the angular equation.

(b) Consider the case $l=0$. Show by differentiation that the solution of the radial equation has the form

$$R(r)=(2\pi a)^{-1/2}\frac{\sin(n\pi r/a)}{r}$$

(c) Now go on to show (by acknowledging the appropriate boundary conditions) that the allowed energies are given by $E_n=n^2h^2/8ma^2$. With substitution of m_e for m and of R for a, this is the equation given above for the energy.

Integrated activities

F3.1 Discuss the correspondence principle and provide two examples.

F3.2 Define, justify, and provide examples of zero-point energy.

F3.3 Explain why the particle in a box and the harmonic oscillator are useful models for quantum mechanical systems: what chemically significant systems can they be used to represent?

F3.4 Discuss the presence or absence of zero-point energy for translational and rotational motions in two and three dimensions.

F3.5 Determine the values of $\Delta x=(\langle x^2\rangle-\langle x\rangle^2)^{1/2}$ and $\Delta p=(\langle p^2\rangle-\langle p\rangle^2)^{1/2}$ for the ground state of (a) a particle in a box of length L and (b) a harmonic oscillator. Discuss these quantities with reference to the uncertainty principle.

F3.6 Repeat Problem F3.5 for (a) a particle in a box and (b) a harmonic oscillator in a general quantum state (n and v, respectively).

F3.7 Use mathematical software, a spreadsheet, or the *Living graphs* (labelled $^{\mathrm{LG}}$) on the website of this book for the following exercises:

(a) $^{\mathrm{LG}}$ Plot the probability density for a particle in a box with $n=1, 2,\ldots 5$ and $n=50$. How do your plots illustrate the correspondence principle?

(b) $^{\mathrm{LG}}$ Plot the transmission probability T against E/V for passage by (i) a hydrogen molecule, (ii) a proton, and (iii) an electron through a barrier of height V.

(c) $^{\mathrm{LG}}$ To gain some insight into the origins of the nodes in the harmonic oscillator wavefunctions, plot the Hermite polynomials $H_v(y)$ for $v=0$ through 5.

(d) Use mathematical software to generate three-dimensional plots of the wavefunctions for a particle confined to a rectangular surface with (i) $n_1=1$, $n_2=1$, the state of lowest energy, (ii) $n_1=1$, $n_2=2$, (iii) $n_1=2$, $n_2=1$, and (iv) $n_1=2$, $n_2=2$. Deduce a rule for the number of nodal lines in a wavefunction as a function of the values of n_1 and n_2.

Mathematical background 3 Complex numbers

We describe here general properties of complex numbers and functions, which are mathematical constructs frequently encountered in quantum mechanics.

MB3.1 Definitions

Complex numbers have the general form

$$z = x + \mathrm{i}y$$

General form of a complex number (MB3.1)

where $\mathrm{i} = (-1)^{1/2}$. The real numbers x and y are, respectively, the real and imaginary parts of z, denoted $\mathrm{Re}(z)$ and $\mathrm{Im}(z)$. When $y=0$, $z=x$ is a real number; when $x=0$, $z=\mathrm{i}y$ is a pure imaginary number. Two complex numbers $z_1 = x_1 + \mathrm{i}y_1$ and $z_2 = x_2 + \mathrm{i}y_2$ are equal when $x_1 = x_2$ and $y_1 = y_2$. Although the general form of the imaginary part of a complex number is written $\mathrm{i}y$, a specific numerical value is typically written in the reverse order; for instance, as 3i.

The **complex conjugate** of z, denoted z^*, is formed by replacing i by –i:

$$z^* = x - \mathrm{i}y$$

Complex conjugate (MB3.2)

The product of z^* and z is denoted $|z|^2$ and is called the **square modulus** of z. From eqns MB3.1 and MB3.2,

$$|z|^2 = (x+\mathrm{i}y)(x-\mathrm{i}y) = x^2 + y^2$$

Square modulus (MB3.3)

since $\mathrm{i}^2 = -1$. The square modulus is a real number. The **absolute value** or **modulus** is itself denoted $|z|$ and is given by:

$$|z| = (z^* z)^{1/2} = (x^2 + y^2)^{1/2}$$

Absolute value or modulus (MB3.4)

Since $zz^* = |z|^2$ it follows that $z \times (z^*/|z|^2) = 1$, from which we can identify the (multiplicative) **inverse** of z (which exists for all nonzero complex numbers):

$$z^{-1} = \frac{z^*}{|z|^2}$$

Inverse of a complex number (MB3.5)

Brief illustration MB3.1 Inverse

Consider the complex number $z = 8 - 3\mathrm{i}$. Its square modulus is

$$|z|^2 = z^* z = (8-3\mathrm{i})*(8-3\mathrm{i}) = (8+3\mathrm{i})(8-3\mathrm{i}) = 64 + 9 = 73$$

The modulus is therefore $|z| = 73^{1/2}$. From eqn MB3.5, the inverse of z is

$$z^{-1} = \frac{8+3\mathrm{i}}{73} = \frac{8}{73} + \frac{3}{73}\mathrm{i}$$

MB3.2 Polar representation

The complex number $z = x + \mathrm{i}y$ can be represented as a point in a plane, the **complex plane**, with $\mathrm{Re}(z)$ along the x-axis and $\mathrm{Im}(z)$ along the y-axis (Fig. MB3.1). If, as shown in the figure, r and ϕ denote the polar coordinates of the point, then since $x = r\cos\phi$ and $y = r\sin\phi$, we can express the complex number in **polar form** as

$$z = r(\cos\phi + \mathrm{i}\sin\phi)$$

Polar form of a complex number (MB3.6)

The angle ϕ, called the **argument** of z, is the angle that z makes with the x-axis. Because $y/x = \tan\phi$, it follows that the polar form can be constructed from

$$r = (x^2 + y^2)^{1/2} = |z| \qquad \phi = \arctan\frac{y}{x} \tag{MB3.7a}$$

To convert from polar to Cartesian form, use

$$x = r\cos\phi \text{ and } y = r\sin\phi \text{ to form } z = x + \mathrm{i}y \tag{MB3.7b}$$

One of the most useful relations involving complex numbers is **Euler's formula**:

$$\mathrm{e}^{\mathrm{i}\phi} = \cos\phi + \mathrm{i}\sin\phi$$

Euler's formula (MB3.8a)

The simplest proof of this relation is to expand the exponential function as a power series and to collect real and imaginary terms. It follows that

$$\cos\phi = \tfrac{1}{2}(\mathrm{e}^{\mathrm{i}\phi} + \mathrm{e}^{-\mathrm{i}\phi}) \qquad \sin\phi = -\tfrac{1}{2}\mathrm{i}(\mathrm{e}^{\mathrm{i}\phi} - \mathrm{e}^{-\mathrm{i}\phi}) \tag{MB3.8b}$$

The polar form in eqn MB3.6 then becomes

$$z = r\mathrm{e}^{\mathrm{i}\phi} \tag{MB3.9}$$

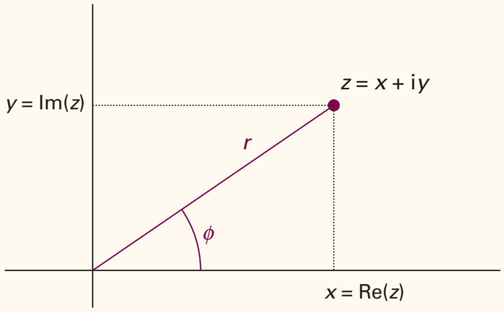


Figure MB3.1 The representation of a complex number z as a point in the complex plane using cartesian coordinates (x,y) or polar coordinates (r,ϕ).

Brief illustration MB3.2 Polar representation

Consider the complex number $z = 8 - 3\text{i}$. From *Brief illustration* MB3.1, $r = |z| = 73^{1/2}$. The argument of z is

$$\theta = \arctan\left(\frac{-3}{8}\right) = -0.359 \text{ rad, or } -20.6°$$

The polar form of the number is therefore

$$z = 73^{1/2}\,\text{e}^{-0.359\text{i}}$$

MB3.3 Operations

The following rules apply for arithmetic operations for the complex numbers $z_1 = x_1 + \text{i}y_1$ and $z_2 = x_2 + \text{i}y_2$.

1 Addition: $z_1 + z_2 = (x_1 + x_2) + \text{i}(y_1 + y_2)$ (MB3.10a)

2 Subtraction: $z_1 - z_2 = (x_1 - x_2) + \text{i}(y_1 - y_2)$ (MB3.10b)

3 Multiplication:

$$\begin{aligned} z_1 z_2 &= (x_1 + \text{i}y_1)(x_2 + \text{i}y_2) \\ &= (x_1x_2 - y_1y_2) + \text{i}(x_1y_2 + y_1x_2) \end{aligned} \qquad \text{(MB3.10c)}$$

4 Division: We interpret z_1/z_2 as $z_1z_2^{-1}$ and use eqn MB3.5 for the inverse:

$$\frac{z_1}{z_2} = z_1 z_2^{-1} = \frac{z_1 z_2^*}{|z_2|^2} \qquad \text{(MB3.10d)}$$

Brief illustration MB3.3 Operations with numbers

Consider the complex numbers $z_1 = 6 + 2\text{i}$ and $z_2 = -4 - 3\text{i}$. Then

$$\begin{aligned} z_1 + z_2 &= (6-4) + (2-3)\text{i} = 2 - \text{i} \\ z_1 - z_2 &= 10 + 5\text{i} \\ z_1 z_2 &= \{6(-4) - 2(-3)\} + \{6(-3) + 2(-4)\}\text{i} = -18 - 26\text{i} \\ \frac{z_1}{z_2} &= (6+2\text{i})\left(\frac{-4+3\text{i}}{25}\right) = -\frac{6}{5} + \frac{2}{5}\text{i} \end{aligned}$$

The polar form of a complex number is commonly used to perform arithmetical operations. For instance the product of two complex numbers in polar form is

$$z_1 z_2 = (r_1 \text{e}^{\text{i}\phi_1})(r_2 \text{e}^{\text{i}\phi_2}) = r_1 r_2 \text{e}^{\text{i}(\phi_1 + \phi_2)} \qquad \text{(MB3.11)}$$

This multiplication is depicted in the complex plane as shown in Fig. MB3.2. The nth power and the nth root of a complex number are

$$z^n = (r\text{e}^{\text{i}\phi})^n = r^n \text{e}^{\text{i}n\phi} \qquad z^{1/n} = (r\text{e}^{\text{i}\phi})^{1/n} = r^{1/n}\text{e}^{\text{i}\phi/n} \qquad \text{(MB3.12)}$$

The depictions in the complex plane are shown in Fig. MB3.3.

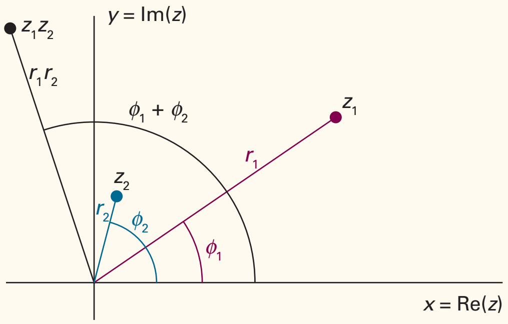


Figure MB3.2 The multiplication of two complex numbers depicted in the complex plane.

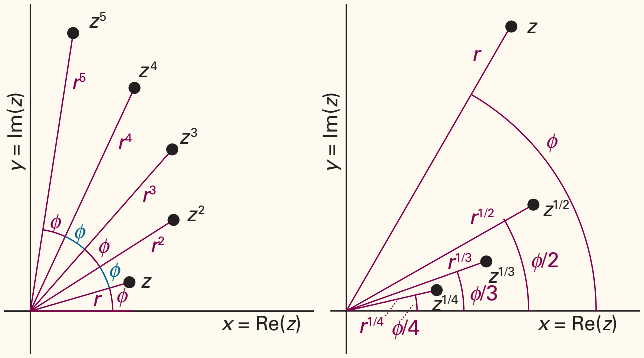


Figure MB3.3 The nth powers ($n = 1, 2, 3, 4, 5$) and the nth roots ($n = 1, 2, 3, 4$) of a complex number depicted in the complex plane.

Brief illustration MB3.4 Roots

To determine the 5th root of $z = 8 - 3\text{i}$, we note that from *Brief illustration* MB3.2 its polar form is

$$z = 73^{1/2}\,\text{e}^{-0.359\text{i}} = 8.544\text{e}^{-0.359\text{i}}$$

The 5th root is therefore

$$z^{1/5} = (8.544\text{e}^{-0.359\text{i}})^{1/5} = 8.544^{1/5}\text{e}^{-0.359\text{i}/5} = 1.536\text{e}^{-0.0718\text{i}}$$

It follows that $x = 1.536 \cos(-0.0718) = 1.532$ and $y = 1.536 \sin(-0.0718) = -0.110$ (note that we work in radians), so

$$(8 - 3\text{i})^{1/5} = 1.532 - 0.110\text{i}$$

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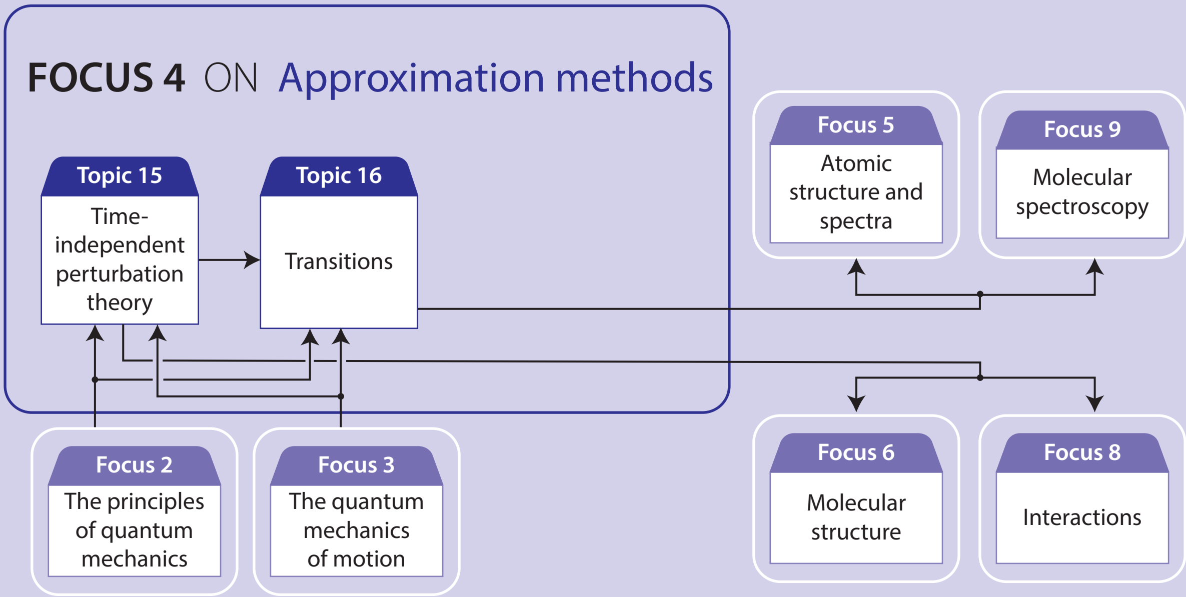
FOCUS 4 ON Approximation methods



Exact solutions of the Schrödinger equation can be found for only a small number of problems, such as the model systems described in *The quantum mechanics of motion*. Almost all the problems of interest in chemistry do not have exact solutions. To make progress with these problems, which include many-electron atoms and molecules, we need to develop techniques of approximation.

There are three major approaches to finding approximate solutions. The first is to try to guess the shape and mathematical form of the wavefunction. 'Variation theory' provides a criterion of success with such an approach and, as it is most commonly encountered in the context of molecular orbital theory, we consider it in *Molecular structure*. The second approach, an iterative method called the 'self-consistent field procedure' which is often used alongside variation theory, is useful to find numerical solutions of the Schrödinger equation for many-electron systems (see *Atomic structure and spectra* and *Molecular structure*). The third approach takes the hamiltonian operator for the problem and separates it into a simple model hamiltonian for which the Schrödinger equation can be solved and a 'perturbation', which is the difference between the true and model hamiltonians. The aim of 'perturbation theory', which provides the mathematical tools for solving complex problems by this approach, is to generate the wavefunction and energy of the perturbed system from knowledge of the model hamiltonian and a systematic procedure for taking into account the presence of the perturbation.

Time-independent perturbation theory (**Topic 15**) begins by identifying a model system that resembles the system of interest, and then shows how to distort the wavefunctions and adjust the energies to approach those of the actual system in the presence of a time-independent perturbation. This analytical procedure is the basis for the many-body perturbation theory method described in *Molecular structure* and is also useful in the discussion of electric and magnetic properties of materials (*Interactions*).

Time-dependent perturbation theory (**Topic 16**) is the basis of the discussion of transitions between states when the system is subjected to a perturbation that varies with time. A very important example of such a system is an atom or molecule exposed to an oscillating electromagnetic field and is the basis of accounting for the transitions observed in *Atomic structure and spectra* and *Molecular spectroscopy*.

TOPIC 15

Time-independent perturbation theory

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➤ Why do you need to know this material?

Perturbation theory is used throughout chemistry where exact solutions of the Schrödinger equation are impossible to find. It is used to find approximate solutions of complicated problems, such as the electric and magnetic properties of matter (Topics 34 and 39) and the interaction between matter and electromagnetic radiation (Topic 16).

➤ What is the key idea?

The hamiltonian of the system is expressed as a sum of a simple model hamiltonian and a perturbation hamiltonian; the latter is then used to develop approximations to the energies and wavefunctions of the system.

➤ What do you need to know already?

You need to be familiar with the concepts introduced in Topics 5–7, particularly the Schrödinger equation, expectation values, hermiticity, normalization, and orthogonality. The calculations in this Topic rely heavily on the description of the particle in a one-dimensional box (Topic 9).

Perturbation theory comes in two formulations, depending on whether or not the perturbation varies with time. In this Topic, we consider only **time-independent perturbation theory**, which is the basis of our discussion of the electric and magnetic properties of molecules. In Topic 16, we discuss **time-dependent perturbation theory**, which is used to discuss the response of atoms and molecules to time-dependent electromagnetic fields and is central to the discussion of spectroscopy.

15.1 Perturbation expansions

We suppose that the hamiltonian for the problem we are trying to solve, $\hat{H}$, can be expressed as a sum of a simple hamiltonian, $\hat{H}^{(0)}$, which has known eigenvalues, $E^{(0)}$, and eigenfunctions, $\psi^{(0)}$, and a contribution, $\hat{H}^{(1)}$, which represents the extent to which the true hamiltonian differs from the 'model' hamiltonian:

$$\hat{H}=\hat{H}^{(0)}+\hat{H}^{(1)} \qquad (15.1)$$

Perturbation theory Partition of the hamiltonian

We seek the energies and eigenvalues of $\hat{H}$. To find them we suppose that the true energy of the system, E, differs from the energy of the model system, $E^{(0)}$, and that we can write

$$E=E^{(0)}+E^{(1)}+E^{(2)}+\ldots \qquad (15.2)$$

Perturbation theory Expansion of the energy where $E^{(1)}$ is the 'first-order' correction to the energy, a contribution proportional to $\hat{H}^{(1)}$, and $E^{(2)}$ is the 'second-order' correction to the energy, a contribution proportional to the square of $\hat{H}^{(1)}$, and so on. The true wavefunction, ψ, also differs from the 'simple' wavefunction of the model system, $\psi^{(0)}$, and we write

$$\psi = \psi^{(0)} + \psi^{(1)} + \psi^{(2)} + \ldots \qquad (15.3)$$

Perturbation theory

Expansion of the wavefunction

where $\psi^{(1)}$ is the 'first-order' correction to the wavefunction and so on. In practice, time-independent perturbation theory typically needs only first- and second-order energy corrections to provide accurate estimates of energies of the perturbed system (as long as the perturbation is weak.) Likewise, it rarely needs to proceed beyond first-order corrections to the wavefunction.

Brief illustration 15.1 The corrections to the energy and wavefunction

Consider an electron in a one-dimensional metallic nanoparticle of length L. A related simple problem is a particle in a one-dimensional box. The model hamiltonian $\hat{H}^{(0)}$ is therefore that of a particle in a one-dimensional box (Topic 9). The effect of the varying potential energy of the electron inside the nanoparticle can be modelled by supposing that it has the form $V(x) = -\varepsilon\sin(\pi x/L)$ (Fig. 15.1). The perturbation is therefore $\hat{H}^{(1)} = -\varepsilon\sin(\pi x/L)$. The corrections $E^{(1)}$ and $\psi^{(1)}$ are proportional to ε and $E^{(2)}$ is proportional to ε^2.

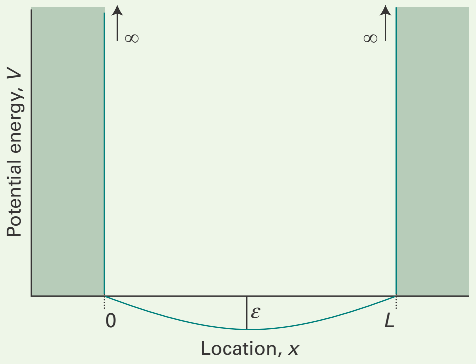

Figure 15.1 A model for the potential energy used to illustrate the application of perturbation theory to a simple system. The potential energy is infinite at the walls of the box and varies as V across the floor of the box.

Self-test 15.1 The vibrational motion of a certain diatomic molecule is known to be described by a potential energy of the form $V = \frac{1}{2}k_f x^2 + ax^3$, where k_f is the force constant, x is the displacement of the internuclear distance from the equilibrium bond length, and a is a constant. Identify the model hamiltonian and the perturbation and predict the dependencies of the corrections $E^{(1)}$, $E^{(2)}$, and $\psi^{(1)}$ on the constant a.

Answer: $\hat{H}^{(0)}$ is that of the harmonic oscillator (Topic 12); $\hat{H}^{(1)} = ax^3$; $E^{(1)}$ and $\psi^{(1)}$ are proportional to a, $E^{(2)}$ to a^2

This Topic is filled with derivations. If you do not require this level of detail and wish to proceed to the key results, they are as follows for the ground state of the system.

- The first-order correction to the energy is given by

$$E_0^{(1)} = \int \psi_0^{(0)*}\,\hat{H}^{(1)}\,\psi_0^{(0)}\,d\tau \qquad (15.4)$$

First-order energy correction

where $\psi_0^{(0)}$ is the ground-state wavefunction for the 'model' system with hamiltonian $\hat{H}^{(0)}$.

See Example 15.1 for an illustration of how this expression is used. The integral is an expectation value (Topic 7); in this case, it is the expectation value of the perturbation calculated using the unperturbed ground-state wavefunction. We can therefore interpret $E_0^{(1)}$ as the average value of the effect of the perturbation. An analogy is the shift in energy of vibration of a violin string when small weights are hung along its length. The weights hanging close to the nodes have little effect on its energy of vibration. Those hanging at the locations of maximum amplitude, however, have a profound effect (Fig. 15.2a). The overall effect is the average of all the weights.

- The wavefunction corrected to first order is given by

$$\psi_0 = \psi_0^{(0)} + \sum_{n\neq 0} c_n \psi_n^{(0)} \qquad c_n = \frac{\int \psi_n^{(0)*}\,\hat{H}^{(1)}\,\psi_0^{(0)}\,d\tau}{E_0^{(0)} - E_n^{(0)}} \qquad (15.5)$$

First-order correction to the wavefunction

where $\psi_n^{(0)}$ and $E_n^{(0)}$ are the eigenfunctions and eigenvalues, respectively, of the model system.

See Example 15.2 for an illustration of how this expression is used. In this case, the wavefunction is distorted by the perturbation. In terms of the violin-string analogy, the weights distort the shape of the vibrating string.

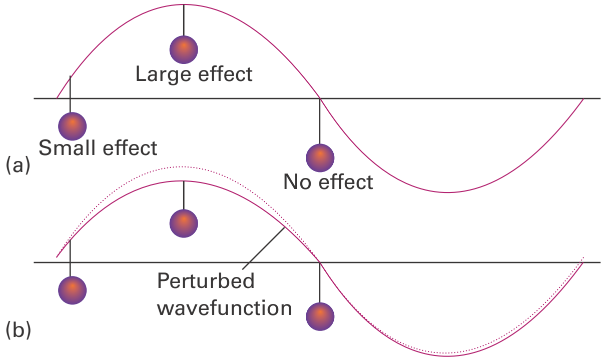

Figure 15.2 (a) The first-order correction to the energy is an average of the perturbation (represented by the hanging weights) over the unperturbed wavefunction. (b) The second-order correction is a similar average, but over the distortion induced by the perturbation.

- The second-order correction to the energy is given by

$$E_0^{(2)} = \sum_{n\neq 0} \frac{\left|\int \psi_n^{(0)*}\hat{H}^{(1)}\psi_0^{(0)}\mathrm{d}\tau\right|^2}{E_0^{(0)} - E_n^{(0)}} \qquad (15.6)$$

Second-order energy correction

See Example 15.3 for an illustration of how this expression is used. The correction also represents an average of the perturbation similar to that for the first-order energy correction, but now it is an average over the *perturbed* wavefunctions. In terms of the violin analogy, the average is now taken over the distorted waveform of the vibrating string, in which the locations of minimum and maximum amplitudes are slightly shifted (Fig. 15.2b).

15.2 The first-order correction to the energy

Although the equations of perturbation theory are applicable to any state of the perturbed system, we focus attention on the ground state for which the wavefunction of the 'model' system is $\psi_0^{(0)}$. We show in the following *Justification* that the first-order correction to the energy of the ground state is given by eqn 15.4.

Justification 15.1 The first-order correction to the energy

To develop expressions for the corrections to the ground-state wavefunction and energy of a system subjected to a time-independent perturbation, we write

$$\psi_0 = \psi_0^{(0)} + \lambda\psi_0^{(1)} + \lambda^2\psi_0^{(2)} + \cdots$$

where λ is a dummy variable that will help us keep track of the order of the correction. At the end of the calculation, we discard it. Likewise we write

$$\hat{H} = \hat{H}^{(0)} + \lambda\hat{H}^{(1)}$$

and

$$E_0 = E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \cdots$$

When these expressions are inserted into the Schrödinger equation, $\hat{H}\psi = E\psi$, we obtain

$$(\hat{H}^{(0)} + \lambda\hat{H}^{(1)})(\psi_0^{(0)} + \lambda\psi_0^{(1)} + \lambda^2\psi_0^{(2)} + \cdots) =$$
$$(E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \cdots)(\psi_0^{(0)} + \lambda\psi_0^{(1)} + \lambda^2\psi_0^{(2)} + \cdots)$$

which, by collecting powers of λ, we can rewrite as

$$\hat{H}^{(0)}\psi_0^{(0)} + \lambda(\hat{H}^{(1)}\psi_0^{(0)} + \hat{H}^{(1)}\psi_0^{(1)}) + \lambda^2(\hat{H}^{(0)}\psi_0^{(2)} + \hat{H}^{(1)}\psi_0^{(1)}) + \cdots$$
$$= E_0^{(0)}\psi_0^{(0)} + \lambda(E_0^{(0)}\psi_0^{(1)} + E_0^{(1)}\psi_0^{(0)}) + \lambda^2(E_0^{(2)}\psi_0^{(0)}$$
$$+ E_0^{(1)}\psi_0^{(1)} + E_0^{(0)}\psi_0^{(2)}) + \cdots$$

By comparing powers of λ, we find

$$\text{Terms in } \lambda^0: \hat{H}^{(0)}\psi_0^{(0)} = E_0^{(0)}\psi_0^{(0)}$$
$$\text{Terms in } \lambda^1: \hat{H}^{(1)}\psi_0^{(0)} + \hat{H}^{(0)}\psi_0^{(1)} = E_0^{(0)}\psi_0^{(1)} + E_0^{(1)}\psi_0^{(0)}$$
$$\text{Terms in } \lambda^2: \hat{H}^{(0)}\psi_0^{(2)} + \hat{H}^{(1)}\psi_0^{(1)} = E_0^{(2)}\psi_0^{(0)} + E_0^{(1)}\psi_0^{(1)} + E_0^{(0)}\psi_0^{(2)}$$

and so on. At this point, λ has served its purpose, and can now be discarded.

The first of the three above equations is the Schrödinger equation for the ground state of the unperturbed system, which we can assume we can solve. To solve the second of the equations (the one in λ^1), we suppose that the first-order correction to the wavefunction can be expressed as a linear combination of the wavefunctions of the unperturbed system, and write

$$\psi_0^{(1)} = \sum_n c_n\psi_n^{(0)}$$

with the coefficients c_n to be determined. We can isolate the term in $E_0^{(1)}$ by making use of the fact that the $\psi_n^{(0)}$ form a complete orthonormal set (eqn 7.3b of Topic 7) in the sense that

$$\int \psi_0^{(0)*}\psi_n^{(0)}\mathrm{d}\tau = \overbrace{\delta_{0n}}^{1\text{ if } n=0,\ 0 \text{ if } n\neq 0}$$

where δ_{ij}, the Kronecker delta (Topic 7), is 1 when $i=j$ and 0 when $i\neq j$. Therefore, when we multiply the equation in λ^1 through by $\psi_0^{(0)*}$ and integrate over all space, we get

$$\int \psi_0^{(0)*}\hat{H}^{(1)}\psi_0^{(0)}\mathrm{d}\tau + \sum_n c_n \overbrace{\int \psi_0^{(0)*}\hat{H}^{(0)}\psi_n^{(0)}\mathrm{d}\tau}^{E_0^{(0)}\text{ if } n=0,\, 0 \text{ otherwise}}$$
$$= \sum_n c_n E_0^{(0)} \overbrace{\int \psi_0^{(0)*}\psi_n^{(0)}\mathrm{d}\tau}^{\delta_{0n}} + E_0^{(1)} \overbrace{\int \psi_0^{(0)*}\psi_0^{(0)}\mathrm{d}\tau}^{1}$$

That is, because the middle two terms are equivalent,

$$\int \psi_0^{(0)*}\hat{H}^{(0)}\psi_0^{(0)}\mathrm{d}\tau = E_0^{(1)}$$

which is eqn 15.4.

Example 15.1 Evaluating the first-order correction to the energy

Use the model described in *Brief illustration* 15.1 for the potential energy of an electron in a one-dimensional nanoparticle to evaluate the first-order correction to the energy of the ground state.

Method Identify the first-order perturbation hamiltonian and evaluate $E_0^{(1)}$ from eqn 15.4. The ground-state wavefunction of the particle in a one-dimensional box is given in Topic 9 (where it corresponds to $n=1$). Use Integral T.3 listed in the *Resource section*.

Answer The perturbation hamiltonian is $\hat{H}^{(1)}=-\varepsilon\sin(\pi x/L)$ and the unperturbed ground-state ($n=1$) wavefunction of the particle in a one-dimensional box is $\psi^{(0)}=(2/L)^{1/2}\sin(\pi x/L)$. Therefore, the first-order correction to the wavefunction is

$$E^{(1)}=\int_0^L \psi^{(0)}\hat{H}^{(1)}\psi^{(0)}\mathrm{d}x=-\frac{2\varepsilon}{L}\overbrace{\int_0^L \sin^3\frac{\pi x}{L}\mathrm{d}x}^{4L/3\pi}=-\frac{8\varepsilon}{3\pi}$$

The energy is lowered by the perturbation, as would be expected for the shape shown in Fig. 15.1.

Self-test 15.2 Evaluate the first-order correction to the energy of the ground state if, in the same model, $V(x)=-\varepsilon\sin^2(\pi x/L)$. Use Integral T.4 listed in the *Resource section*.

Answer: $E^{(1)}=-\frac{3}{4}\varepsilon$

15.3 The first-order correction to the wavefunction

We show in the following *Justification* that the wavefunction corrected to first order in the perturbation is quoted in eqn 15.5. The first-order correction to the wavefunction is a linear combination of the unperturbed wavefunctions of the system. Equation 15.5 shows that a particular state $\psi_n^{(0)}$

- makes no contribution to the linear combination if $\int\psi_n^{(0)*}\hat{H}^{(1)}\psi_0^{(0)}\mathrm{d}\tau=0$
- makes a larger contribution the smaller the energy difference $|E_0^{(0)}-E_n^{(0)}|$ (absolute values used because $E_n^{(0)}$ is greater than the ground-state energy $E_0^{(0)}$).

Physical interpretation

Justification 15.2 The first-order correction to the wavefunction

To find the first-order correction to the wavefunction, we continue the work of *Justification* 15.1 and seek the coefficients c_n of the first-order correction to the wavefunction:

$$\psi_0^{(1)}=\sum_n c_n\psi_n^{(0)}$$

When we multiply the equation in λ^1 (rewritten here)

$$\hat{H}^{(1)}\psi_0^{(0)}+\hat{H}^{(0)}\psi_0^{(1)}=E_0^{(0)}\psi_0^{(1)}+E_0^{(1)}\psi_0^{(0)}$$

through by $\psi_k^{(0)*}$, where now $k\neq0$, and integrate over all space, we get

$$\int\psi_k^{(0)*}\hat{H}^{(1)}\psi_0^{(0)}\mathrm{d}\tau+\overbrace{\sum_n c_n\underbrace{\int\psi_k^{(0)*}\hat{H}^{(0)}\psi_n^{(0)}\mathrm{d}\tau}_{}}^{c_kE_k^{(0)}}$$

$E_k^{(0)}$ if $n=k$, 0 otherwise

$$=\overbrace{\sum_n c_nE_0^{(0)}\overbrace{\int\psi_k^{(0)*}\psi_n^{(0)}\mathrm{d}\tau}^{\delta_{kn}}}^{c_kE_0^{(0)}}+E_0^{(1)}\overbrace{\int\psi_k^{(0)*}\psi_0^{(0)}\mathrm{d}\tau}^{0}$$

That is,

$$\int\psi_k^{(0)*}\hat{H}^{(1)}\psi_0^{(0)}\mathrm{d}\tau+c_kE_k^{(0)}=c_kE_0^{(0)}$$

which we can rearrange into

$$c_k=\frac{\int\psi_k^{(0)*}\hat{H}^{(1)}\psi_0^{(0)}\mathrm{d}\tau}{E_0^{(0)}-E_k^{(0)}}$$

Although this expression is for the coefficient c_k, it applies to all coefficients: to get c_n, simply change the index k wherever it occurs to n. The result is eqn 15.5.

Example 15.2 Evaluating the first-order correction to the wavefunction

Once again, use the model described in *Brief illustration* 15.1, this time to evaluate the contribution from the state with $n=3$ to the first-order correction to the wavefunction of the ground state.

Method The first-order correction to the wavefunction is given by the sum in eqn 15.5. The ground state of the particle in the box (denoted $\psi_0^{(0)}$ in the equation) is ψ_1; we seek the contribution from ψ_3. The wavefunctions and energies of the particle in a box are given in Topic 9. All the wavefunctions are real, so the * can be ignored. Use Integral T.6 listed in the *Resource section*.

Answer The contribution from the $n=3$ state to the first-order correction to the wavefunction is given by the coefficient

$$c_3=\frac{\int\psi_3\hat{H}^{(1)}\psi_1\mathrm{d}\tau}{E_1-E_3}$$

The energies of the particle (an electron) in a box are $E_n=n^2h^2/8m_eL^2$, so the denominator is $E_1-E_3=-h^2/m_eL^2$. The numerator is

$$\int \psi_3 \hat{H}^{(1)} \psi_1 \mathrm{d}\tau$$

$$= \int_0^L \overbrace{\left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{3\pi x}{L}\right)}^{\psi_3} \times \overbrace{\left\{-\varepsilon \sin\left(\frac{\pi x}{L}\right)\right\}}^{\hat{H}^{(1)}} \overbrace{\left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right)}^{\psi_1} \mathrm{d}x$$

$$= -\frac{2\varepsilon}{L} \int_0^L \sin\left(\frac{3\pi x}{L}\right) \sin^2\left(\frac{\pi x}{L}\right) \mathrm{d}x$$

$$\overbrace{=}^{\text{Integral T.6}} \left(-\frac{2\varepsilon}{L}\right) \times \left(-\frac{L}{2\pi}\right) \left\{\frac{1}{3} - \frac{1}{2(3+2)} - \frac{1}{2(3-2)}\right\} \{(-1)^3 - 1\}$$

$$= \frac{8\varepsilon}{15\pi}$$

Therefore, the contribution from the $n=3$ state is

$$c_3 = \frac{8\varepsilon/15\pi}{-h^2/m_e L^2} = -\frac{8\varepsilon m_e L^2}{15\pi h^2}$$

and the corrected ground-state wavefunction is

$$\psi_1 = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right) - \frac{8\varepsilon m_e L^2}{15\pi h^2} \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{3\pi x}{L}\right)$$

which, as Fig. 15.3 shows, corresponds to a greater accumulation of amplitude in the middle of the well. Notice that there are no contributions from even-n states because the integral $\int \psi_n \hat{H}^{(1)} \psi_1 \mathrm{d}\tau$ vanishes unless n is odd.

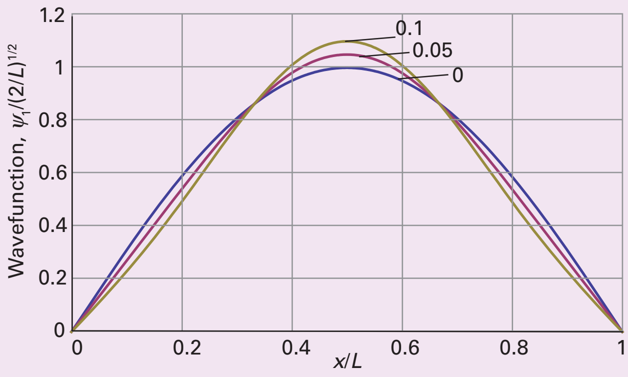

Figure 15.3 The ground-state wavefunction corrected to first order as evaluated in Example 15.2 for different values of $8\varepsilon m_e L^2/15\pi h^2$. Notice the progressive accumulation of amplitude in the middle of the well as the perturbation increases.

Self-test 15.3 Use the same model to evaluate the contribution from the $n=5$ state to the first-order correction to the wavefunction of the ground state.

Answer: $c_5 = -8\varepsilon m_e L^2/315\pi h^2$

15.4 The second-order correction to the energy

The second-order correction to the energy (eqn 15.6), which is derived in the following *Justification*, is rather more complicated, but we can note three important features:

- Because $E_n^{(0)} > E_0^{(0)}$, all the terms in the denominator are negative, and because the numerators are all positive, $E_0^{(2)}$ is negative. That is, the second-order energy correction, but not necessarily the first-order correction, always *lowers* the energy of the ground state.
- The perturbation appears (as its square) in the numerator; so, the stronger the perturbation, the greater the lowering of the ground-state energy.
- If the energy levels of the system are widely spaced, all the denominators are large, so the sum is likely to be small. In this case, the perturbation has little effect on the second-order correction to the energy of the system: the system is 'stiff', and unresponsive to perturbations. The opposite is true when the energy levels lie close together.

Physical interpretation

Justification 15.3 The second-order correction to the energy

We continue the work on the previous two *Justifications*. To isolate the second-order energy correction $E_0^{(2)}$ we multiply both sides of the equation (with terms λ^2):

$$\hat{H}^{(0)} \psi_0^{(2)} + \hat{H}^{(1)} \psi_0^{(1)} = E_0^{(2)} \psi_0^{(0)} + E_0^{(1)} \psi_0^{(1)} + E_0^{(0)} \psi_0^{(2)}$$

by $\psi_0^{(0)*}$ and integrate over all space to obtain

$$\overbrace{\int \psi_0^{(0)*} \hat{H}^{(0)} \psi_0^{(2)} \mathrm{d}\tau}^{E_0^{(0)} \int \psi_0^{(0)*} \psi_0^{(2)} \mathrm{d}\tau} + \int \psi_0^{(0)*} \hat{H}^{(1)} \psi_0^{(1)} \mathrm{d}\tau$$

$$= E_0^{(2)} \overbrace{\int \psi_0^{(0)*} \psi_0^{(0)} \mathrm{d}\tau}^{1} + E_0^{(1)} \int \psi_0^{(0)*} \psi_0^{(1)} \mathrm{d}\tau + E_0^{(0)} \int \psi_0^{(0)*} \psi_0^{(2)} \mathrm{d}\tau$$

In the first term, we have used the hermiticity (Topic 6) of $\hat{H}^{(0)}$. The first and last terms cancel, and we are left with

$$E_0^{(2)} = \int \psi_0^{(0)*} \hat{H}^{(1)} \psi_0^{(1)} \mathrm{d}\tau - E_0^{(1)} \int \psi_0^{(0)*} \psi_0^{(1)} \mathrm{d}\tau$$

We have already found the first-order corrections to the energy and wavefunction (eqns 15.4 and 15.5), so this expression could be regarded as an explicit expression for the second-order energy correction. However, we can go one step further by substituting $\psi_0^{(1)} = \sum_n c_n \psi_n^{(0)}$:

$$E_0^{(2)} = \sum_n c_n \int \psi_0^{(0)\star} \hat{H}^{(1)} \psi_n^{(0)} \mathrm{d}\tau - \overbrace{\sum_n c_n E_0^{(1)} \overbrace{\int \psi_0^{(0)\star} \psi_n^{(0)} \mathrm{d}\tau}^{\delta_{0n}}}^{c_0 E_0^{(1)}}$$

The final term cancels the $n=0$ term in the sum, and we are left with

$$E_0^{(2)} = \sum_{n \neq 0} c_n \int \psi_0^{(0)\star} \hat{H}^{(1)} \psi_n^{(0)} \mathrm{d}\tau$$

Substitution of the expression for c_n (see *Justification* 15.2) produces the final result, eqn 15.6.

Example 15.3 Evaluating the second-order correction to the energy

Continue to use the model in previous Examples and evaluate the contribution from the state with $n=3$ to the second-order correction to the energy of the ground state.

Method The second-order correction to the wavefunction is given by eqn 15.6. The ground state of the particle in the box (denoted $\psi_0^{(0)}$ in the equation) is ψ_1; we seek the contribution from ψ_3. All the integrals needed have been evaluated in Example 15.2.

Answer Using the results in Example 15.2 gives

$$\frac{\left| \int \psi_3 \hat{H}^{(1)} \psi_1 \mathrm{d}\tau \right|^2}{E_1 - E_3} = \frac{(8\varepsilon/15\pi)^2}{-h^2/m_e L^2} = -\frac{64\varepsilon^2 m_e L^2}{225\pi^2 h^2}$$

which corresponds to a lowering of the energy due to the perturbation. We can now collect the first and second-order corrections to the energy and write the perturbed energy of the ground state as

$$E_0 = \frac{h^2}{8m_e L^2} - \frac{8\varepsilon}{3\pi} - \frac{64\varepsilon^2 m_e L^2}{225\pi^2 h^2}$$

Self-test 15.4 Evaluate the contribution from the $n=5$ state to the second-order correction to the energy of the ground state in this model.

Answer: $-64\varepsilon^2 m_e L^2/33075\pi^2 h^2$

Checklist of concepts

☐ 1. In **perturbation theory**, the hamiltonian operator for the problem is separated into a simple model hamiltonian, for which the Schrödinger equation can be solved exactly, and a 'perturbation', which is the difference between the true and model hamiltonians.

☐ 2. In **time-independent perturbation theory**, the perturbation does not vary with time.

☐ 3. The **first-order correction to the energy** can be interpreted as the average value of the effect of the perturbation.

☐ 4. An unperturbed state makes a larger contribution to the first-order correction to the ground-state wavefunction the smaller its energy difference with the unperturbed ground-state energy.

☐ 5. The **second-order correction to the energy** is an average of the perturbation over the perturbed wavefunctions.

☐ 6. The second-order energy correction always lowers the energy of the ground state.

☐ 7. The stronger the perturbation and the smaller the spacings of the energy levels in the unperturbed system, the greater the lowering of the ground-state energy.

Checklist of equations

Property	Equation	Comment	Equation number
Division of the hamiltonian	$\hat{H}=\hat{H}^{(0)}+\hat{H}^{(1)}$	$\hat{H}^{(1)}$ is the perturbation	15.1
Expansion of the energy	$E=E^{(0)}+E^{(1)}+E^{(2)}+\ldots$	$E^{(N)}$ is the Nth-order energy correction	15.2
Expansion of the wavefunction	$\psi=\psi^{(0)}+\psi^{(1)}+\psi^{(2)}+\ldots$	$\psi^{(N)}$ is the Nth-order correction to the wavefunction	15.3
First-order energy correction	$E_0^{(1)}=\int\psi_0^{(0)*}\hat{H}^{(1)}\psi_0^{(0)}\,\mathrm{d}\tau$	Ground-state energy	15.4
Wavefunction corrected to first order	$\psi_0=\psi_0^{(0)}+\sum_{n\neq0}c_n\psi_n^{(0)}$ $c_n=\left(\int\psi_n^{(0)*}\hat{H}^{(1)}\psi_0^{(0)}\,\mathrm{d}\tau\right)/\left(E_0^{(0)}-E_n^{(0)}\right)$	Ground state	15.5
Second-order energy correction	$E_0^{(2)}=\sum_{n\neq0}\left\|\int\psi_n^{(0)*}\hat{H}^{(1)}\psi_0^{(0)}\,\mathrm{d}\tau\right\|^2/\left(E_0^{(0)}-E_n^{(0)}\right)$	Ground-state energy	15.6

TOPIC 16

Transitions

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➤ Why do you need to know this material?

One of the most important ways of exploring the structure of matter is spectroscopy, in which the radiation absorbed, emitted, or scattered by molecules is analysed. To understand the processes involved, we need to know how wavefunctions change when molecules are exposed to perturbations of various kinds, such as an oscillating electromagnetic field or the impact of a collision.

➤ What is the key idea?

A selection rule results from analysis of the expression for the transition rate, which is proportional to the square of the strength of the perturbation.

➤ What do you need to know already?

You need to be familiar with the general principles of quantum mechanics (Topics 5–7) and the Schrödinger equation, as well as the basic concepts of perturbation theory (Topic 15). An example draws on information about the harmonic oscillator (Topic 12).

When the potential energy that occurs in a hamiltonian is independent of time the wavefunctions are solutions of the time-independent Schrödinger equation (Topic 6). However, that doesn't mean that they do not vary with time. In fact, if the energy corresponding to a wavefunction $\psi(\boldsymbol{r})$ is E, then the time-dependent wavefunction is

$$\psi(\boldsymbol{r},t)=\psi(\boldsymbol{r})\mathrm{e}^{-\mathrm{i}Et/\hbar} \qquad \text{Stationary-state wavefunction} \qquad (16.1)$$

and, because $\mathrm{e}^{-\mathrm{i}Et/\hbar}=\mathrm{e}^{-\mathrm{i}(E/\hbar)t}=\cos(Et/\hbar)-\mathrm{i}\sin(Et/\hbar)$ (Euler's formula, *Mathematical background* 3), the time-dependent wavefunction oscillates in time with a frequency $E/\hbar$. Although the wavefunction oscillates, the physical observable it represents, the probability density, does not, for

$$\Psi(\boldsymbol{r},t)^{\star}\Psi(\boldsymbol{r},t)=(\psi(\boldsymbol{r})^{\star}\mathrm{e}^{\mathrm{i}Et/\hbar})(\psi(\boldsymbol{r})\mathrm{e}^{-\mathrm{i}Et/\hbar})=\psi(\boldsymbol{r})^{\star}\psi(\boldsymbol{r}).$$

which is independent of time. It is for this reason that $\Psi(\boldsymbol{r},t)$ describes a **stationary state**, a state with a probability density that persists unchanged in time.

Matters are very different when the potential energy varies with time, either because an external influence, a perturbation, is switched on or because it is always present but changing with time, as is the case when an atom or molecule is exposed to an electromagnetic field. The states are no longer stationary, and a molecule in one state might be forced into another state. That is, **transitions,** changes of state, occur in the presence of time-dependent perturbations.

Time-dependent perturbation theory provides a technique for analysing transitions between states, allowing us to identify the conditions under which transitions can occur and to develop expressions for their rates. Consequently, our discussion begins with time-dependent perturbation theory and then describes one of its most important applications, an initial exploration of the absorption and emission of electromagnetic radiation. This material is fundamental to the detailed account of atomic and molecular spectra.

16.1 Time-dependent perturbation theory

To predict the outcome of the presence of a time-dependent perturbation we have to solve the **time-dependent Schrödinger equation**:

$$\hat{H}(t)\Psi(\boldsymbol{r},t)=\mathrm{i}\hbar\frac{\partial\Psi(\boldsymbol{r},t)}{\partial t}$$

Time-dependent Schrödinger equation (16.2)

(a) The general procedure

As in Topic 15 we use a perturbation procedure to find approximate solutions, and begin by supposing that the hamiltonian can be partitioned into a simple, solvable part and a perturbation, which now is taken to be time-dependent:

$$\hat{H}=\hat{H}^{(0)}+\hat{H}^{(1)}(t) \tag{16.3a}$$

For instance, when a molecule is exposed to an electromagnetic field of frequency ω and strength $\mathcal{E}$ parallel to the z-direction, the perturbation is

$$\hat{H}^{(1)}(t)=-\hat{\mu}_z\mathcal{E}\cos\omega t$$

Oscillating electric field Time-dependent perturbation (16.3b)

where $\hat{\mu}_z$ is the z-component of the **dipole moment operator** $\hat{\mu}$ and is proportional to z. The underlying classical idea is that for an atom or molecule to be able to interact with the electromagnetic field and absorb or create a photon of a specific frequency, it must possess, at least transiently, a dipole oscillating at that frequency.

As in the case of time-independent perturbation theory, we suppose that the solutions of eqn 16.2 can be expressed as linear combinations of the eigenfunctions of the unperturbed hamiltonian, the only difference being that the coefficients are allowed to vary with time. For instance, although initially an electron in a hydrogenic atom might be in a 1s orbital, as time goes on the probability increases that it will be found in a 2p orbital, so the coefficient of that orbital grows with time while the coefficient of the 1s orbital decreases. In general, we write

$$\Psi(\boldsymbol{r},t)=\sum_n c_n(t)\Psi_n^{(0)}(\boldsymbol{r},t)=\sum_n c_n(t)\psi_n^{(0)}(\boldsymbol{r})\mathrm{e}^{-\mathrm{i}E_n^{(0)}t/\hbar}$$

where, as usual, the $\psi_n^{(0)}(\boldsymbol{r})$ are the eigenfunctions of $\hat{H}^{(0)}$ and the $E_n^{(0)}$ are their energies.

The challenge is to find explicit expressions for the coefficients. We do not give the details here,[1] but it turns out that if we confine our attention to the first-order effect of the perturbation, then the coefficients of all the wavefunctions other than the one occupied initially, which we take to be $\psi_0^{(0)}(\boldsymbol{r})$ (for instance, the 1s orbital in the previous example), is given by

$$c_n(t)=\frac{1}{\mathrm{i}\hbar}\int_0^t H_{n0}^{(1)}(t)\mathrm{e}^{\mathrm{i}\omega_{n0}t}\mathrm{d}t$$

First-order time-dependent perturbation theory Coefficient of initially unoccupied state *n* (16.4a)

where

$$H_{n0}^{(1)}(t)=\int\psi_n^{(0)*}\hat{H}^{(1)}(t)\psi_0^{(0)}\mathrm{d}\tau \tag{16.4b}$$

We have supposed that the perturbation is applied at $t=0$ and have written $\omega_{n0}=(E_n^{(0)}-E_0^{(0)})/\hbar$. All it is necessary to do, therefore, is to introduce the form of the perturbation and evaluate these integrals, one over space (in eqn 16.4b) and the other over time (after substituting the outcome into eqn 16.4a).

A perturbation that is suddenly applied is like an impact and can be expected to knock the system into a variety of states; one that is applied slowly and grows to its final value produces a less violent effect and, well after it has been switched on, gives results equivalent to those obtained from time-independent perturbation theory where the perturbation is always present. Even oscillating perturbations are often best treated as being switched on slowly, for a sudden application will introduce transient responses that are hard to treat mathematically.

Example 16.1 Using time-dependent perturbation theory for a slowly switched perturbation

To explore the slowly switched case, write $\hat{H}^{(1)}(t)=\hat{H}^{(1)}(1-\mathrm{e}^{-t/\tau_0})$ where the time constant τ_0 is very long (Fig. 16.1). Show that at times $t >> \tau_0$ (at which the perturbation has reached the constant value $\hat{H}^{(1)}$), the square modulus of the coefficient $c_n(t)$ is the same as we obtain from time-independent perturbation theory (Topic 15).

Method Use eqn 16.4 to evaluate $c_n(t)$ and compare its square modulus to that of eqn 15.5 from time-independent perturbation theory. We use τ_0 for the time constant to avoid confusion with the τ in the volume element, $\mathrm{d}\tau$.

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[1] For a full account of the solution, see our *Molecular quantum mechanics*, Oxford University Press (2011).

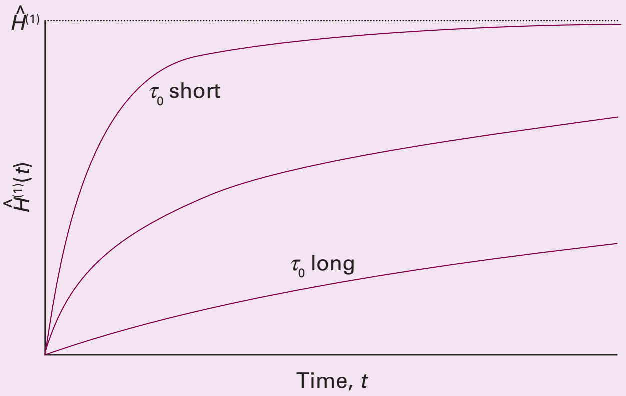

Figure 16.1 The time dependence of a slowly switched perturbation. A large value of τ_0 corresponds to very slow switching.

Answer Substitution of $\hat{H}^{(1)}(t)=\hat{H}^{(1)}(1-\mathrm{e}^{-t/\tau_0})$ into eqn 16.4b gives

$$H^{(1)}_{n0}(t)=\int\psi_n^{(0)*}\hat{H}^{(1)}(1-\mathrm{e}^{-t/\tau_0})\psi_0^{(0)}\mathrm{d}\tau$$

$$=(1-\mathrm{e}^{-t/\tau_0})\overbrace{\int\psi_n^{(0)*}\hat{H}^{(1)}\psi_0^{(0)}\mathrm{d}\tau}^{H^{(1)}_{n0}}$$

$$=(1-\mathrm{e}^{-t/\tau_0})H^{(1)}_{n0}$$

Now substitute this expression into eqn 16.4a, recognizing that $H^{(1)}_{n0}$ is independent of time:

$$c_n(t)=\frac{H^{(1)}_{n0}}{\mathrm{i}\hbar}\int_0^t(1-\mathrm{e}^{-t/\tau_0})\mathrm{e}^{\mathrm{i}\omega_{n0}t}\mathrm{d}t$$

$$=\frac{H^{(1)}_{n0}}{\mathrm{i}\hbar}\int_0^t(\mathrm{e}^{\mathrm{i}\omega_{n0}t}-\mathrm{e}^{-(1/\tau_0-\mathrm{i}\omega_{n0})t})\mathrm{d}t$$

Now use

$$\int_0^t\mathrm{e}^{\mathrm{i}\omega_{n0}t}\mathrm{d}t=\frac{\mathrm{e}^{\mathrm{i}\omega_{n0}t}-1}{\mathrm{i}\omega_{n0}}\quad\text{and}\quad\int_0^t\mathrm{e}^{-(1/\tau_0-\mathrm{i}\omega_{n0})t}\mathrm{d}t=-\frac{\mathrm{e}^{-(1/\tau_0-\mathrm{i}\omega_{n0})t}-1}{1/\tau_0-\mathrm{i}\omega_{n0}}$$

At this point, we suppose that the perturbation is switched slowly, in the sense that $\tau_0>>1/\omega_{n0}$ so that the (blue) $1/\tau_0$ in the second denominator can be ignored. Note that the assumption $\tau_0>>1/\omega_{n0}$ provides a quantitative criterion of 'slow'. We also suppose that we are interested in the coefficients long after the perturbation has settled down into its final value, when $t>>\tau_0$, so that the (blue) exponential in the second numerator is close to zero and can be ignored. Under these conditions,

$$c_n(t)=-\frac{\mathrm{e}^{\mathrm{i}\omega_{n0}t}}{\hbar\omega_{n0}}H^{(1)}_{n0}$$

Now we recognize that $\hbar\omega_{n0}=E_n^{(0)}-E_0^{(0)}$, which gives

$$c_n(t)=-\frac{\mathrm{e}^{\mathrm{i}\omega_{n0}t}H^{(1)}_{n0}}{E_n^{(0)}-E_0^{(0)}}$$

When we form the square modulus of c_n, the factor $\mathrm{e}^{\mathrm{i}\omega_{n0}t}$ disappears (its square modulus is 1) and we obtain a result identical to the square modulus of the coefficient in eqn 15.5.

Self-test 16.1 What is the form of $c_n(t)$ if a system is exposed to the oscillating perturbation $\hat{H}^{(1)}(t)=2\hat{H}^{(1)}\cos\omega t=\hat{H}^{(1)}(\mathrm{e}^{\mathrm{i}\omega t}+\mathrm{e}^{-\mathrm{i}\omega t})$?

Answer: $(1/\mathrm{i}\hbar)H^{(1)}_{n0}\{(\mathrm{e}^{\mathrm{i}(\omega_{n0}+\omega)t}-1)/[\mathrm{i}(\omega_{n0}+\omega)]+(\mathrm{e}^{\mathrm{i}(\omega_{n0}-\omega)t}-1)/[\mathrm{i}(\omega_{n0}-\omega)]\}$

The probability that at time t the perturbation has induced a transition from the initial state $\psi_0^{(0)}$ to the state $\psi_n^{(0)}$ is

$$P_n(t)=|c_n(t)|^2\qquad\text{Transition probability}\qquad(16.5)$$

The **transition rate**, w, is the rate of change of the probability of being in the final state $\psi_n^{(0)}$ due to transitions from the initial state $\psi_0^{(0)}$:

$$w_n(t)=\frac{\mathrm{d}P_n}{\mathrm{d}t}\qquad\text{Transition rate}\qquad(16.6)$$

We can now develop an important relation between the transition rate and the strength of the perturbation. We consider time-dependent perturbations of the form

$$\hat{H}^{(1)}(t)=\hat{H}^{(1)}f(t)$$

where all time dependence is contained in $f(t)$, as we illustrated in a specific case in Example 16.1 and we have also seen for the perturbation of eqn 16.3b, $\hat{H}^{(1)}=-\hat{\mu}_z\mathcal{E}$ and $f(t)=\cos\omega t$. Because the probability, P_n, is proportional to the square modulus of the coefficient, c_n, of the state (eqn 16.5) and the coefficient is itself proportional to the magnitude of the perturbation (eqn 16.4), we conclude that the transition rate, a time derivative, is proportional to the square modulus of the strength of the perturbation:

$$w_n(t)\propto|H^{(1)}_{n0}|^2=\left|\int\psi_n^{(0)*}\hat{H}^{(1)}\psi_0^{(0)}\mathrm{d}\tau\right|^2\qquad\textit{Oscillating electric field}\qquad\text{Transition rate}\qquad(16.7)$$

(b) Oscillating perturbations and spectroscopic transitions

When the perturbation has the form given in eqn 16.3b, the transition rate is of the form

$$w_n(t) \propto \mathcal{E}^2 \left|\int \psi_n^{(0)*}\hat{\mu}_z\psi_0^{(0)}\,\mathrm{d}\tau\right|^2 \qquad \text{Transition rate} \qquad (16.8\text{a})$$

which includes a factor of the form

$$\mu_{z,n0} = \int \psi_n^{(0)*}\hat{\mu}_z\psi_0^{(0)}\,\mathrm{d}z \qquad \text{Transition dipole moment } (z\text{-component}) \qquad (16.8\text{b})$$

Such an integral is called a **transition dipole moment**. It is a measure of the electric dipole moment associated with the migration of charge from the initial state to the final state. The size of the transition dipole can be regarded as a measure of the charge redistribution that accompanies a transition: a transition is active (and generates or absorbs photons) only if the accompanying charge redistribution is dipolar (Fig. 16.2). Clearly, if there is no such dipole moment, then $w_n = 0$ and no transition occurs. If the transition dipole moment is not zero, then $w_n \neq 0$ and we infer that a transition to n has occurred. A transition is **forbidden** if the transition dipole moment is zero; it is **allowed** if any one of the components of the transition dipole moment (there are, in the most general case, also components $\mu_{x,n0}$ and $\mu_{y,n0}$) is nonzero.

To summarize the discussion so far, we interpret eqn 16.8 as follows: the *intensity of absorption or emission of radiation in a transition*, which is proportional to the transition rate, *is proportional to the square modulus of the transition dipole moment*. A detailed study of the transition dipole moment leads to the **specific selection rules** that express the allowed transitions in terms of the changes in quantum numbers. A **gross selection rule** specifies the general features a molecule must have if it is to have a spectrum of a given kind. Selection rules, and others like it for other types of transition, are explained in relevant Topics (see, for example, Topics 42–44).

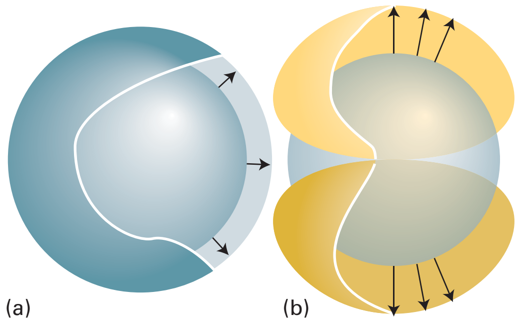

Figure 16.2 (a) When a 1s electron becomes a 2s electron, there is a spherical migration of charge. There is no dipole moment associated with this migration of charge, so this transition is electric-dipole forbidden. (b) In contrast, when a 1s electron becomes a 2p electron, there is a dipole associated with the charge migration; this transition is allowed.

Example 16.2 Analysing spectroscopic transitions of a harmonic oscillator

Suppose a hydrogen atom adsorbed on the surface of a gold nanoparticle undergoes harmonic motion perpendicular to the surface. Can the absorption of electromagnetic radiation result in a transition from the ground vibrational state of the oscillator to the first excited vibrational state?

Method The harmonic oscillator wavefunctions are given in Topic 12; they depend on the displacement, z, of the oscillator from its equilibrium position. Consider the component of the electromagnetic radiation along the axis perpendicular to the surface (that is, along z). Proceed to determine if the transition dipole moment $\int \psi_1^{(0)*}\mu_z\psi_0^{(0)}\mathrm{d}z$ is nonzero; $\mu_z \propto z$. Use Integral G.3 listed in the *Resource section*.

Answer The ground-state and first excited-state harmonic oscillator wavefunctions are the real functions

$$\psi_0^{(0)} = N_0\mathrm{e}^{-z^2/2\alpha^2} \qquad \psi_1^{(0)} = N_1\left(\frac{2}{\alpha}\right)z\mathrm{e}^{-z^2/2\alpha^2}$$

where N_0 and N_1 are normalization constants and $\alpha = (\hbar^2/\mu k_\mathrm{f})^{1/4}$ with μ and k_f the effective mass and force constant, respectively, of the oscillator. The transition dipole moment is therefore

$$\mu_{z,10} \propto \int_{-\infty}^{\infty}\psi_1^{(0)}z\psi_0^{(0)}\mathrm{d}z = \frac{2N_0N_1}{\alpha}\int_{-\infty}^{\infty}z^2\mathrm{e}^{-z^2/\alpha^2}\mathrm{d}z$$
$$= \frac{4N_0N_1}{\alpha}\int_0^{\infty}z^2\mathrm{e}^{-z^2/\alpha^2}\mathrm{d}z \overset{\text{Integral G.3}}{=} N_0N_1\alpha^2\pi^{1/2}$$

Because the integral is not zero, the spectroscopic transition is allowed.

Self-test 16.2 Can the absorption of electromagnetic radiation result in a transition from the ground state of the harmonic oscillator to the second excited vibrational state? (*Hint*: Consider the symmetry of the integrand in the transition dipole moment.)

Answer: No; the integrand $\psi_2^{(0)}z\psi_0^{(0)}$ is an odd function of z

(c) The energy of time-varying states

The energy of a time-varying state (not a stationary state) cannot be specified exactly. To see why this is so, suppose that the wavefunction has the form

$$\Psi(\boldsymbol{r},t)=\psi(\boldsymbol{r})\mathrm{e}^{-\mathrm{i}Et/\hbar}\times\mathrm{e}^{-t/2\tau}$$

so that it oscillates and decays and the probability density decays exponentially with a time constant τ. An exponential function can be expressed as a superposition of sine and cosine functions, and therefore as a superposition of functions of the form $\mathrm{e}^{-\mathrm{i}\varepsilon t/\hbar}$ with a wide range of values of ε. Therefore, the decaying function has the form

$$\Psi(\boldsymbol{r},t)=\psi(\boldsymbol{r})\sum_{\varepsilon}c_{\varepsilon}\mathrm{e}^{-\mathrm{i}(E+\varepsilon)t/\hbar}$$

The probability that the energy $E+\varepsilon$ is measured is proportional to $|c_{\varepsilon}|^2$, and it is no longer possible to say with certainty that the energy of the decaying state is E. Indeed, the shorter the time constant τ, the **lifetime** of the state, the wider the spread of energies that must be included in the sum, as is illustrated in Fig. 16.3, where we have shown how a decaying exponential function with various decay rates can be expressed as a superposition of cosine functions. The relation between the lifetime and the spread of energies ΔE is summarized by the expression

$$\Delta E\approx\frac{\hbar}{\tau}$$

Energy – time uncertainty (16.9)

This expression is reminiscent of the Heisenberg uncertainty principle (Topic 8), and consequently it is often referred to as 'the energy–time uncertainty principle'. However, its derivation is quite different, and a better term is simply **energy–time uncertainty**. We see in Topic 40 that it plays an important role in governing the widths of spectral lines.

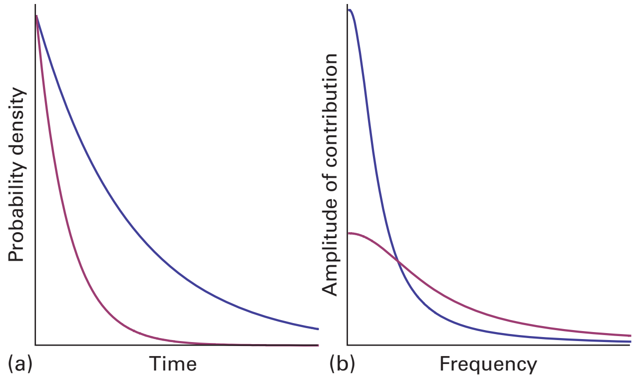

Figure 16.3 (a) Two wavefunctions that decay at different rates; the purple curve has a faster decay rate and shorter lifetime than the blue curve. (b) The spread of frequencies (and therefore energies) that when superimposed re-creates the decaying wavefunctions; the state with the shorter lifetime has a wider spread of contributions (purple).

Brief illustration 16.1 Energy–time uncertainty

Consider an excited electronic state which has a lifetime of 25 ns. The state corresponds to a spread of energies

$$\Delta E\approx\frac{\hbar}{\tau}=\frac{1.055\times10^{-34}\,\mathrm{J\,s}}{25\times10^{-9}\,\mathrm{s}}=4.2\times10^{-27}\,\mathrm{J}$$

or, by dividing by hc, to the wavenumber $2.1\times10^{-4}\,\mathrm{cm}^{-1}$.

Self-test 16.3 Determine the lifetime of a short-lived excited state that corresponds to a range of wavenumbers $1.0\times10^{-2}\,\mathrm{cm}^{-1}$.

Answer: 530 ps

16.2 The absorption and emission of radiation

The rates of transitions between states induced by an electromagnetic field (or any other kind of perturbation) can be calculated from eqns 16.4–16.6 by inserting the appropriate perturbation. However, Einstein was able to carry out an analysis that led to a surprising conclusion: transitions took place even in the apparent absence of a perturbation!

His argument went as follows. First, he recognized that the transition from a low-energy state to one of higher energy that is driven by the electromagnetic field oscillating at the transition frequency is called **stimulated absorption**. This transition rate is proportional to $\mathcal{E}^2$ (eqn 16.8a) and therefore to the intensity of the incident radiation. Therefore, the more intense the incident radiation, the stronger is the absorption by the sample (Fig. 16.4). Einstein wrote this transition rate as

$$w_{\mathrm{f}\leftarrow\mathrm{i}}=B_{\mathrm{fi}}\rho$$

Stimulated absorption Transition rate (16.10)

The constant B_{fi} is the **Einstein coefficient of stimulated absorption** and $\rho\mathrm{d}\nu$ is the energy density of radiation in the frequency range from ν to $\nu+\mathrm{d}\nu$, where ν is the frequency of the transition. For instance, when the atom or molecule is exposed to black-body radiation from a source of temperature T, ρ is given by the Planck distribution (Topic 4):

$$\rho=\frac{8\pi h\nu^3/c^3}{\mathrm{e}^{h\nu/kT}-1}$$

Planck distribution (16.11)

At this stage B_{fi} as an empirical parameter that characterizes the transition: if it is large, then a given intensity of incident radiation will induce transitions strongly and the sample will be strongly absorbing. The **total rate of absorption**, $W_{\mathrm{f}\leftarrow\mathrm{i}}$, is the

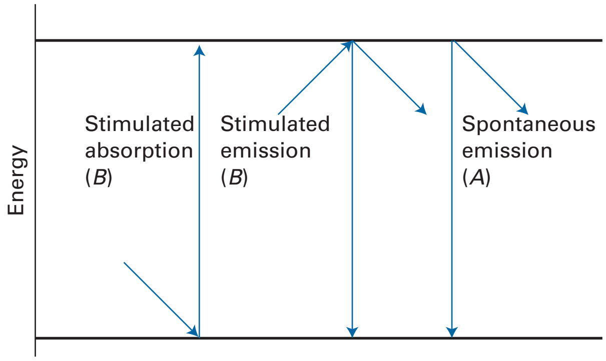

Figure 16.4 The transitions analysed by Einstein in his theory of stimulated and spontaneous processes.

transition rate of a single molecule multiplied by the number of molecules N_i in the lower state:

$$W_{f\leftarrow i}=N_i w_{f\leftarrow i}=N_i B_{fi}\rho \qquad \text{Total absorption rate} \qquad (16.12)$$

Einstein considered that the radiation was also able to induce the molecule in the upper state to undergo a transition to the lower state, and hence to generate a photon of frequency ν. Thus, he wrote the rate of this **stimulated emission** as

$$w_{f\to i}=B_{if}\rho \qquad \textit{Stimulated emission} \quad \text{Transition rate} \qquad (16.13)$$

where B_{if} is the **Einstein coefficient of stimulated emission**. This coefficient is in fact equal to the coefficient of stimulated absorption, as we shall see below. Moreover, only radiation of the same frequency as the transition can stimulate an excited state to fall to a lower state.

At this point, it is tempting to suppose that the total rate of emission is this individual rate multiplied by the number of molecules in the upper state, N_f, and therefore to write $W_{f\to i}=N_f B_{if}\rho$. But here we encounter a problem: at equilibrium (as in a black-body container), the rate of emission is equal to the rate of absorption, so $N_i B_{fi}\rho=N_f B_{if}\rho$ and therefore, since $B_{if}=B_{fi}$, $N_i=N_f$. The conclusion that the populations must be equal at equilibrium is in conflict with another very fundamental conclusion, that the ratio of populations is given by the Boltzmann distribution (Topics 2 and 51).

Einstein realized that to bring the analysis of transition rates into alignment with the Boltzmann distribution there must be another route for the upper state to decay into the lower state, and wrote

$$w_{f\to i}=A+B_{if}\rho \qquad \text{Emission rate} \qquad (16.14)$$

The constant A is the **Einstein coefficient of spontaneous emission**. The **total rate of emission,** $W_{f\to i}$, is therefore

$$W_{f\to i}=N_f w_{f\to i}=N_f(A+B_{if}\rho) \qquad \text{Total emission rate} \qquad (16.15)$$

At thermal equilibrium, N_i and N_f do not change over time. This condition is reached when the total rate of emission and absorption are equal:

$$N_i B_{fi}\rho=N_f(A+B_{if}\rho) \qquad \text{Thermal equilibrium} \qquad (16.16)$$

and therefore

$$\rho=\frac{N_f A}{N_i B_{fi}-N_f B_{if}} \overset{\text{divide by } N_f B_{fi}}{\overbrace{=}} \frac{A/B_{fi}}{N_i/N_f-B_{if}/B_{fi}}=\frac{A/B_{fi}}{e^{h\nu/kT}-B_{if}/B_{fi}} \qquad (16.17)$$

We have used the Boltzmann expression (Topic 2) for the ratio of populations of the upper state (of energy E_f) and lower state (of energy E_i):

$$\frac{N_f}{N_i}=e^{-\overbrace{(E_f-E_i)}^{h\nu}/kT}$$

This result has the same form as the Planck distribution (eqn 16.11), which describes the radiation density at thermal equilibrium. Indeed when we compare eqns 16.11 and 16.17, we can conclude that $B_{if}=B_{fi}$ and that

$$A=\left(\frac{8\pi h\nu^3}{c^3}\right)B \qquad (16.18)$$

The important point about eqn 16.18 is that it shows that the relative importance of spontaneous emission increases as the cube of the transition frequency and therefore that it is therefore potentially of great importance at very high frequencies. Conversely, spontaneous emission can be ignored at low transition frequencies, in which case intensities of those transitions can be discussed in terms of stimulated emission and absorption.

Brief illustration 16.2 The Einstein coefficients

For a transition in the X-ray region of the electromagnetic spectrum (corresponding to an excitation of a core electron in a molecule), a typical wavelength is 100 pm, corresponding to a frequency of $3.00\times10^{18}\,s^{-1}$. The ratio of the Einstein coefficients of spontaneous and stimulated emission is

$$\frac{A}{B}=\frac{8\pi\times(6.626\times10^{-34}\,J\,s)\times(3.00\times10^{18}\,s^{-1})^3}{(2.998\times10^{8}\,m\,s^{-1})^3}=1.67\times10^{-2}\,kg\,m^{-1}\,s$$

Self-test 16.4 Calculate the ratio of the Einstein coefficients of spontaneous and stimulated emission for a transition in the microwave region of the electromagnetic spectrum with wavelength 1.0 cm.

Answer: $A/B=1.7\times10^{-26}\,kg\,m^{-1}\,s$

The presence of so-called spontaneous emission, in which, contrary to our earlier discussion, a transition occurs in the absence of a perturbation, might seem paradoxical. But in fact there is an unseen perturbation at work. The electromagnetic field can be modelled as a collection of harmonic oscillators, one for each of the infinite range of frequencies that can be stimulated. This is the basis of the original derivation of Planck's expression for the density of states. Then, the presence of radiation is equivalent to the excitation of oscillators of the appropriate frequency, and the absence of that frequency in the radiation corresponds to the oscillator being in its ground state. But an oscillator has a zero-point energy (Topic 12), and is never truly still. Therefore, even in the absence of observable radiation, the electromagnetic fields are oscillating. It is these 'unseen' zero-point oscillations of the electromagnetic field that act as a perturbation and drive the so-called 'spontaneous' emission of radiation.

Checklist of concepts

☐ 1. A **stationary state** corresponds to a wavefunction with a probability density that does not change with time.
☐ 2. **Transitions** are changes in the state of the system; they often occur in the presence of time-dependent perturbations.
☐ 3. In the classical picture, for an atom or molecule to be able to interact with the electromagnetic field and absorb or create a photon of a specific frequency, it must possess, at least transiently, a dipole oscillating at that frequency.
☐ 4. The **transition dipole moment** is a measure of the electric dipole moment associated with the migration of charge from the initial state to the final state.
☐ 5. A transition is **forbidden** if the transition dipole moment is zero; it is **allowed** if any one of the components of the transition dipole moment is nonzero.
☐ 6. The **transition rate** is proportional to the square modulus of the strength of the perturbation.
☐ 7. The **intensity** of absorption or emission of radiation in a transition is proportional to the square modulus of the transition dipole moment.
☐ 8. A **specific selection rule** expresses the allowed transitions in terms of the changes in quantum numbers.
☐ 9. A **gross selection rule** specifies the general features a molecule must have if it is to have a spectrum of a given kind.
☐ 10. The shorter the **lifetime** of a state, the wider is the spread of energies to which the state corresponds.
☐ 11. A transition from a low-energy state to one of higher energy that is driven by an oscillating electromagnetic field is called **stimulated absorption.**
☐ 12. A transition driven from high energy to low energy is called **stimulated emission**.
☐ 13. The relative importance of spontaneous emission increases as the cube of the transition frequency.

Checklist of equations

Property	Equation	Comment	Equation number
Time-dependent Schrödinger equation	$\hat{H}(t)\Psi(\boldsymbol{r},t)=\mathrm{i}\hbar\partial\Psi(\boldsymbol{r},t)/\partial t$		16.2
Perturbation due to oscillating electric field	$\hat{H}^{(1)}(t)=-\hat{\mu}_z\mathcal{E}\cos\omega t$	$\hat{\mu}_z$ is z-component of dipole moment operator	16.3b
Coefficient of initially unoccupied state n	$c_n(t)=(1/\mathrm{i}\hbar)\int_0^t H_{n0}^{(1)}(t)\mathrm{e}^{\mathrm{i}\omega_{n0}t}\mathrm{d}t$ $H_{n0}^{(1)}(t)=\int\psi_n^{(0)*}\hat{H}^{(1)}(t)\psi_0^{(0)}\mathrm{d}\tau$	First-order time-dependent perturbation theory	16.4
Transition probability	$P_n(t)=\lvert c_n(t)\rvert^2$		16.5
Transition rate	$w_n(t)=\mathrm{d}P_n/\mathrm{d}t$		16.6
Transition dipole moment	$\mu_{z,n0}=\int\psi_n^{(0)*}\breve{\mu}_z\psi_0^{(0)}\mathrm{d}z$	z-component	16.8b
Energy–time uncertainty	$\Delta E\approx\hbar/\tau$	τ is the lifetime of the state	16.9
Planck distribution	$\rho=(8\pi h\nu^3/c^3)/(\mathrm{e}^{h\nu/kT}-1)$		16.11
Ratio of Einstein coefficients of spontaneous and stimulated emission	$A/B=8\pi h\nu^3/c^3$	Einstein coefficients of stimulated emission and absorption are equal	16.18

Focus 4 on Approximation methods

Topic 15 Time-independent perturbation theory

Discussion questions

15.1 Identify the two different forms of perturbation theory and explain why they are useful.

15.2 Describe what is meant by 'first-order' and 'second-order' corrections in perturbation theory.

15.3 Provide a physical interpretation for the expression for the first-order correction in the wavefunction.

15.4 Provide a physical interpretation for the expression for the second-order correction in the energy.

Exercises

15.1(a) Calculate the first-order correction to the energy of an electron in a one-dimensional nanoparticle modelled as a particle in a box when the perturbation is $V(x) = -\varepsilon \sin(2\pi x/L)$ and $n = 1$.
15.1(b) Calculate the first-order correction to the energy of an electron in a one-dimensional nanoparticle modelled as a particle in a box when the perturbation is $V(x) = -\varepsilon \sin(3\pi x/L)$ and $n = 1$.

15.2(a) Calculate the first-order correction to the energy of a particle in a box when the perturbation is $V(x) = -\varepsilon \cos(2\pi x/L)$ and $n = 1$.
15.2(b) Calculate the first-order correction to the energy of a particle in a box when the perturbation is $V(x) = -\varepsilon \cos(3\pi x/L)$ and $n = 1$.

15.3(a) Suppose that the 'floor' of a one-dimensional box slopes up from $x = 0$ to ε at $x = L$. Calculate the first-order effect on the energy of the state $n = 1$.
15.3(b) Suppose that the 'floor' of a one-dimensional box slopes up from $x = 0$ to ε at $x = L$. Calculate the first-order effect on the energy of the state $n = 2$.

15.4(a) Does the vibrational frequency of an O–H bond depend on whether it is horizontal or vertical at the surface of the Earth? Suppose that a harmonic oscillator of mass m is held vertically, so that it experiences a perturbation $V(x) = mgx$, where g is the acceleration of free fall. Calculate the first-order correction to the energy of the ground state.
15.4(b) Repeat the previous exercise to find the change in excitation energy from $v = 1$ to $v = 2$ in the presence of the perturbation.

15.5(a) Evaluate the second-order correction to the energy of the harmonic oscillator for the perturbation described in Exercise 15.4(a). *Hint*: You will find that there is only one term that contributes to the sum in eqn 15.6.
15.5(b) Evaluate the second-order correction to the energy of a particle in a one-dimensional square well for the perturbation described in Exercise 15.2(a). *Hint*: The only term that contributes to the sum in eqn 15.6 is $n = 3$.

Problems

15.1 Suppose that the floor of a one-dimensional nanoparticle has an imperfection that can be represented by a small step in the potential energy, as in Fig. F4.1. (a) Write a general expression for the first-order correction to the ground-state energy, $E_0^{(1)}$. (b) Evaluate the energy correction for $a = L/10$ (so the blip in the potential occupies the central 10 per cent of the well), with $n = 1$.

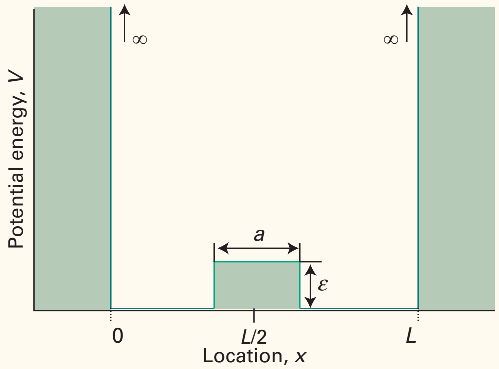

Figure F4.1 The definition of the potential energy in Problem 15.1.

15.2 We normally think of the one-dimensional well as being horizontal. Suppose it is vertical; then the potential energy of the particle depends on x because of the presence of the gravitational field. Calculate the first-order correction to the zero-point energy, and evaluate it for an electron in a box on the surface of the Earth. Account for the result. *Hint*: The energy of the particle depends on its height as mgh, where $g = 9.81\ \text{m s}^{-2}$. Because g is so small, the energy correction is small; but it would be significant if the box were near a very massive star.

15.3 Calculate the second-order correction to the energy for the system described in Problem 15.2 and calculate the ground-state wavefunction. Account for the shape of the distortion caused by the perturbation. *Hint*: The integrals required are listed in the *Resource section*.

15.4 The vibrations of molecules are only approximately harmonic because the energy of a bond is not exactly parabolic. Calculate the first-order correction to the energy of the ground state of a harmonic oscillator subjected to an anharmonic potential of the form $ax^3 + bx^4$, where a and b are small (anharmonicity) constants. Consider the three cases in which the anharmonic perturbation is present: (a) during bond expansion ($x \geq 0$) and compression ($x \leq 0$); (b) during expansion only; (c) during compression only.

Topic 16 Transitions

Discussion questions

16.1 What are likely to be the differences in outcome of the application of sudden and slowly switched perturbations?

16.2 What is the physical interpretation of a selection rule?

16.3 Identify some perturbations that are likely to be encountered in the discussion of the properties of molecules.

Exercises

16.1(a) Calculate the ratio of the Einstein coefficients of spontaneous and stimulated emission, A and B, for transitions with the following characteristics: (a) 70.8 pm X-rays; (b) 500 nm visible light; (c) 3000 cm^{-1} infrared radiation.

16.1(b) Calculate the ratio of the Einstein coefficients of spontaneous and stimulated emission, A and B, for transitions with the following characteristics: (a) 500 MHz radiofrequency radiation; (b) 3.0 cm microwave radiation.

Problem

16.1 The motion of a pendulum can be thought of as representing the location of a wavepacket that migrates from one turning point to the other periodically. Show that whatever superposition of harmonic oscillator states is used to construct a wavepacket, it is localized at the same place at the times 0, T, $2T$, …, where T is the classical period of the oscillator.

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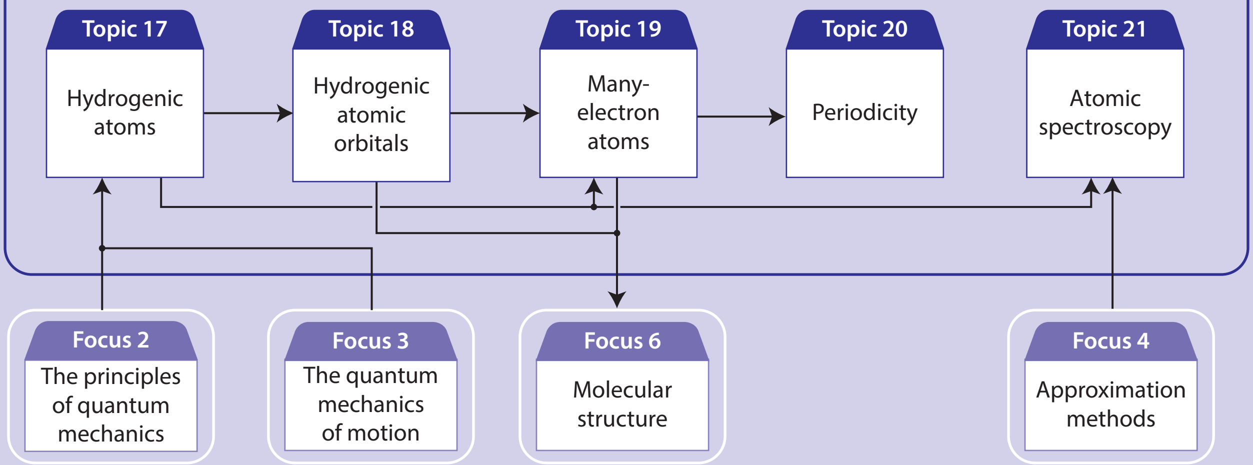
FOCUS 5 ON Atomic structure and spectra



Atoms are the currency of chemistry. They are the building blocks of all the forms of matter that chemists consider and it is essential to understand their structure. To do so, we draw on *The quantum mechanics of motion*, especially but not only rotational motion in three dimensions, and apply it to progressively more complex atoms.

The simplest atom of all is a hydrogen atom with its single electron, and its generalization to 'hydrogenic atoms' of general atomic number but still only one electron (**Topic 17**). When the Schrödinger equation is solved for hydrogenic atoms we obtain the wavefunctions known as 'atomic orbitals' (**Topic 18**). These orbitals play a central role in the description of chemical bonding, as is explained in *Molecular structure*, and, in combination with the 'Pauli exclusion principle', are the basis of the description of the structures of many-electron atoms (**Topic 19**). With the structures of these atoms understood, the structure of the periodic table and the 'periodicity' of the properties of the elements fall into place (**Topic 20**).

The experimental investigation of the structure of atoms is largely through 'atomic spectroscopy' (**Topic 21**). The origin of the transitions that give rise to spectral lines is time-dependent perturbation theory, which is described in *Approximation methods*. These transitions reveal details about the interactions between electrons and the coupling of the various sources of angular momentum in an atom.

What is the impact of this material?

Atomic spectroscopy is widely used by astronomers to determine the chemical composition of stars (*Impact* 5.1). Stellar material consists of neutral and ionized forms of atoms, such as hydrogen, helium, carbon, and iron, and each element, and indeed each isotope of an element, has a characteristic spectral signature that is transmitted through space by the star's light.

To read more about the impact of this material, scan the QR code, or go to http://bcs.whfreeman.com/webpub/chemistry/qmc2e/impact/qchem_impact5.html.

TOPIC 17

Hydrogenic atoms

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➤ Why do you need to know this material?

To set the stage for your study of the structure of atoms and molecules, you need to know how the Schrödinger equation is solved for the hydrogen atom. Moreover, the solutions for the hydrogen atom underlie the entire discussion of many-electron atoms, periodicity, and the formation of chemical bonds.

➤ What is the key idea?

Solution of the Schrödinger equation for the hydrogen atom subject to the appropriate boundary conditions results in one-electron wavefunctions, known as atomic orbitals, that are defined by three quantum numbers, n, l, and m_l, and energies that depend only on n.

➤ What do you need to know already?

You should be familiar with the form of the Schrödinger equation (Topic 6), its solution by the separation of variables technique (*Mathematical background* 2), and the quantum mechanical description of rotation in three dimensions (Topic 14).

In this Topic we begin to describe the **electronic structure** of an atom, the distribution of electrons around its nuclei. We need to distinguish between two types of atoms. A **hydrogenic atom** is a one-electron atom or ion of general atomic number Z such as H, He^+, Li^{2+}, O^{7+}, and even U^{91+}. A **many-electron atom** (or *polyelectronic atom*) is an atom or ion with more than one electron, such as all neutral atoms other than H. This Topic, which focuses exclusively on hydrogenic atoms, provides a set of concepts that are used to describe the structure of many-electron atoms (Topic 19).

17.1 The structure of hydrogenic atoms

To describe a hydrogenic atom using quantum theory, we need to write and solve the Schrödinger equation. The potential-energy term in the Schrödinger equation arises from the Coulomb interaction between the electron and the nucleus of charge Ze (see *Foundations*, Topic 2):

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} \qquad \textit{Hydrogenic atom} \quad \text{Potential energy} \qquad (17.1)$$

where r is the distance of the electron from the nucleus and ε_0 is the vacuum permittivity. Because this expression depends only on the distance from a single point (here, the nucleus), it is an example of a *central potential*. The hamiltonian operator for the electron and a nucleus of mass m_N is therefore

$$\hat{H} = \overbrace{-\frac{\hbar^2}{2m_e}\nabla_e^2}^{\text{electronic kinetic energy}} \overbrace{-\frac{\hbar^2}{2m_N}\nabla_N^2}^{\text{nuclear kinetic energy}} \overbrace{-\frac{Ze^2}{4\pi\varepsilon_0 r}}^{\text{potential energy}}$$

Hydrogenic atom Hamiltonian operator (17.2)

The subscripts on ∇^2 indicate differentiation with respect to the electronic or nuclear coordinates (Fig. 17.1).

(a) The separation of variables

As shown in the following *Justification*, the Schrödinger equation for a hydrogenic atom can be separated into two equations, one for the motion of the atom as a whole through space and the other for the motion of the electron relative to the nucleus. The Schrödinger equation for the internal motion of the electron relative to the nucleus is

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi$$

Internal motion of electron Schrödinger equation (17.3a)

$$\mu = \frac{m_e m_N}{m_e + m_N}$$

Hydrogenic atom Reduced mass (17.3b)

where differentiation is now with respect to the coordinates of the electron relative to the nucleus (Fig. 17.2). The quantity μ, which is called the **reduced mass,** is very similar in value to the electron mass because m_N, the mass of the nucleus, is much larger than the mass of an electron, so $\mu \approx m_e$. In all except the most precise work, the reduced mass can be replaced by m_e.

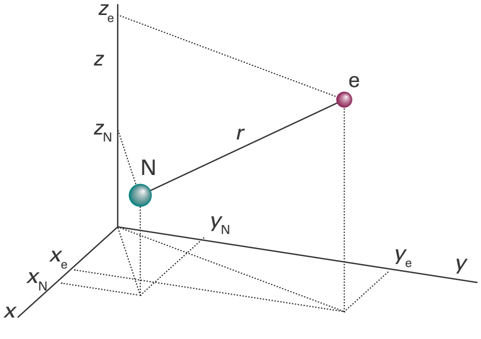

Figure 17.1 The coordinate system for describing the positions of the electron and nucleus in a hydrogenic atom.

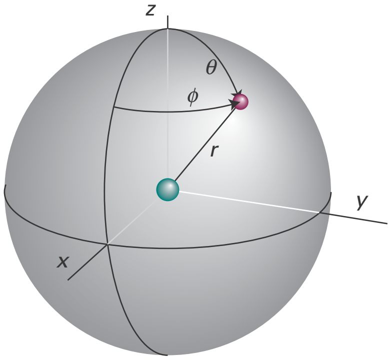

Figure 17.2 The coordinate system for describing the position of the electron relative to the nucleus. The nucleus is placed at the origin, and spherical polar coordinates are used for describing the position of the electron relative to the nucleus.

Justification 17.1 The separation of internal and external motion

We consider a one-dimensional system in which the potential energy depends only on the separation of the two particles, and then generalize to three dimensions. The total classical energy is

$$E = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V$$

where $p_1 = m_1\dot{x}_1$ and $p_2 = m_2\dot{x}_2$ (where the dot indicates differentiation with respect to time) are the linear momenta of the two particles. The centre of mass (Fig. 17.3) is located at

$$X = \frac{m_1}{m}x_1 + \frac{m_2}{m}x_2$$

where $m = m_1 + m_2$. Because the separation of the particles is $x = x_1 - x_2$, it follows that

$$X = \frac{m_1}{m}x_1 + \frac{m_2}{m}(x_1 - x)$$

giving

$$x_1 = X + \frac{m_2}{m}x \quad \text{and} \quad x_2 = x_1 - x = X - \frac{m_1}{m}x$$

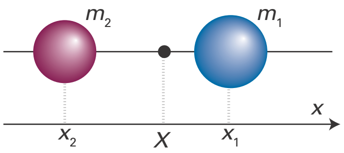

Figure 17.3 The coordinates used for discussing the separation of the relative motion of two particles from the motion of the centre of mass.

The linear momenta of the particles in terms of the rates of change of x and X are

$$p_1=m_1\dot{x}_1=m_1\dot{X}+\frac{m_1m_2}{m}\dot{x}$$
$$p_2=m_2\dot{x}_2=m_2\dot{X}-\frac{m_1m_2}{m}\dot{x}$$

Then it follows that

$$\frac{p_1^2}{2m_1}+\frac{p_2^2}{2m_2}=\frac{1}{2m_1}\left(m_1\dot{X}+\frac{m_1m_2}{m}\dot{x}\right)^2+\frac{1}{2m_2}\left(m_2\dot{X}-\frac{m_1m_2}{m}\dot{x}\right)^2$$
$$=\frac{1}{2}m\dot{X}^2+\frac{1}{2}\left(\frac{m_1m_2}{m}\right)\dot{x}^2$$

By writing $P=m\dot{X}$ for the linear momentum of the system as a whole and defining p as $\mu\dot{x}$, where the reduced mass $\mu=m_1m_2/m$, we find

$$E=\frac{P^2}{2m}+\frac{p^2}{2\mu}+V$$

The corresponding hamiltonian is therefore

$$\hat{H}=\frac{\hat{P}^2}{2m}+\frac{\hat{p}^2}{2\mu}+V$$

which, generalized to three dimensions, is

$$\hat{H}=-\frac{\hbar^2}{2m}\nabla_{\text{cm}}^2-\frac{\hbar^2}{2\mu}\nabla^2+V$$

where the first term differentiates with respect to the centre of mass coordinates and the second with respect to the relative coordinates.

Now we write the overall wavefunction as the product $\psi_{\text{total}}=\psi_{\text{cm}}\psi$, where ψ_{cm} is a function of only the centre of mass coordinates and ψ is a function of only the relative coordinates. The overall Schrödinger equation, $\hat{H}\psi_{\text{total}}=E_{\text{total}}\psi_{\text{total}}$, then separates by the argument presented in *Mathematical background* 2 with $E_{\text{total}}=E_{\text{cm}}+E$.

The centrosymmetric Coulomb potential energy has spherical symmetry in the sense that at a given distance its value is independent of angle. We can therefore suspect that the Schrödinger equation will separate into an angular component that mirrors the equation for a particle on a sphere treated in Topic 14 and, new to this system, an equation for the radial factor. That is, we can think of the electron as free to move around the nucleus on a spherical surface with the additional freedom to move between concentric surfaces of different radii. The following *Justification* confirms that the wavefunction can indeed be written as a product of functions

$$\psi(r,\theta,\phi)=R(r)Y(\theta,\phi) \tag{17.4}$$

Hydrogenic atom Electronic wavefunction

where the Y are the spherical harmonics that occur for a particle on a sphere and are labelled with the quantum numbers l and m_l that specify the angular momentum of the particle. The factor R, the **radial wavefunction**, is a solution of the **radial wave equation**

$$-\frac{\hbar^2}{2\mu R}\left(r^2\frac{\mathrm{d}^2R}{\mathrm{d}r^2}+2r\frac{\mathrm{d}R}{\mathrm{d}r}\right)+Vr^2-Er^2=-\frac{l(l+1)\hbar^2}{2\mu} \tag{17.5}$$

Hydrogenic atom Radial wave equation

Justification 17.2 The solutions of the Schrödinger equation for a hydrogenic atom

Substitution of the wavefunction $\psi=RY$ into eqn 17.3 gives

$$-\frac{\hbar^2}{2\mu}\overbrace{\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\Lambda^2\right)}^{\nabla^2\text{ in spherical coordinates}}RY+VRY=ERY$$

Because R depends only on r and Y depends only on the angular coordinates, this equation becomes

$$-\frac{\hbar^2}{2\mu}\left(Y\frac{\mathrm{d}^2R}{\mathrm{d}r^2}+\frac{2Y}{r}\frac{\mathrm{d}R}{\mathrm{d}r}+\frac{R}{r^2}\Lambda^2Y\right)+VRY=ERY$$

Multiplication through by r^2/RY gives

$$-\frac{\hbar^2}{2\mu R}\left(r^2\frac{\mathrm{d}^2R}{\mathrm{d}r^2}+2r\frac{\mathrm{d}R}{\mathrm{d}r}\right)+Vr^2-\frac{\hbar^2}{2\mu Y}\Lambda^2Y=Er^2$$

and therefore

$$\overbrace{-\frac{\hbar^2}{2\mu R}\left(r^2\frac{\mathrm{d}^2R}{\mathrm{d}r^2}+2r\frac{\mathrm{d}R}{\mathrm{d}r}\right)+(V-E)r^2}^{\text{Depends on }r\text{ alone}}=\overbrace{\frac{\hbar^2}{2\mu Y}}^{\text{Depends on }\theta,\phi\text{ alone}}\Lambda^2Y$$

At this point we employ the usual argument for the separation of variables (*Mathematical background* 2), that each term on either side of the equals sign must be a constant, and conclude that the differential equation separates into two equations:

$$-\frac{\hbar^2}{2\mu Y}\Lambda^2Y=\text{constant}$$
$$-\frac{\hbar^2}{2\mu R}\left(r^2\frac{\mathrm{d}^2R}{\mathrm{d}r^2}+2r\frac{\mathrm{d}R}{\mathrm{d}r}\right)+(V-E)r^2=-\text{constant}$$

The first of these two equations is encountered in Topic 14, where it is noted that

$$\Lambda^2Y=-l(l+1)Y$$

and that the solutions (subject to cyclic boundary conditions) are the spherical harmonics.

Brief illustration 17.1 The angular part of the hydrogenic wavefunction

Consider an electron in a hydrogen atom with the angular part of its wavefunction given by the spherical harmonic $Y_{2,-1}(\theta,\phi)$. Because $l=2$ and $m_l=-1$, the magnitude of the angular momentum is $6^{1/2}\hbar$ and the z-component is $-\hbar$; the negative sign indicates that, in classical terms, the electron is circulating in an anticlockwise sense as seen from below. Furthermore, because (Table 14.1) $Y_{2,-1}(\theta,\phi) \propto \cos\theta \sin\theta$, there are angular nodes at $\theta=0, \pi/2, \pi$: the probability of finding the electron anywhere on the z-axis and in the xy-plane is therefore zero.

Self-test 17.1 If the angular part of the electronic wavefunction is given by $Y_{1,+1}(\theta,\phi)$, determine the magnitude and z-component of the angular momentum as well as the locations of any angular nodes.

Answer: $2^{1/2}\hbar$, $+\hbar$, $\theta=0, \pi$

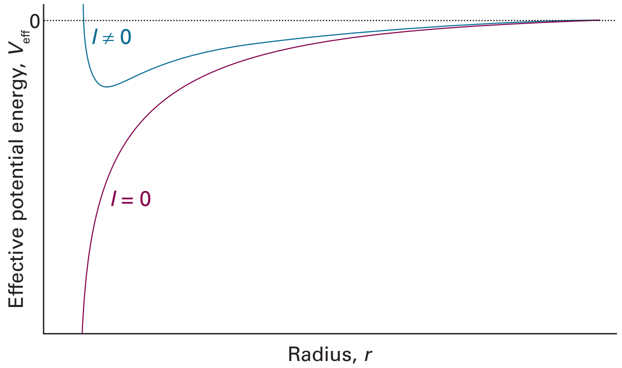

Figure 17.4 The effective potential energy of an electron in a hydrogenic atom. When the electron has zero orbital angular momentum, the effective potential energy is the Coulombic potential energy. When the electron has nonzero orbital angular momentum, the centrifugal effect gives rise to a positive contribution which is very large close to the nucleus. The $l=0$ and $l\neq 0$ wavefunctions are therefore very different near the nucleus.

(b) The radial solutions

The appearance of the radial wave equation (eqn 17.5) is simplified by writing $R=u/r$, with u a function of r, for it then becomes (see Problem 17.4)

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2u}{\mathrm{d}r^2}+V_{\text{eff}}u=Eu$$

Hydrogenic atom Radial wave equation (17.6a)

where

$$V_{\text{eff}}=-\frac{Ze^2}{4\pi\varepsilon_0 r}+\frac{l(l+1)\hbar^2}{2\mu r^2}$$

Hydrogenic atom Effective potential energy (17.6b)

Equation 17.6 describes the motion of a particle of mass μ in a one-dimensional region $0\le r<\infty$ where the potential energy is V_{eff}.

The first term in eqn 17.6b is the Coulomb potential energy of the electron in the field of the nucleus. The second term, which depends on the angular momentum of the electron around the nucleus, stems from what in classical physics would be called the 'centrifugal effect'. When $l=0$, the electron has no angular momentum, and the effective potential energy is purely Coulombic and attractive at all radii (Fig. 17.4). When $l\neq 0$, the centrifugal term gives a positive (repulsive) contribution to the effective potential energy. When the electron is close to the nucleus ($r\approx 0$), this repulsive term, which is proportional to $1/r^2$, dominates the attractive Coulombic component, which is proportional to $1/r$, and the net result is an effective repulsion of the electron from the nucleus. The two effective potential energies, the one for $l=0$ and the one for $l\neq 0$, are qualitatively very different close to the nucleus. However, they are similar at large distances because the centrifugal contribution tends to zero more rapidly (as $1/r^2$) than the Coulombic contribution (as $1/r$). Therefore, we can expect the solutions with $l=0$ and $l\approx 0$ to be quite different near the nucleus but similar far away from it.

We show in the following *Justification* that:

- Close to the nucleus the radial wavefunction is proportional to r^l.
- Far from the nucleus all radial wavefunctions approach zero exponentially.

It follows that when $l\neq 0$ (and $r^l=0$ when $r=0$) there is a zero probability density for finding the electron at the nucleus, and the higher the orbital angular momentum, the less likely the electron is to be found near the nucleus (Fig. 17.5). However, when $l=0$ (and $r^l=1$ even when $r=0$) there is a nonzero probability density of finding the electron at the nucleus. The contrast in behaviour has profound implications for chemistry, for it underlies the structure of the periodic table (Topic 20). The exponential decay of wavefunctions has a further important implication: it means that atoms can, to a good approximation, be represented by spheres with reasonably well defined radii. This feature is especially important in the discussion of solids (Topic 37), which are commonly modelled as aggregates of spheres representing their atoms and ions.

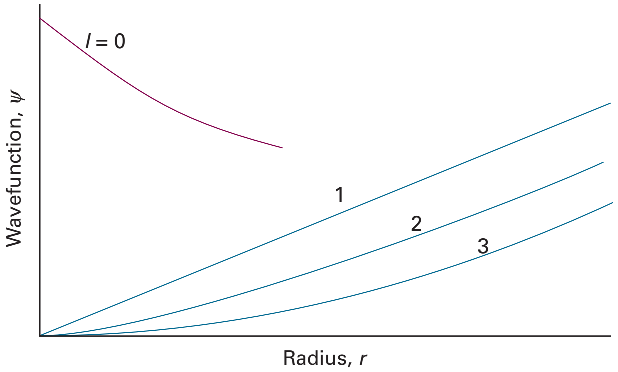

Figure 17.5 Close to the nucleus, orbitals with $l=1$ are proportional to r, orbitals with $l=2$ are proportional to r^2, and orbitals with $l=3$ are proportional to r^3. Electrons are progressively excluded from the neighbourhood of the nucleus as l increases. An orbital with $l=0$ has a finite, nonzero value at the nucleus.

Justification 17.3 The radial wavefunctions close to and far from the nucleus

When r is very small (close to the nucleus), $u=rR\approx 0$, so the right-hand side of eqn 17.6a is zero. We can also ignore all but the largest terms (those depending on $1/r^2$) in eqn 17.6b and write

$$-\frac{\mathrm{d}^2u}{\mathrm{d}r^2}+\frac{l(l+1)}{r^2}u\approx 0$$

The solution of this equation (for $r\approx 0$) is

$$u\approx Ar^{l+1}+\frac{B}{r^l}$$

as may be verified by substitution of the solution into the differential equation. Because $R=u/r$, and R cannot be infinite anywhere and specifically at $r=0$, we must set $B=0$. Therefore we obtain $u\approx Ar^{l+1}$ or $R\approx Ar^l$, as we wanted to show.

Far from the nucleus, when r is very large and we can ignore all terms in $1/r$ and $1/r^2$, eqn 17.6a becomes

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2u}{\mathrm{d}r^2}\simeq Eu$$

where $\simeq$ means 'asymptotically equal to' (that is, the two sides of the expression become equal as $r\to\infty$). Because

$$\frac{\mathrm{d}^2u}{\mathrm{d}r^2}=\frac{\mathrm{d}^2(rR)}{\mathrm{d}r^2}=\frac{\mathrm{d}}{\mathrm{d}r}\frac{\mathrm{d}}{\mathrm{d}r}(rR)=\frac{\mathrm{d}}{\mathrm{d}r}\left(r\frac{\mathrm{d}R}{\mathrm{d}r}+R\right)$$

$$=\overset{\text{This factor is very large}}{\overset{\uparrow}{r}}\frac{\mathrm{d}^2R}{\mathrm{d}r^2}+2\frac{\mathrm{d}R}{\mathrm{d}r}\simeq r\frac{\mathrm{d}^2R}{\mathrm{d}r^2}$$

this equation has the form

$$-\frac{\hbar^2}{2\mu}r\frac{\mathrm{d}^2R}{\mathrm{d}r^2}\simeq ErR$$

or, after cancelling the r,

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2R}{\mathrm{d}r^2}\simeq ER$$

Because R must be finite and the energy is negative for a **bound state**, a state in which the energy of the electron is lower than when the electron is infinitely distant and stationary, the acceptable solution for r large is

$$R\simeq \mathrm{e}^{-(2\mu|E|/\hbar^2)^{1/2}r}$$

as may be verified by substitution. That is, all the bound-state wavefunctions decay exponentially towards zero as r increases.

We shall not go through the technical steps of solving the radial wave equation (eqn 17.6) for the full range of radii, and see how the form r^l close to the nucleus blends into the exponentially decaying form at great distances.[1] It is sufficient to know that:

- The two limits can be matched only for integral values of a new quantum number n.
- The allowed energies corresponding to the allowed solutions are

$$E_{nlm_l}=-\frac{Z^2\mu e^4}{32\pi^2\varepsilon_0^2\hbar^2n^2}\qquad n=1,2,\ldots \tag{17.7}$$

Hydrogenic atom Energy

- The allowed energies are independent of the values of l and m_l; to avoid overburdening the notation, henceforth we denote them simply E_n.
- The radial wavefunctions depend on the values of both n and l (but not on m_l) with l restricted to values 0, 1, …, $n-1$.
- All radial wavefunctions have the form

$$R(r)=r^l\times(\text{polynomial in } r)\times(\text{decaying exponential in } r)$$

These functions are most simply written in terms of the dimensionless quantity ρ (rho), where

$$\rho=\frac{2Zr}{na}\qquad a=\frac{4\pi\varepsilon_0\hbar^2}{\mu e^2} \tag{17.8}$$

---

[1] For a full account of the solution, see our *Molecular quantum mechanics*, Oxford University Press (2011).

For simplicity, and introducing negligible error, the μ in eqn 17.8 is often replaced by m_e, in which case $\rho = 2Zr/na_0$ and

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} \qquad \text{Definition} \quad \text{Bohr radius} \qquad (17.9)$$

The **Bohr radius**, a_0, has the value 52.9 pm; it is so called because the same quantity appeared in Bohr's early model of the hydrogen atom as the radius of the electron orbit of lowest energy. Specifically, the radial wavefunctions for an electron with quantum numbers n and l are the (real) functions

$$R_{nl}(r) = N_{nl}\rho^l L_{n+1}^{2l+1}(\rho)e^{-\rho/2} \qquad \text{Hydrogenic atom} \quad \text{Radial wavefunctions} \qquad (17.10)$$

where N_{nl} is a normalization constant (with a value that depends on n and l) and L is a polynomial in ρ called an **associated Laguerre polynomial**. The polynomial L connects the $r \approx 0$ solutions on its left (corresponding to $R \propto \rho^l$) to the exponentially decaying function on its right. The notation might look fearsome, but the polynomials have quite simple forms, such as 1, ρ, and $2-\rho$ (they can be picked out in Table 17.1).

The components of eqn 17.10 can be interpreted as follows:

Physical interpretation

- The exponential factor ensures that the wavefunction approaches zero far from the nucleus.
- The factor ρ^l ensures that (provided $l > 0$) the wavefunction vanishes at the nucleus.
- The associated Laguerre polynomial is a function that oscillates from positive to negative values and accounts for the presence of radial nodes.

Expressions for some radial wavefunctions are given in Table 17.1 and illustrated in Fig. 17.6. Note that because r is never negative, the zero in the radial wavefunctions at $r = 0$ (for $l > 0$) is not a node: the wavefunction does not pass *through* zero there.

Brief illustration 17.2 The radial nodes of the wavefunction

Consider an electron in a hydrogen atom with $n = 2$, $l = 0$, $m_l = 0$. Because the radial wavefunction $R_{2,0} \propto (2-\rho)$ (see Table 17.1), the radial node is found at $\rho = 2$. Using eqns 17.8 and 17.9, we find, with $Z = 1$ and $n = 2$,

$$r = \frac{na_0\rho}{2Z} = 2a_0$$

Therefore, there is zero probability of finding the electron in a small volume element at a distance 105.8 pm from the nucleus in the hydrogen atom.

Table 17.1 Hydrogenic radial wavefunctions

n	l	R_{nl}
1	0	$2\left(\frac{Z}{a}\right)^{3/2} e^{-\rho/2}$
2	0	$\frac{1}{8^{1/2}}\left(\frac{Z}{a}\right)^{3/2} (2-\rho)e^{-\rho/2}$
2	1	$\frac{1}{24^{1/2}}\left(\frac{Z}{a}\right)^{3/2} \rho e^{-\rho/2}$
3	0	$\frac{1}{243^{1/2}}\left(\frac{Z}{a}\right)^{3/2} (6-6\rho+\rho^2)e^{-\rho/2}$
3	1	$\frac{1}{486^{1/2}}\left(\frac{Z}{a}\right)^{3/2} (4-\rho)\rho e^{-\rho/2}$
3	2	$\frac{1}{2430^{1/2}}\left(\frac{Z}{a}\right)^{3/2} \rho^2 e^{-\rho/2}$

$\rho = (2Z/na)r$ with $a = 4\pi\varepsilon_0\hbar^2/\mu e^2$. For an infinitely heavy nucleus (or one that may be assumed to be), $\mu = m_e$ and $a = a_0$, the Bohr radius.

Self-test 17.2 Find the radial nodes for an electron in Li^{2+} ion with $n = 3$, $l = 0$, $m_l = 0$.

Answer: $(3 \pm 3^{1/3})a_0/2$, 125 and 33.5 pm

17.2 The atomic orbitals and their energies

The wavefunctions of hydrogenic atoms are called 'atomic orbitals'. More precisely, an **atomic orbital** is a one-electron wavefunction for an electron in an atom.

(a) The atomic orbitals

Each hydrogenic atomic orbital (eqn 17.4) is defined by three quantum numbers, designated n, l, and m_l:

$$\psi_{nlm_l}(r,\theta,\phi) = R_{nl}(r)Y_{lm_l}(\theta,\phi) \qquad \text{Hydrogenic atom} \quad \text{Atomic orbital} \qquad (17.11)$$

When an electron is described by one of these wavefunctions, we say that it 'occupies' that orbital.

The quantum number n is called the **principal quantum number**; it can take the values $n = 1, 2, 3, \ldots$ and determines the energy of the electron, as in eqn 17.7. The two other quantum numbers, l and m_l, come from the angular solutions and specify the angular momentum of the electron around the nucleus, as explained in Topic 14. However, the various boundary

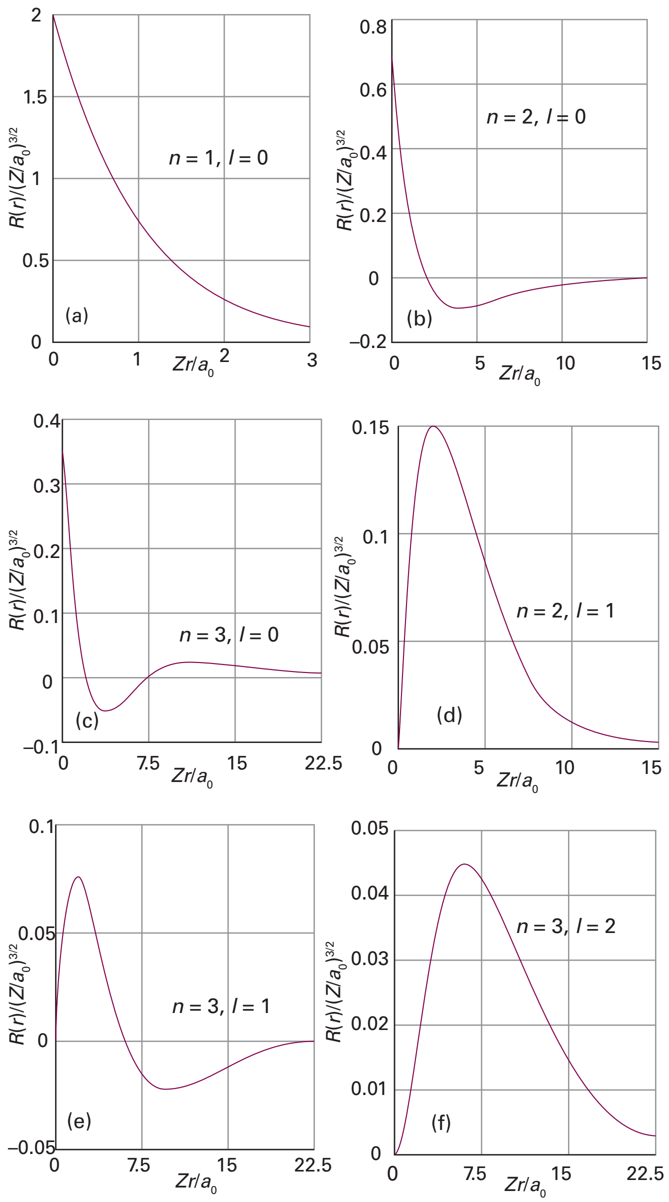

Figure 17.6 The radial wavefunctions of the first few states of hydrogenic atoms of atomic number Z. Note that the orbitals with $l=0$ have a nonzero and finite value at the nucleus. The horizontal scales are different in each case: orbitals with high principal quantum numbers are relatively distant from the nucleus.

conditions that the angular and radial wavefunctions must satisfy put additional constraints on their values:

> An electron in an orbital with quantum number l has an angular momentum of magnitude $\{l(l+1)\}^{1/2}\hbar$, with $l=0, 1, 2, \ldots, n-1$.
>
> An electron in an orbital with quantum number m_l has a z-component of angular momentum $m_l\hbar$, with $m_l=0,\pm1,\pm2,\ldots,\pm l$.

Note how the value of the principal quantum number, n, controls the maximum value of l and how, in turn, l restricts the range of values of m_l. For example, if $n=3$, the allowed values of l (and corresponding m_l) are 0 (0), 1 (0, ±1), and 2 (0, ±1, ±2).

Brief illustration 17.3 The probability density for an electron

To calculate the probability density at the nucleus for an electron occupying the $n=1$, $l=0$, $m_l=0$ orbital, we begin by evaluating $\psi_{1,0,0}$ at $r=0$ (see Tables 14.1 and 17.1):

$$\psi_{1,0,0}(0,\theta,\phi)=R_{1,0}(0)Y_{0,0}(\theta,\phi)=2\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{1}{4\pi}\right)^{1/2}$$

The probability density is therefore

$$\psi_{1,0,0}(0,\theta,\phi)^2=\frac{Z^3}{\pi a_0^3}$$

which evaluates to $2.15\times10^{-6}\,\text{pm}^{-3}$ when $Z=1$. Therefore, the probability of finding the electron inside a region of volume $1.00\,\text{pm}^3$ located at the nucleus, ignoring the variation of ψ within the very small region, is 2.15×10^{-6} or about 1 part in 5×10^5.

Self-test 17.3 Evaluate the probability density at the nucleus for an electron occupying the $n=2$, $l=0$, $m_l=0$ orbital. What is the probability of finding the electron inside a region of volume $1.00\,\text{pm}^3$ located at the nucleus of the H atom?

Answer: $Z^3/(8\pi a_0^3)$, 2.69×10^{-7}

(b) The energy levels

The energy levels predicted by eqn 17.7 are depicted in Fig. 17.7. The energies, and also the separation of neighbouring levels, are proportional to Z^2; therefore, the levels are four times as wide apart in He^+ ($Z=2$) as in H ($Z=1$) and the ground state ($n=1$) is four times deeper in energy. All the energies given by eqn 17.7 are negative because they refer to the bound states of the atom, in which the energy of the atom is lower than that of the infinitely separated, stationary electron and nucleus (the $n=\infty$ limit). There are also solutions of the Schrödinger equation (eqn 17.3) with positive energies. These solutions correspond to **unbound states** of the electron, the states to which an electron is raised when it is ejected from the atom by a high-energy collision or photon. The energies of the unbound electron are not quantized (the boundary condition that the wavefunction must vanish at infinity is no longer relevant) and form the **continuum states** of the atom.

For the hydrogen atom, the expression for the energy in eqn 17.7 can be written in the form

$$E_n=-\frac{hc\tilde{R}_{\text{H}}}{n^2}\qquad n=1,2,\ldots \tag{17.12a}$$

Alternative form

Energy, hydrogen atom

where $\tilde{R}_{\mathrm{H}}$ is the Rydberg constant for hydrogen

$$\tilde{R}_{\mathrm{H}}=\frac{\mu_{\mathrm{H}}e^4}{8\varepsilon_0^2h^3c}\qquad\text{Rydberg constant for H}\tag{17.12b}$$

with a value of 109 677 cm^{-1}. The **Rydberg constant** itself, $\tilde{R}_\infty$, is defined by the same expression as eqn 17.12b except for the replacement of μ_{H} by the mass of an electron, m_{e}, corresponding to a nucleus of infinite mass:

$$\tilde{R}_\infty=\frac{m_{\mathrm{e}}e^4}{8\varepsilon_0^2h^3c}\qquad\textit{Definition}\quad\text{Rydberg constant}\tag{17.13}$$

Example 17.1 Determining the energy for an electron occupying an atomic orbital

The single electron in a certain excited state of a hydrogenic He$^+$ ion ($Z=2$) is described by the wavefunction $R_{3,2}(r)\times Y_{2,-1}(\theta,\phi)$. What is the energy of its electron?

Method Because the energy of a hydrogenic atom depends on n but is independent of the values of l and m_l, we need identify only the quantum number n, which is done by noting the form of the wavefunction given in eqn 17.11. Then use eqn 17.7 to calculate the energy. To a good approximation, the reduced mass in eqn 17.7 can be replaced by m_{e} and the energy can be written in terms of the Rydberg constant of eqn 17.13. (For greater accuracy, use the reduced mass of the electron and helium nucleus.)

Answer Replacing μ by m_{e} and using $\hbar=h/2\pi$, we can write the expression for the energy (eqn 17.7) as

$$E_n=-\frac{Z^2m_{\mathrm{e}}e^4}{8\varepsilon_0^2h^2n^2}=-\frac{Z^2hc\tilde{R}_\infty}{n^2}$$

with

$$\tilde{R}_\infty=\frac{\overbrace{9.109\,38\times10^{-31}\,\mathrm{kg}}^{m_{\mathrm{e}}}\times\overbrace{(1.602\,176\times10^{-19}\,\mathrm{C})^4}^{e^4}}{8\times\underbrace{(8.854\,19\times10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}})^2}_{\varepsilon_0^2}\times\underbrace{(6.626\,08\times10^{-34}\,\mathrm{J\,s})^3}_{h^3}\times\underbrace{2.997\,926\times10^{10}\,\mathrm{cm\,s^{-1}}}_{c}}$$

$$=109\,737\,\mathrm{cm^{-1}}$$

and

$$\begin{aligned}hc\tilde{R}_\infty&=(6.626\,08\times10^{-34}\,\mathrm{J\,s})\times(2.997\,926\times10^{10}\,\mathrm{cm\,s^{-1}})\\&\quad\times(109\,737\,\mathrm{cm^{-1}})\\&=2.179\,87\times10^{-18}\,\mathrm{J}\end{aligned}$$

Therefore, for $n=3$, the energy is

$$\begin{aligned}E_3&=-\frac{\overbrace{4}^{Z^2}\times\overbrace{2.179\,87\times10^{-18}\,\mathrm{J}}^{hc\tilde{R}_\infty}}{\underbrace{9}_{n^2}}\\&=-9.688\,31\times10^{-19}\,\mathrm{J}\end{aligned}$$

or $-0.968\,831$ aJ (a, for atto, is the prefix that denotes 10^{-18}). In some applications it is useful to express the energy in electronvolts ($1\,\mathrm{eV}=1.602\,176\times10^{-19}\,\mathrm{J}$); in this case, $E_3=-6.046\,97\,\mathrm{eV}$.

Self-test 17.4 What is the energy of the electron in an excited state of a Li^{+2} ion ($Z=3$) for which the wavefunction is $R_{4,3}(r)\times Y_{3,-2}(\theta,\phi)$?

Answer: $-1.226\,18$ aJ, $-7.653\,22$ eV

Equation 17.12 is a convenient expression for analyses of the emission spectrum of atomic hydrogen, as shown in the following Example, and explored in more detail in Topic 21.

Example 17.2 Calculating the wavenumber of a line in the emission spectrum of H

When an electric discharge is passed through gaseous hydrogen, the H$_2$ molecules are dissociated and energetically excited H atoms are produced. If the electron in an excited H atom makes a transition from $n=2$ to $n=1$, calculate the wavenumber of the corresponding line in the emission spectrum.

Method When an excited electron makes a transition from a state with quantum number n_2 to a lower energy state with quantum number n_1, it loses an energy

$$\Delta E=E_{n_2}-E_{n_1}=-hc\tilde{R}_{\mathrm{H}}\left(\frac{1}{n_2^2}-\frac{1}{n_1^2}\right)$$

The frequency of the emitted photon is $\nu=\Delta E/h$; the wavenumber is $\tilde{\nu}=\nu/c=\Delta E/hc$.

Answer The wavenumber of the photon emitted when an electron makes a transition from $n_2=2$ to $n_1=1$ is given by

$$\begin{aligned}\tilde{\nu}&=-\tilde{R}_{\mathrm{H}}\left(\frac{1}{n_2^2}-\frac{1}{n_1^2}\right)\\&=-(109677\,\mathrm{cm^{-1}})\times\left(\frac{1}{2^2}-\frac{1}{1^2}\right)\\&=82\,258\,\mathrm{cm^{-1}}\end{aligned}$$

The emitted photon has a wavelength of 122 nm, corresponding to ultraviolet radiation.

Self-test 17.5 Calculate the wavelength and wavenumber of the emitted photon if the electron in H makes a transition from $n=3$ to $n=2$.

Answer: 656 nm, 15 233 cm^{-1}, visible

(c) Ionization energies

The **ionization energy**, I, of an element is the minimum energy required to remove an electron from the ground state, the state of lowest energy, of one of its atoms in the gas phase. Because the ground state of hydrogen is the state with $n=1$, with energy $E_1=-hc\tilde{R}_H$, and the atom is ionized when the electron has been excited to the level corresponding to $n=\infty$ (see Fig. 17.7), the energy that must be supplied is

$$I = hc\tilde{R}_H \qquad \textit{Hydrogen atom} \quad \text{Ionization energy} \tag{17.14}$$

The value of I is 2.179 aJ, which corresponds to 13.60 eV.

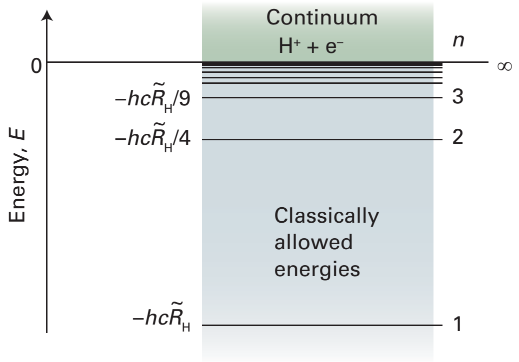

Figure 17.7 The energy levels of a hydrogen atom. The values are relative to an infinitely separated, stationary electron and a proton.

Example 17.3 Measuring an ionization energy spectroscopically

The emission spectrum of atomic hydrogen shows a series of lines at 82 259, 97 492, 102 824, 105 292, 106 632, and 107 440 cm^{-1}, which correspond to transitions to the same lower state. Determine (a) the ionization energy of the lower state, (b) the value of the Rydberg constant.

Method The spectroscopic determination of ionization energies depends on the determination of the 'series limit', the wavenumber at which the series terminates and becomes a continuum. If the upper state lies at an energy $-hc\tilde{R}_H/n^2$, then when the atom makes a transition to E_{lower}, a photon of wavenumber

$$\tilde{\nu} = -\frac{\tilde{R}_H}{n^2} - \frac{E_{\text{lower}}}{hc}$$

is emitted. However, because $I=-E_{\text{lower}}$, it follows that

$$\tilde{\nu} = \frac{I}{hc} - \frac{\tilde{R}_H}{n^2}$$

A plot of the wavenumbers against $1/n^2$ should give a straight line of slope $-\tilde{R}_H$ and intercept I/hc. Use mathematical software to make a least-squares fit of the data to get a result that reflects the precision of the data.

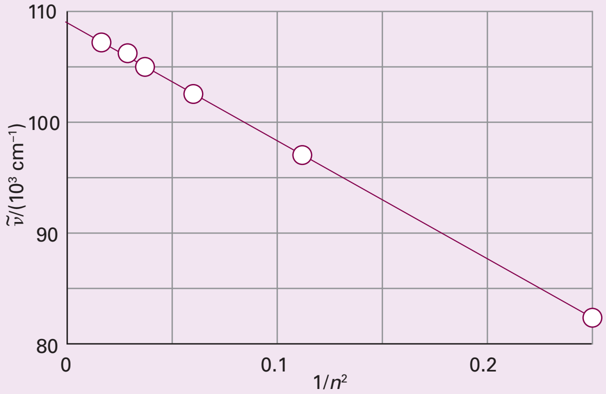

Figure 17.8 The plot of the data in Example 17.3 used to determine the ionization energy of an atom (in this case, of H).

Answer The wavenumbers are plotted against $1/n^2$ in Fig. 17.8. The (least-squares) intercept lies at 109 679 cm^{-1}, so the ionization energy is 2.1788 aJ (1317.1 kJ mol^{-1}). The slope is, in this instance, numerically the same, so the experimentally determined value of the Rydberg constant is 109 679 cm^{-1}, very close to the actual value of 109 677 cm^{-1}.

Self-test 17.6 The emission spectrum of atomic deuterium shows lines at 15 238, 20 571, 23 039, and 24 380 cm^{-1}, which correspond to transitions to the same lower state. Determine (a) the ionization energy of the lower state, (b) the ionization energy of the ground state, (c) the mass of the deuteron (by expressing the Rydberg constant in terms of the reduced mass of the electron and the deuteron, and solving for the mass of the deuteron).

Answer: (a) 328.1 kJ mol^{-1}, (b) 1317.4 kJ mol^{-1}, (c) 2.8×10^{-27} kg, a result very sensitive to R_D

Checklist of concepts

☐ 1. A **hydrogenic atom** is a one-electron atom or ion of general atomic number Z. A many-electron atom is an atom or ion with more than one electron.

☐ 2. The wavefunction of a hydrogenic atom is the product of a radial wavefunction and an angular wavefunction (spherical harmonic) and is labelled by the quantum numbers n, l, and m_l.

☐ 3. An **atomic orbital** is a one-electron wavefunction for an electron in an atom.

☐ 4. The **principal quantum number** n determines the energy of an electron in a hydrogenic atom; $n = 1, 2, \ldots$.

☐ 5. The **quantum numbers** l **and** m_l specify the magnitude (as $\{l(l+1)\}^{1/2}\hbar$) and the z-component (as $m_l\hbar$), respectively, of the angular momentum of the electron around the nucleus. The allowed values are $l = 0, 1, 2, \ldots, n-1$; $m_l = 0, \pm 1, \pm 2, \ldots, \pm l$.

☐ 6. The energy of an infinitely separated, stationary electron and nucleus is zero. Electron energies which are negative correspond to bound states of the atom. Positive energies correspond to unbound or continuum states.

☐ 7. The **ionization energy** of an element is the minimum energy required to remove an electron from the ground state of one of its atoms in the gas phase.

Checklist of equations

Property	Equation	Comment	Equation number
Coulomb potential energy	$V(r) = -Ze^2/4\pi\varepsilon_0 r$		17.1
Reduced mass	$\mu = m_e m_N/(m_e + m_N)$		17.3b
Radial wave equation	$-(\hbar^2/2\mu)(d^2u/dr^2) + V_{eff}u = Eu$	Hydrogenic atom	17.6a
Effective potential energy	$V_{eff} = -Ze^2/4\pi\varepsilon_0 r + l(l+1)\hbar^2/2\mu r^2$	Hydrogenic atom	17.6b
Electronic energy	$E_n = -Z^2\mu e^4/32\pi^2\varepsilon_0^2\hbar^2 n^2$ $n = 1, 2, \ldots$	Hydrogenic atom	17.7
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	52.9 pm	17.9
Atomic orbital	$\psi_{nlm_l}(r,\theta,\phi) = R_{nl}(r)Y_{lm_l}(\theta,\phi)$		17.11
Rydberg constant for hydrogen	$\tilde{R}_H = \mu_H e^4/8\varepsilon_0^2 h^3 c$	109 677 cm^{-1}	17.12b
Rydberg constant	$\tilde{R}_\infty = m_e e^4/8\varepsilon_0^2 h^3 c$	109 737 cm^{-1}	17.13
Ionization energy of hydrogen	$I = hc\tilde{R}_H$	2.179 aJ, 13.60 eV	17.14

TOPIC 18

Hydrogenic atomic orbitals

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➤ Why do you need to know this material?

The properties of hydrogenic atomic orbitals figure prominently in the discussion of electronic structure of many-electron atoms and, by extension, molecules. Therefore, to understand the form of the periodic table, molecular structure, and chemical reactivity, you need a firm understanding of atomic orbitals.

➤ What is the key idea?

Atomic orbitals describe the probability density distribution of an electron in an atom.

➤ What do you need to know already?

You need to know what is meant by the terms probability density (Topic 5), expectation value (Topic 7), and node (Topic 9). This Topic draws heavily on the forms of the radial wavefunctions given in Table 17.1 of Topic 17 and the spherical harmonics given in Table 14.1 of Topic 14. Various techniques of integration are used; they are reviewed in *Mathematical background* 1.

Hydrogenic atomic orbitals, which are the electronic wavefunctions for one-electron atoms with atomic number Z, are defined by the three quantum numbers n, l, and m_l (Topic 17). They have the form $\psi_{nlm_l} = R_{nl}Y_{lm_l}$ where the radial wavefunction R is given in Table 17.1 and the spherical harmonic Y in Table 14.1. The probability densities $|\psi_{nlm_l}|^2$ result in the shapes of atomic orbitals familiar from introductory chemistry courses. Here we explore the properties of hydrogenic atomic orbitals because they provide the basis for describing the electronic structure and periodic properties of many-electron atoms (Topic 19) and, by extension, molecules (Topics 22–30).

18.1 Shells and subshells

All atomic orbitals of a given value of n are said to form a single **shell** of the atom; in a hydrogenic atom, all orbitals of given n, and therefore belonging to the same shell, have the same energy. It is common to refer to successive shells by uppercase letters:

$$\begin{array}{lllll} n = & 1 & 2 & 3 & 4\ldots \\ & \mathrm{K} & \mathrm{L} & \mathrm{M} & \mathrm{N}\ldots \end{array}$$

Thus, all the orbitals of the shell with $n=2$ form the L shell of the atom, and so on. The orbitals with the same value of n but different values of l (allowed values are 0, 1, …, $n-1$) are said to form a **subshell** of a given shell.The subshells are generally referred to by lowercase letters:

$$\begin{array}{llllllll} l = & 0 & 1 & 2 & 3 & 4 & 5 & 6\ldots \\ & \mathrm{s} & \mathrm{p} & \mathrm{d} & \mathrm{f} & \mathrm{g} & \mathrm{h} & \mathrm{i}\ldots \end{array}$$

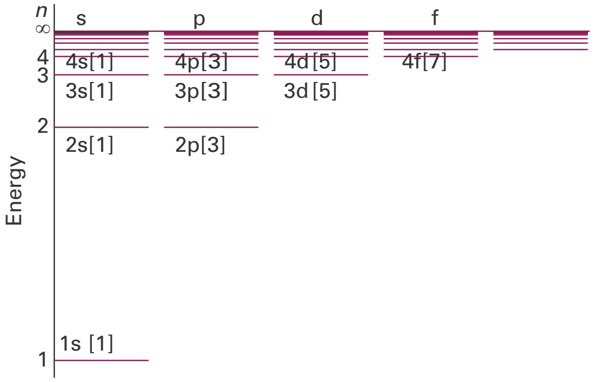


Figure 18.1 The energy levels of a hydrogenic atom showing the subshells and (in square brackets) the numbers of orbitals in each subshell. All orbitals of a given shell have the same energy.

The letters then run alphabetically omitting j (because some languages do not distinguish between i and j). Figure 18.1 shows the energy levels of the subshells explicitly for a hydrogenic atom. Because l can range from 0 to $n-1$, giving n values in all, it follows that there are n subshells of a shell with principal quantum number n. Thus,

- when $n=1$, there is only one subshell, the one with $l=0$ (the 1s subshell);
- when $n=2$, there are two subshells, the 2s subshell (with $l=0$) and the 2p subshell (with $l=1$).

When $n=1$ there is only one subshell, that with $l=0$, and that subshell contains only one orbital, with $m_l=0$ (the only value of m_l permitted). When $n=2$, there are four orbitals, one in the s subshell with $l=0$ and $m_l=0$, and three in the $l=1$ subshell with $m_l=+1, 0, -1$. In general, the number of orbitals in a shell of principal quantum number n is n^2, so in a hydrogenic atom each energy level is n^2-fold degenerate. The organization of orbitals in the shells is summarized in Fig. 18.2.

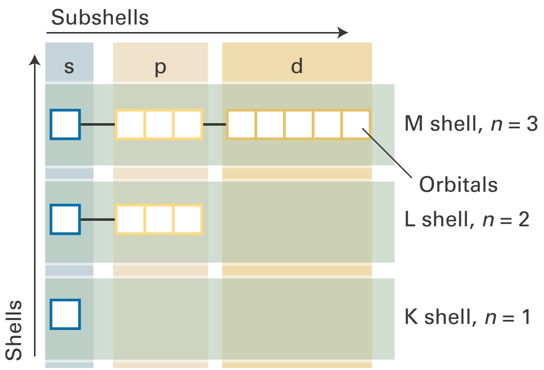


Figure 18.2 The organization of orbitals (white squares) into subshells (characterized by l) and shells (characterized by n).

Brief illustration 18.1 The number of orbitals in a shell

When $n=3$ there are three subshells, $l=0$ (3s), $l=1$ (3p), and $l=2$ (3d). Since the s, p, and d subshells contain one, three, and five orbitals, respectively, there are a total of $9=3^2$ orbitals in the M shell.

Self-test 18.1 Identify the orbitals in the N shell.

Answer: one 4s, three 4p, five 4d, seven 4f orbitals; 16 in total

(a) s Orbitals

The orbital occupied in the ground state of a hydrogenic atom is the one with $n=1$ and therefore with $l=0$ and $m_l=0$. The wavefunction $\psi_{1,0,0}$ is the product of the radial wavefunction $R_{1,0}$ and the spherical harmonic $Y_{0,0}$, so from Tables 14.1 and 17.1 it follows that

$$\psi = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/a_0} \quad \textit{Hydrogenic atom} \quad \text{1s wavefunction} \qquad (18.1)$$

This wavefunction is independent of the angular location of the electron and has the same value at all points of constant radius; that is, the 1s orbital is 'spherically symmetrical'. The wavefunction decays exponentially from a maximum value of $(Z^3/\pi a_0^3)^{1/2}$ at the nucleus (at $r=0$), and therefore the greatest probability density is at the nucleus.

A note on good practice Always keep in mind the distinction between the *probability density* (dimensions: 1/volume) at a point, ψ^2, and the *probability* (dimensionless) of the electron being in an infinitesimal region $d\tau$ at that point, $\psi^2 d\tau$.

The general form of the ground-state wavefunction can be understood by considering the contributions of the potential and kinetic energies to the total energy of the atom. The closer the electron is to the nucleus, the lower (that is, more negative) its potential energy. This dependence suggests that the lowest potential energy is obtained with a sharply peaked wavefunction that has a large amplitude at the nucleus and is very small everywhere else (Fig. 18.3a). However, this shape implies a high kinetic energy, because such a wavefunction has a very high average curvature. The electron would have very low kinetic energy if its wavefunction had only a very low average curvature. However, such a wavefunction (Fig. 18.3b) spreads to great distances from the nucleus and the average potential energy of the electron is correspondingly high (that is, less negative). The actual ground-state wavefunction is a compromise between these two extremes (Fig. 18.3c): the wavefunction spreads away from the nucleus (so the expectation value of the potential energy is not as low as in the first example, but nor is it very high) and has a reasonably low average curvature (so the expectation value of the kinetic energy is not very low, but nor is it as high as in the first example). The contributions of

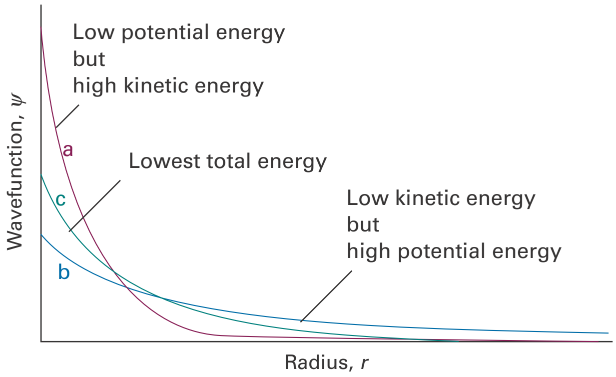


Figure 18.3 The balance of kinetic and potential energies that accounts for the structure of the ground state of hydrogenic atoms. (a) The sharply curved but localized orbital has high mean kinetic energy, but low mean potential energy; (b) the mean kinetic energy is low, but the potential energy is not very favourable; (c) the compromise of moderate kinetic energy and moderately favourable potential energy.

the kinetic energy and the potential energy to the ground-state energy can also be understood by using the virial theorem, as shown in the following *Justification*.

One way of depicting the probability density of the electron is to represent $|\psi|^2$ by the density of shading (Fig. 18.4).

Justification 18.1 The virial theorem and the energies of hydrogenic atomic orbitals

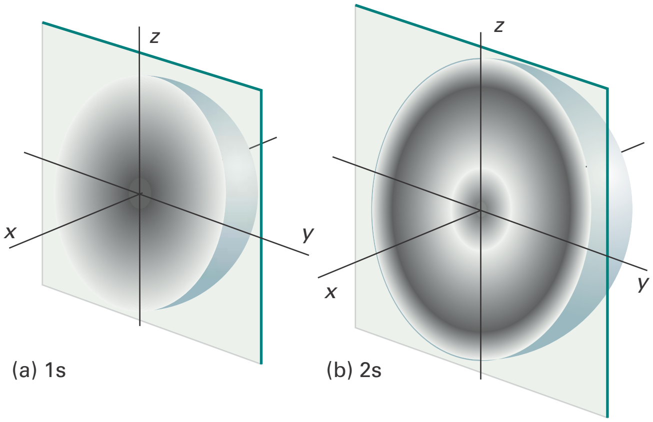
The virial theorem (Topic 12) states that if the potential energy of the system is of the form $V=ax^b$, where a and b are constants, then the average kinetic and potential energies are related by $2\langle E_k\rangle=\langle V\rangle$. For the Coulomb potential energy ($V \propto -1/r$), $b=-1$; therefore

$$\langle E_k\rangle=-\frac{1}{2}\langle V\rangle$$

As the average distance of the electron from the nucleus increases, $\langle V\rangle$ increases (becomes less negative) so $\langle E_k\rangle$ decreases (becomes less positive), as described in the text.

A simpler procedure is to show only the **boundary surface**, the surface that captures a high proportion (typically about 90 per cent) of the electron probability density. For the 1s orbital, the boundary surface is a sphere centred on the nucleus (Fig. 18.5).

All s orbitals are spherically symmetric, but differ in the number of radial nodes. For example, the 1s, 2s, and 3s orbitals, which are collected in Table 18.1, have 0, 1, and 2 radial nodes, respectively (see Fig. 17.6 and note the number of zeroes in the radial wavefunction). The radial nodes for the 2s and 3s orbitals are calculated in *Brief illustration* 17.2. In general, an *n*s orbital has $n-1$ radial nodes.



(a) 1s (b) 2s

Figure 18.4 Representations of cross-sections through the (a) 1s and (b) 2s hydrogenic atomic orbitals in terms of their electron probability densities (as represented by the density of shading).

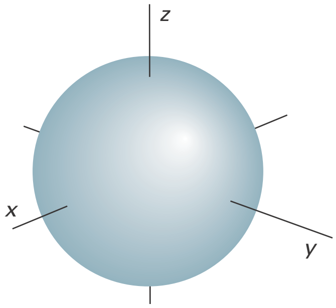


Figure 18.5 The boundary surface of a 1s orbital, within which there is a 90 per cent probability of finding the electron. All s orbitals have spherical boundary surfaces.

Example 18.1 Calculating the mean radius of an s orbital

Evaluate the mean radius of a 1s orbital of a hydrogenic atom of atomic number *Z*.

Method The mean radius is the expectation value

$$\langle r\rangle=\int\psi^{*}r\psi\,\mathrm{d}\tau=\int r|\psi|^{2}\,\mathrm{d}\tau$$

We therefore need to evaluate the integral using the hydrogenic 1s wavefunction (Tables 14.1 and 17.1); the volume element in spherical polar coordinates is $\mathrm{d}\tau=r^2\mathrm{d}r\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$ (see *The chemist's toolkit* 14.1). The angular parts of the wavefunction are normalized in the sense that

$$\int_0^{\pi}\int_0^{2\pi}\left|Y_{lm_l}\right|^2\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi=1$$

where the limits on the first integral sign refer to θ, and those on the second to ϕ (recall the procedure for multiple integration in *Mathematical background* 1). Use Integral E.1 listed in the *Resource section*.

Answer With the wavefunction written in the form $\psi_{nlm_l}=R_{nl}Y_{lm_l}$, the expectation value $\langle r\rangle$ is

$$\langle r\rangle=\int_0^\infty\int_0^\pi\int_0^{2\pi} r\overbrace{R_{nl}^2\left|Y_{lm_l}\right|^2}^{|\psi|^2}\overbrace{r^2\mathrm{d}r\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi}^{\mathrm{d}\tau}$$

$$=\int_0^\infty r^3R_{nl}^2\mathrm{d}r\times\overbrace{\int_0^\pi\int_0^{2\pi}\left|Y_{lm_l}\right|^2\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi}^{1}$$

$$=\int_0^\infty r^3R_{nl}^2\mathrm{d}r$$

For a 1s orbital (Table 17.1),

$$R_{1,0}=2\left(\frac{Z}{a_0}\right)^{3/2}\mathrm{e}^{-Zr/a_0}$$

Hence, by using Integral E.1 given in the *Resource section* with $n=3$ and $a=2Z/a_0$,

$$\langle r\rangle=4\left(\frac{Z}{a_0}\right)^3\int_0^\infty r^3\mathrm{e}^{-2Zr/a_0}\mathrm{d}r\overset{\text{Integral E.1}}{=}4\left(\frac{Z}{a_0}\right)^3\times\frac{3!}{(2Z/a_0)^4}$$

$$=\frac{3a_0}{2Z}$$

For H, $\langle r\rangle=79.4$ pm, and for He$^+$, $\langle r\rangle=39.7$ pm. In general, the higher the nuclear charge, the closer the electron is drawn to the nucleus.

Self-test 18.2 Evaluate the mean radius of (a) a 3s orbital and (b) a 3p orbital for a hydrogenic atom of atomic number Z.

Answer: (a) $(27/2)a_0/Z$; (b) $(25/2)a_0/Z$

(b) p Orbitals

The three p orbitals are distinguished by the three different values that m_l can take when $l=1$. Because the quantum number m_l tells us the projection of the orbital angular momentum onto a particular axis (by convention, the z-axis), these different values of m_l denote orbitals in which the electron has different orbital angular momenta around an arbitrary z-axis. The orbital with $m_l=0$, for instance, has zero angular momentum around the z-axis. Its angular variation is proportional to cos θ (Table 14.1), so the probability density, which is proportional to $\cos^2\theta$, has its maximum value on either side of the nucleus along the z-axis (at $\theta=0$ and 180°, where $\cos^2\theta=1$).

The hydrogenic 2p orbital with $m_l=0$ is

$$\psi_{2\mathrm{p}_0}=R_{2,1}Y_{1,0}=\frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a_0}\right)^{5/2}r\cos\theta\,\mathrm{e}^{-Zr/2a_0}$$
$$=r\cos\theta\,f(r)\qquad(18.2\mathrm{a})$$

2p$_z$ atomic orbital

where $f(r)$ is a function only of r. Because in spherical polar coordinates $z=r\cos\theta$, this wavefunction may also be written

$$\psi_{2\mathrm{p}_z}=zf(r)\qquad(18.2\mathrm{b})$$

All p orbitals with $m_l=0$ have wavefunctions of this form regardless of the value of n (with different forms of f for different values of n). This way of writing the orbital is the origin of the name 'p$_z$ orbital'. The boundary surface (for $n=2$) is shown in Fig. 18.6. The wavefunction is zero everywhere in the xy-plane, where $z=0$, so the xy-plane is a **nodal plane** of the orbital: the wavefunction changes sign on going from one side of the nodal plane to the other.

The hydrogenic 2p orbitals with $m_l=\pm1$ are

$$\psi_{2\mathrm{p}_{\pm1}}=R_{2,1}Y_{1,\pm1}$$
$$=\mp\frac{1}{8\pi^{1/2}}\left(\frac{Z}{a_0}\right)^{5/2}r\,\mathrm{e}^{-Zr/2a_0}\sin\theta\,\mathrm{e}^{\pm\mathrm{i}\phi}$$
$$=\mp\frac{1}{2^{1/2}}r\sin\theta\,\mathrm{e}^{\pm\mathrm{i}\phi}f(r)\qquad(18.3)$$

with $f(r)$ a function only of r (but not the same function as in eqn 18.2). These functions correspond to nonzero angular

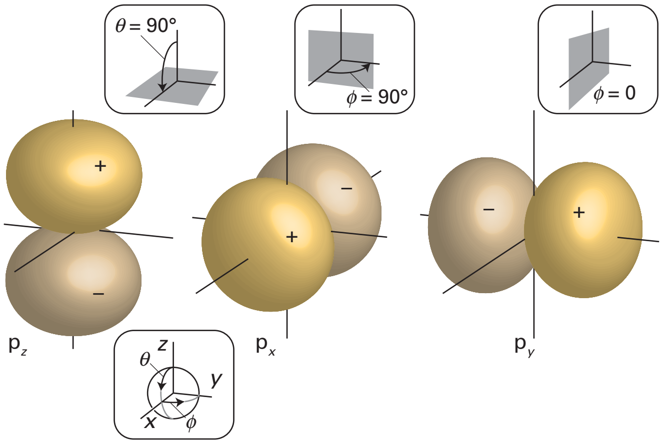


Figure 18.6 The boundary surfaces of 2p orbitals. A nodal plane passes through the nucleus and separates the two lobes of each orbital. The dark and light areas denote regions of opposite sign of the wavefunction. The angles of the spherical polar coordinate system are also shown. All p orbitals have boundary surfaces like those shown here.

momentum about the z-axis: $e^{+i\phi}$ corresponds to clockwise rotation when viewed from below, and $e^{-i\phi}$ corresponds to anticlockwise rotation (from the same viewpoint). They have zero amplitude where $\theta=0$ and 180° (along the z-axis) and maximum amplitude at $\theta=90°$, which is in the xy-plane.

To draw the functions in eqn 18.3, it is customary to construct two *real* wavefunctions that are linear combinations of the degenerate functions $\psi_{2p_{\pm1}}$. We show in the following *Justification* that it is permissible to take linear combinations of degenerate orbitals. In particular, we form the real linear combinations (using $e^{+i\phi}=\cos\phi\pm i\sin\phi$)

$$\psi_{2p_x}=-\frac{1}{2^{1/2}}(\psi_{2p_{+1}}-\psi_{2p_{-1}})=\overbrace{r\sin\theta\cos\phi}^{x}f(r) \qquad \text{2p}_x \text{ atomic orbital} \qquad (18.4a)$$
$$=xf(r)$$

$$\psi_{2p_y}=\frac{i}{2^{1/2}}(\psi_{2p_{+1}}+\psi_{2p_{-1}})=\overbrace{r\sin\theta\sin\phi}^{y}f(r) \qquad \text{2p}_y \text{ atomic orbital} \qquad (18.4b)$$
$$=yf(r)$$

Because the functions in eqn 18.4 are superpositions of states with equal and opposite values of m_l (namely, +1 and −1), the linear combinations are standing waves with no *net* orbital angular momentum around the z-axis.

Justification 18.2 The linear combination of degenerate wavefunctions

The freedom to take linear combinations of degenerate functions rests on the fact that whenever two or more wavefunctions correspond to the same energy (as is the case with $\psi_{2p_{+1}}$ and $\psi_{2p_{-1}}$), any linear combination of them (such as ψ_{2p_x} or ψ_{2p_y}) is an equally valid solution of the Schrödinger equation.

Suppose ψ_1 and ψ_2 are both solutions of the Schrödinger equation with energy E; then we know that $\hat{H}\psi_1=E\psi_1$ and $\hat{H}\psi_2=E\psi_2$. Now consider the linear combination $\psi=c_1\psi_1+c_2\psi_2$, where c_1 and c_2 are arbitrary coefficients. Then it follows that

$$\begin{aligned}\hat{H}\psi&=\hat{H}(c_1\psi_1+c_2\psi_2)=c_1\hat{H}\psi_1+c_2\hat{H}\psi_2\\&=c_1E\psi_1+c_2E\psi_2=E(c_1\psi_1+c_2\psi_2)=E\psi\end{aligned}$$

Hence, the linear combination is also a solution corresponding to the same energy E. The result that any linear combination of eigenfunctions of an operator all having the same eigenvalue is also an eigenfunction of the operator with the same eigenvalue applies to all quantum mechanical operators, not just the hamiltonian.

The $2p_x$ orbital has the same shape as a $2p_z$ orbital, but it is directed along the x-axis (see Fig. 18.6); the $2p_y$ orbital is similarly directed along the y-axis. The wavefunction of any p orbital of a given shell can be written as a product of x, y, or z and the same radial function (which depends on the value of n). The 2p hydrogenic wavefunctions presented in eqns 18.2–18.4 are collected in Table 18.1 as well as the 3p hydrogenic wavefunctions. All 2p orbitals have no radial nodes; 3p orbitals have one radial node, and np orbitals have $n-2$ radial nodes. These numbers, including that for s orbitals given earlier, are special cases of

Table 18.1 Hydrogenic atomic orbitals

s orbitals		
1s	$\psi_{1s}=\left(\frac{Z^3}{\pi a_0^3}\right)^{1/2}e^{-Zr/a_0}$	
2s	$\psi_{2s}=\left(\frac{Z^3}{32\pi a_0^3}\right)^{1/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$	
3s	$\psi_{3s}=\left(\frac{Z^3}{972\pi a_0^3}\right)^{1/2}\left(6-\frac{4Zr}{a_0}+\frac{4Z^2r^2}{9a_0^2}\right)e^{-Zr/3a_0}$	
p orbitals		
2p	With $f(r)=\frac{1}{(32\pi)^{1/2}}\left(\frac{Z}{a_0}\right)^{5/2}e^{-Zr/2a_0}$	
	Polar form	**Cartesian form**
	$\psi_{2p_0}=r\cos\theta f(r)$	$\psi_{2p_x}=xf(r)$
	$\psi_{2p_{\pm1}}=\mp\frac{1}{2^{1/2}}r\sin\theta e^{\pm i\phi}f(r)$	$\psi_{2p_y}=yf(r)$
		$\psi_{2p_z}=zf(r)$
3p	With $f(r)=\left(\frac{2}{729\pi}\right)^{1/2}\left(\frac{Z}{a_0}\right)^{5/2}\left(2-\frac{Zr}{3a_0}\right)e^{-Zr/3a_0}$	
	$\psi_{3p_0}=r\cos\theta f(r)$	$\psi_{3p_x}=xf(r)$
	$\psi_{3p_{\pm1}}=\mp\frac{1}{2^{1/2}}r\sin\theta e^{\pm i\phi}f(r)$	$\psi_{3p_y}=yf(r)$
		$\psi_{3p_z}=zf(r)$
d orbitals		
3d	With $f(r)=\left(\frac{2}{6561\pi}\right)^{1/2}\left(\frac{Z}{a_0}\right)^{7/2}e^{-Zr/3a_0}$	
	$\psi_{3d_0}=\left(\frac{1}{12}\right)^{1/2}r^2(3\cos^2\theta-1)f(r)$	$\psi_{3d_{z^2}}=\left(\frac{1}{12}\right)^{1/2}(3z^2-r^2)f(r)$
		$\psi_{3d_{x^2-y^2}}=\frac{1}{2}(x^2-y^2)f(r)$
	$\psi_{3d_{\pm1}}=\mp\left(\frac{1}{2}\right)^{1/2}r^2\cos\theta\sin\theta e^{\pm i\phi}f(r)$	$\psi_{3d_{xy}}=xyf(r)$
		$\psi_{3d_{yz}}=yzf(r)$
		$\psi_{3d_{zx}}=zxf(r)$
	$\psi_{3d_{\pm2}}=\left(\frac{1}{8}\right)^{1/2}r^2\sin^2\theta e^{\pm2i\phi}f(r)$	

the general expression that a hydrogenic orbital with quantum numbers n and l has $n-l-1$ radial nodes and l nodal planes.

Brief illustration 18.2 The 2p$_x$ orbital

The angular variation of the 2p$_x$ orbital is proportional to $\sin\theta\cos\phi$, so the probability density, which is proportional to $\sin^2\theta\cos^2\phi$, has its maximum values at $\theta=90°$ (where $\sin^2\theta=1$) and $\phi=0$ and 180° (where $\cos^2\phi=1$). Therefore, the electron is most likely to be found on either side of the nucleus along the x-axis (Fig. 18.6). In addition, the wavefunction is zero (and passes through zero) at $\theta=0$, 180° and $\phi=90°$, 270°, so the yz-plane is a nodal plane.

Self-test 18.3 Identify the nodal plane of the 2p$_y$ orbital.

Answer: xz-plane

(c) d Orbitals

When $n=3$, l can be 0, 1, or 2. As a result, this shell consists of one 3s orbital, three 3p orbitals, and five 3d orbitals. The five d orbitals have $m_l=+2, +1, 0, -1, -2$ and correspond to five different components of the angular momenta around the z-axis (but the same *magnitude* of angular momentum, because $l=2$ in each case). As for the p orbitals, d orbitals with opposite values of m_l (and hence opposite senses of motion around the z-axis) may be combined in pairs to give real standing waves (the d orbital with $m_l=0$ is real and designated d$_{z^2}$). The boundary surfaces of the resulting 3d orbitals are shown in Fig. 18.7. The 3d orbitals and their real combinations are collected in Table 18.1.

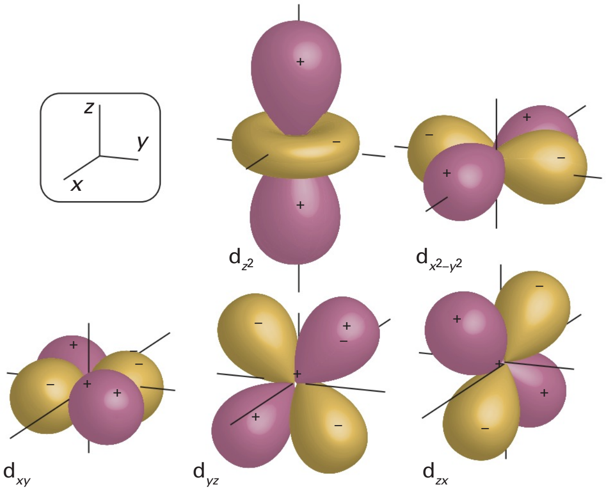


Figure 18.7 The boundary surfaces of 3d orbitals. Two nodal planes in each orbital intersect at the nucleus and separate the lobes of each orbital. The dark and light areas denote regions of opposite sign of the wavefunction. All d orbitals have boundary surfaces like those shown here.

Example 18.2 Finding the most probable locations of an electron

Find the most probable location of an electron occupying the 3d$_{z^2}$ orbital in the hydrogen atom.

Method The 3d$_{z^2}$ orbital corresponds to $n=3$, $l=2$, $m_l=0$. To find the most probable location of the electron, construct the probability density $|\psi_{nlm_l}|^2$ by using Table 18.1 and then find its maxima by finding where the first derivative of the probability density vanishes.

Answer The 3d$_{z^2}$ hydrogen atomic orbital is

$$\psi_{3d_{z^2}}=R_{3,2}(r)Y_{2,0}(\theta,\phi)=\left(\frac{1}{7776\pi a_0^3}\right)^{1/2}\left(\frac{2r}{3a_0}\right)^2\mathrm{e}^{-r/3a_0}(3\cos^2\theta-1)$$

$$=Nr^2\mathrm{e}^{-r/3a_0}(3\cos^2\theta-1)\qquad N=\left(\frac{1}{39366\pi a_0^7}\right)^{1/2}$$

Therefore,

$$\psi_{3d_{z^2}}^2=N^2r^4\mathrm{e}^{-2r/3a_0}(3\cos^2\theta-1)^2$$

The probability density, which is independent of ϕ, has maxima at $\theta=0$, 180° (where $\cos\theta=\pm1$, $\cos^2\theta=1$, and $3\cos^2\theta-1=2$), so the electron is most likely to be found on either side of the z-axis. To find the most probable distance r from the electron to the nucleus, we need to find, by differentiation, the maximum in the function $r^4\mathrm{e}^{-2r/3a_0}$:

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(\overbrace{r^4}^{f}\,\overbrace{\mathrm{e}^{-2r/3a_0}}^{g}\right)=\overbrace{4r^3\mathrm{e}^{-2r/3a_0}}^{(\mathrm{d}f/\mathrm{d}r)g}-\overbrace{\frac{2}{3a_0}r^4\mathrm{e}^{-2r/3a_0}}^{f(\mathrm{d}g/\mathrm{d}r)}$$

$$=2r^3\mathrm{e}^{-2r/3a_0}(2-r/3a_0)$$

where we have used the product rule of differentiation ($\mathrm{d}fg=f\mathrm{d}g+g\mathrm{d}f$; *Mathematical background* 1). This function is zero where the term in parenthesis is zero (ignore $r=0$ which corresponds to a minimum in the function), which is at $r=6a_0$. Therefore the most probable locations of the electron are at a distance of $6a_0$ from the nucleus on either side of the z-axis.

Self-test 18.4 Identify the nodal planes of the 3d$_{xy}$ orbital for the hydrogen atom.

Answer: xz- and yz-planes

18.2 Radial distribution functions

The wavefunction tells us, through the value of $|\psi|^2$, the probability of finding an electron in any region in space. Imagine a probe with a volume $\mathrm{d}\tau$ that is sensitive to electrons and can move around near the nucleus of a hydrogenic atom. Because

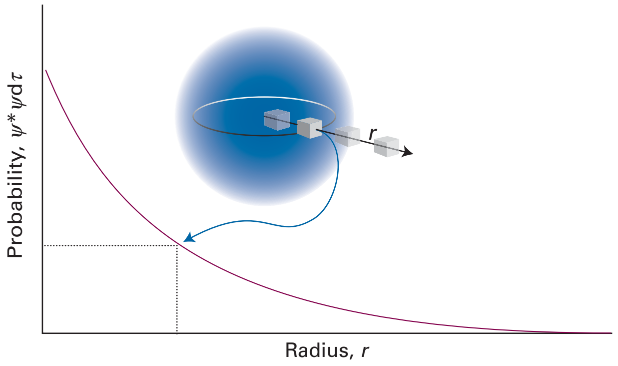


Figure 18.8 A constant-volume electron-sensitive detector (the small cube) gives its greatest reading at the nucleus, and a smaller reading elsewhere. The same reading is obtained anywhere on a circle of given radius: the s orbital is spherically symmetrical.

the probability density in the ground state of the atom is $|\psi_{1s}|^2 \propto \mathrm{e}^{-2Zr/a_0}$, the reading from the probe decreases exponentially as the probe is moved out along any radius but is constant if the probe is moved on a circle of constant radius (Fig. 18.8).

Now consider the probability of finding the ground-state electron *anywhere* between the two walls of a spherical shell of thickness dr at a radius r. The sensitive volume of the probe is now the volume of the shell (Fig. 18.9), which is $4\pi r^2\mathrm{d}r$ (the product of its surface area, $4\pi r^2$, and its thickness, dr). The probability that the 1s electron will be found between the inner and outer surfaces of this shell is the probability density at the radius r multiplied by the volume of the probe, or $|\psi_{1s}|^2\times 4\pi r^2\,\mathrm{d}r$. This expression has the form $P(r)\mathrm{d}r$, where

$$P(r)=4\pi r^2|\psi_{1s}|^2 \qquad (18.5\text{a})$$

Ground-state hydrogenic orbital Radial distribution function

In the following *Justification* we show that the more general expression, which applies to any orbital, is

$$P(r)=r^2R(r)^2 \qquad (18.5\text{b})$$

Definition Radial distribution function

where $R(r)$ is the radial wavefunction for the orbital in question.

Justification 18.3 The general form of the radial distribution function

The probability of finding an electron in a volume element dτ when its wavefunction is $\psi=RY$ is $R^2|Y|^2\,\mathrm{d}\tau$ with $\mathrm{d}\tau=r^2\,\mathrm{d}r\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$ (recall that R is real). The total probability of finding the electron at any angle at a constant radius is the integral of this probability over the surface of a sphere of radius r, and is written $P(r)\mathrm{d}r$; so

$$\begin{aligned}P(r)\mathrm{d}r&=\int_0^{\pi}\int_0^{2\pi}\overbrace{R(r)^2|Y(\theta,\phi)|^2}^{|\psi|^2}\overbrace{r^2\mathrm{d}r\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi}^{\mathrm{d}\tau}\\&=r^2R(r)^2\,\mathrm{d}r\overbrace{\int_0^{\pi}\int_0^{2\pi}|Y(\theta,\phi)|^2\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi}^{1}\\&=r^2R(r)^2\,\mathrm{d}r\end{aligned}$$

The last equality follows from the fact that the spherical harmonics are normalized to 1 (see Example 18.1). It follows that $P(r)=r^2R(r)^2$, as stated in the text.

The **radial distribution function**, $P(r)$, is a probability density in the sense that when it is multiplied by dr, it gives the probability of finding the electron anywhere between the two walls of a spherical shell of thickness dr at the radius r. For a 1s orbital, with $R_{1,0}$ given in Table 17.1,

$$P(r)=\frac{4Z^3}{a_0^3}r^2\mathrm{e}^{-2Zr/a_0} \qquad (18.6)$$

Ground-state hydrogenic orbital Radial distribution function

We can interpret this expression as follows:

- Because $r^2=0$ at the nucleus, $P(0)=0$. Although the probability density itself is a maximum at the nucleus, the radial distribution function is zero at $r=0$ on account of the r^2 factor.
- As $r\to\infty$, $P(r)\to 0$ on account of the exponential term.
- The increase in r^2 and the decrease in the exponential factor means that $P(r)$ passes through a maximum at an intermediate radius (see Fig. 18.9).

Physical interpretation

The maximum of $P(r)$, which can be found by differentiation, marks the most probable distance from the nucleus at which the electron will be found.

The radial distribution functions of the hydrogen atom for $n=1, 2, 3$ are shown in Fig.18.10. Note how the most probable distance of the electron from the nucleus increases with n but it shifts to lower values as the quantum number l increases within a given shell. The small secondary maxima close to the nucleus might seem insignificant, but in Topic 20 we see that they have great significance for the structure of the periodic table.

Example 18.3 Identifying the most probable radius

Identify the most probable radius, r^*, at which an electron will be found when it occupies a 1s orbital of a hydrogenic atom of atomic number Z, and tabulate the values for the one-electron species from H to Ne^{9+}.

Method Find the radius at which the radial distribution function of the hydrogenic 1s orbital has a maximum value by solving $\mathrm{d}P/\mathrm{d}r=0$. You will need to use the rule for differentiating a product of functions (*Mathematical background* 1: $\mathrm{d}(fg)/\mathrm{d}x=f(\mathrm{d}g/\mathrm{d}x)+g(\mathrm{d}f/\mathrm{d}x)$).

Answer The radial distribution function is given in eqn 18.6. It follows (by using the product rule again) that

$$\frac{\mathrm{d}P}{\mathrm{d}r}=\frac{4Z^3}{a_0^3}\frac{\mathrm{d}}{\mathrm{d}r}\left(\overbrace{r^2}^{f}\,\overbrace{\mathrm{e}^{-2Zr/a_0}}^{g}\right)=\frac{4Z^3}{a_0^3}\left(\overbrace{2r\mathrm{e}^{-2Zr/a_0}}^{(\mathrm{d}f/\mathrm{d}r)g}-\overbrace{\frac{2Zr^2}{a_0}\mathrm{e}^{-2Zr/a_0}}^{f(\mathrm{d}g/\mathrm{d}r)}\right)$$

$$=\frac{8Z^3}{a_0^3}r\left(1-\frac{Zr}{a_0}\right)\mathrm{e}^{-2Zr/a_0}$$

This function is zero where the term in parentheses is zero (reject $r=0$, which corresponds to a minimum in P), which is at

$$r^*=\frac{a_0}{Z}$$

That is, the most probable distance of the electron from the nucleus in a hydrogen atom ($Z=1$) is the Bohr radius itself, $a_0=52.9$ pm. For other hydrogenic species, the most probable radius lies at

Notice how the 1s orbital is drawn towards the nucleus as the nuclear charge increases. At uranium the most probable radius is only 0.58 pm, almost 100 times closer than for hydrogen. (On a scale where $r^*=10$ cm for H, $r^*=1$ mm for U^{91+}.) The electron then experiences strong accelerations and relativistic effects are important.

	He^{+}	Li^{2+}	Be^{3+}	B^{4+}	C^{5+}	N^{6+}	O^{7+}	F^{8+}	Ne^{9+}
r^*/pm	26.5	17.6	18.2	10.6	8.82	7.56	6.61	5.88	5.29

Self-test 18.5 Find the most probable distance of an electron from the nucleus in a hydrogenic atom when it occupies a 2s orbital.

Answer: $[(3+5^{1/2})a_0/Z$; for H: 277 pm

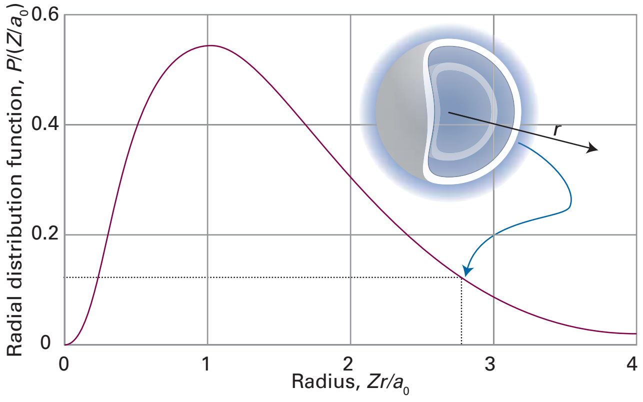


Figure 18.9 The radial distribution function P is the probability density that the electron will be found anywhere in a shell of radius r; the probability itself is $P\mathrm{d}r$, where $\mathrm{d}r$ is the thickness of the shell. For a 1s electron in hydrogen, P is a maximum when r is equal to the Bohr radius a_0. The value of $P\mathrm{d}r$ is equivalent to the reading that a detector shaped like a spherical shell of thickness $\mathrm{d}r$ would give as its radius is varied.

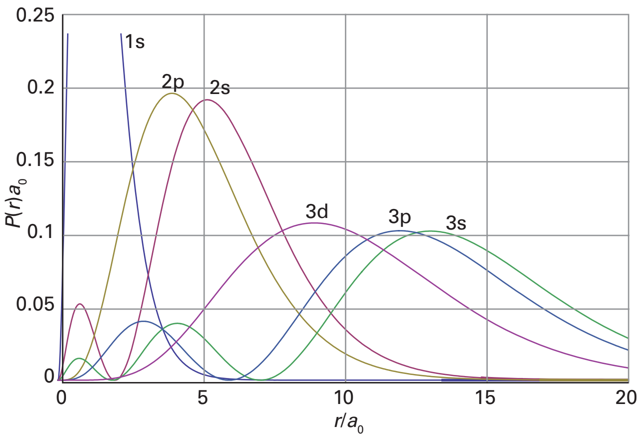


Figure 18.10 The radial distribution functions of the hydrogen atom for $n=1, 2, 3$ and the allowed values of l in each case.

We have taken only the first steps in our exploration of atomic structure. The preceding discussion of hydrogenic atomic orbitals provides the basis for understanding the electronic structure and periodic properties of many-electron atoms (Topic 19), as well as aspects of atomic spectroscopy (Topic 21). Furthermore, an elaboration of the concept of an orbital is used in the description of the electronic structure of molecules (Topics 22–30).

Checklist of concepts

☐ 1. A **shell** of an atom consists of all the orbitals of a given value of n: K($n=1$); L ($n=2$); M ($n=3$); N ($n=4$); …

☐ 2. A **subshell** of a shell of an atom consists of all the orbitals with the same value of n but different values of l: s ($l=0$); p ($l=1$); d ($l=2$); f ($l=3$); g ($l=4$); …

☐ 3. Each shell consists of n^2 orbitals.

☐ 4. Each subshell consists of $2l+1$ orbitals.

☐ 5. A **boundary surface** is the surface that captures a high proportion (typically about 90 per cent) of the electron probability density.

☐ 6. The **radial distribution function** is the probability density of finding the electron anywhere at a distance r from the nucleus.

Checklist of equations

Property	Equation	Comment	Equation number
Ground-state (1s) wavefunction	$\psi=(Z^3/\pi a_0^3)^{1/2}\mathrm{e}^{-Zr/a_0}$	Hydrogenic atom	18.1
Radial distribution function	$P(r)=4\pi r^2\lvert\psi_{1s}\rvert^2$	Ground state of hydrogenic atom	18.5a
Radial distribution function	$P(r)=r^2R(r)^2$	Definition	18.5b

TOPIC 19

Many-electron atoms

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➤ Why do you need to know this material?

Atoms are the currency of chemistry, and although hydrogenic atoms provide an excellent introduction to atomic orbitals, it is essential to see how to adapt those concepts to the description of the electronic structure of many-electron atoms as a basis for understanding chemical periodicity, which is treated in Topic 20.

➤ What is the key idea?

Electrons occupy orbitals in such a way as to achieve the lowest total energy subject to the requirements of the Pauli principle.

➤ What do you need to know already?

You need to be familiar with the concept of atomic orbitals (Topic 18), which are the basis of the discussion in this Topic. The introduction to electron spin makes use of some of the conclusions about angular momentum in Topic 14.

The Schrödinger equation for a many-electron atom is highly complicated because all the electrons interact with one another. Even for a helium atom, with its two electrons, no analytical expression for the wavefunctions and energies can be given, and we are forced to make approximations. We shall adopt a simple approach, called the 'orbital approximation', based on the structure of hydrogenic atoms and the energies of orbitals.

19.1 The orbital approximation

The wavefunction of a many-electron atom is a very complicated function of the coordinates of all the electrons, and we should write it $\psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots)$, where $\boldsymbol{r}_i$ is the vector from the nucleus to electron *i*. However, in the **orbital approximation** we suppose that a reasonable first approximation to this exact wavefunction is obtained by thinking of each electron as occupying its 'own' orbital, and write the product

$$\psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots)=\psi(\boldsymbol{r}_1)\psi(\boldsymbol{r}_2)\ldots \qquad \text{Orbital approximation} \qquad (19.1)$$

We can think of the individual orbitals as resembling the hydrogenic orbitals of Topic 18, but corresponding to nuclear charges modified by the presence of all the other electrons in the atom. This description is only approximate, as explained in the following *Justification*, but it is a useful model for discussing the chemical properties of atoms, and is the starting point for more sophisticated descriptions of atomic structure.

Justification 19.1 The orbital approximation

The orbital approximation would be exact if there were no interactions between electrons. To demonstrate the validity of this remark for a two-electron atom, we need to consider a system in which the hamiltonian for the energy is the sum of two contributions, one for electron 1 and the other for electron 2:

$$\hat{H}=\hat{H}_1+\hat{H}_2$$

In an actual atom (such as helium), there is an additional term corresponding to the interaction of the two electrons, but we are ignoring that term. We now show that if $\psi(r_1)$ is an eigenfunction of $\hat{H}_1$ with energy E_1, and $\psi(r_2)$ is an eigenfunction of $\hat{H}_2$ with energy E_2, then the product $\psi(r_1,r_2)=\psi(r_1)\psi(r_2)$ is an eigenfunction of the combined hamiltonian $\hat{H}$. To do so we write

$$\begin{aligned}\hat{H}\psi(r_1,r_2)&=(\hat{H}_1+\hat{H}_2)\psi(r_1)\psi(r_2)=\hat{H}_1\psi(r_1)\psi(r_2)+\psi(r_1)\hat{H}_2\psi(r_2)\\&=E_1\psi(r_1)\psi(r_2)+\psi(r_1)E_2\psi(r_2)=(E_1+E_2)\ \psi(r_1)\psi(r_2)\\&=E\psi(r_1,r_2)\end{aligned}$$

where $E=E_1+E_2$. This is the result we need to prove. However, if the electrons interact (as they do in fact), then the proof fails; nevertheless, it remains a reasonable and almost universally used starting point for the discussion of atomic structure.

The orbital approximation allows us to express the electronic structure of an atom by reporting its **configuration**, the list of occupied orbitals (usually, but not necessarily, in its ground state).

Brief illustration 19.1 Atomic configurations

As the ground state of a hydrogenic atom consists of the single electron in a 1s orbital, we report its configuration as $1s^1$ (read 'one s one'). The He atom has two electrons. We can imagine forming the atom by adding the electrons in succession to the orbitals of the bare nucleus (of charge $2e$). The first electron occupies a 1s hydrogenic orbital, but because $Z=2$ that orbital is more compact than in H itself. The second electron joins the first in the 1s orbital, so the electron configuration of the ground state of He is $1s^2$ ('one s two').

Self-test 19.1 Show that for the actual hamiltonian for a helium atom, with electron–electron repulsion included, that the proof in *Justification* 19.1 fails.

Answer: e^2/r_{12} term interferes with the argument

19.2 Factors affecting electronic structure

It is tempting to suppose that the electronic configurations of the atoms of successive elements with atomic numbers $Z=3, 4, \ldots$, and therefore with Z electrons, are simply $1s^Z$. That, however, is not the case. The reason lies in two aspects of nature: that electrons possess 'spin' and must obey the very fundamental 'Pauli principle'.

(a) Spin

The quantum mechanical property of electron **spin**, the possession of an intrinsic angular momentum, was identified by the experiment performed in 1921 by Otto Stern and Walther Gerlach, who shot a beam of silver atoms through an inhomogeneous magnetic field (Topic 14). Stern and Gerlach observed *two* bands of Ag atoms in their experiment. This observation seems to conflict with one of the predictions of quantum mechanics, because an angular momentum l gives rise to $2l+1$ orientations, which is equal to 2 only if $l=\frac{1}{2}$, contrary to the conclusion that l must be an integer. The conflict was resolved by the suggestion that the angular momentum they were observing was not due to orbital angular momentum (the motion of an electron around the atomic nucleus) but arose instead from an intrinsic angular momentum of the electron, which classically can be thought of as the rotation of the electron on its own axis. This intrinsic angular momentum, or 'spin', also emerged when Dirac combined quantum mechanics with special relativity and established the theory of relativistic quantum mechanics.

The spin of an electron does not have to satisfy the same boundary conditions as those for a particle circulating around a central point, so the quantum number for spin angular momentum is subject to different restrictions. To distinguish this spin angular momentum from orbital angular momentum we use the **spin quantum number** s (in place of the l in Topic 14; like l, s is a non-negative number) and m_s, the **spin magnetic quantum number**, for the projection on the z-axis. The magnitude of the spin angular momentum is $\{s(s+1)\}^{1/2}\hbar$ and the component $m_s\hbar$ is restricted to the $2s+1$ values $m_s=s, s-1, \ldots, -s$. To account for Stern and Gerlach's observation, $s=\frac{1}{2}$ and $m_s=\pm\frac{1}{2}$.

A note on good practice You will sometimes see the quantum number s used in place of m_s, and written $s=\pm\frac{1}{2}$. That is wrong: like l, s is never negative and denotes the magnitude of the spin angular momentum. For the z-component, use m_s.

The picture of spin as an actual spinning motion can be very useful when used with care. However, that is a classical picture of a quantum mechanical property, and it is better to regard spin as an intrinsic property of the electron, like its rest mass and its charge, with every electron having exactly the same unchangeable, characteristic value. On the vector model of angular momentum (Topic 14), the spin may lie in two different orientations (Fig. 19.1). One orientation corresponds to $m_s=+\frac{1}{2}$ (this state is often denoted α or $\uparrow$); the other orientation corresponds to $m_s=-\frac{1}{2}$ (this state is denoted β or $\downarrow$).

Other elementary particles have characteristic spin. For example, protons and neutrons are spin-$\frac{1}{2}$ particles (that is, $s=\frac{1}{2}$) and invariably spin with the same angular momentum. Because the masses of a proton and a neutron are so much greater than the mass of an electron, yet they all have the same spin angular momentum, the classical picture would be of these

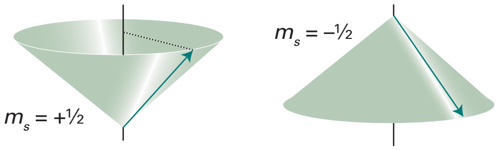

Figure 19.1 The vector representation of the spin of an electron. The length of the side of the cone is $3^{1/2}/2$ units and the projections are $\pm\frac{1}{2}$ units.

two particles spinning much more slowly than an electron. Some mesons are spin-1 particles (that is, $s=1$, as are some atomic nuclei), but for our purposes the most important spin-1 particle is the photon. The importance of photon spin in spectroscopy is explained in Topic 40; proton spin is the basis of Topic 47 (Magnetic resonance).

Brief illustration 19.2 Spin

The magnitude of the spin angular momentum, like any angular momentum, is $\{s(s+1)\}^{1/2}\hbar$. For any spin-$\frac{1}{2}$ particle, not only electrons, this angular momentum is $(\frac{3}{4})^{1/2}\hbar = 0.866\hbar$, or 9.13×10^{-35} J s. The component on the z-axis is $m_s\hbar$, which for a spin-$\frac{1}{2}$ particle is $\pm\frac{1}{2}\hbar$, or $\pm5.27\times10^{-35}$ J s.

Self-test 19.2 Evaluate the spin angular momentum of a photon.

Answer: $2^{1/2}\hbar = 1.49\times10^{-34}$ J s

Particles with half–integral spin are called **fermions** and those with integral spin (including 0) are called **bosons**. Thus, electrons and protons are fermions and photons are bosons. It is a very deep feature of nature that all the elementary particles that constitute matter are fermions whereas the elementary particles that are responsible for the forces that bind fermions together are all bosons. Photons, for example, transmit the electromagnetic force that binds together electrically charged particles. Matter, therefore, is an assembly of fermions held together by forces conveyed by bosons.

(b) The Pauli principle

The role of spin in determining electronic structure becomes apparent as soon as we consider lithium, $Z=3$, and its three electrons. The first two occupy a 1s orbital drawn even more closely than in He around the more highly charged nucleus. The third electron, however, does not join the first two in the 1s orbital because that configuration is forbidden by the **Pauli exclusion principle**:

> No more than two electrons may occupy any given orbital, and if two do occupy one orbital, then their spins must be paired.

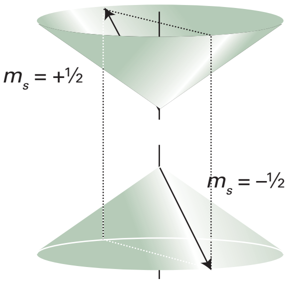

Figure 19.2 Electrons with paired spins have zero resultant spin angular momentum. They can be represented by two vectors that lie at an indeterminate position on the cones shown here, but wherever one lies on its cone, the other points in the opposite direction; their resultant is zero.

Electrons with paired spins, denoted ↑↓, have zero net spin angular momentum because the spin of one electron is cancelled by the spin of the other. Specifically, one electron has $m_s=+\frac{1}{2}$, the other has $m_s=-\frac{1}{2}$, and they are orientated on their respective cones so that the resultant spin is zero (Fig. 19.2). The exclusion principle is the key to the structure of complex atoms, to chemical periodicity, and to molecular structure. It was proposed by Wolfgang Pauli in 1924 when he was trying to account for the absence of some lines in the spectrum of helium. Later he was able to derive a very general form of the principle from theoretical considerations.

The Pauli exclusion principle in fact applies to any pair of identical fermions. Thus it applies to protons, neutrons, and ^{13}C nuclei (all of which have spin $\frac{1}{2}$) and to ^{35}Cl nuclei (which have spin $\frac{3}{2}$). It does not apply to identical bosons, which include photons (spin 1) and ^{12}C nuclei (spin 0). Any number of identical bosons may occupy the same state.

The Pauli exclusion principle is a special case of a general statement called the **Pauli principle**:

> When the labels of any two identical fermions are exchanged, the total wavefunction changes sign; when the labels of any two identical bosons are exchanged, the total wavefunction retains the same sign.

By 'total wavefunction' is meant the entire wavefunction, including the spin of the particles; that is, the total wavefunction must be a function of the positions as well as spins of the particles. To see that the Pauli principle implies the Pauli exclusion principle, we consider the (total) wavefunction for two electrons, $\psi(1,2)$. The Pauli principle implies that it is a fact of nature (which has its roots in the theory of relativity) that the wavefunction must change sign if we interchange the labels 1 and 2 wherever they occur in the function: $\psi(2,1) = -\psi(1,2)$. That the Pauli principle implies the Pauli exclusion principle is shown in the following *Justification*.

Justification 19.2 The Pauli exclusion principle

To derive the Pauli exclusion principle from the more fundamental Pauli principle we need to infer what spin states are allowed when two electrons in an atom occupy the same orbital ψ. According to the orbital approximation, the overall spatial wavefunction is $\psi(1)\psi(2)$. There are several possibilities for two spins: both electrons can be in state α, denoted $\alpha(1)\alpha(2)$; both β, denoted $\beta(1)\beta(2)$; and one α the other β, denoted either $\alpha(1)\beta(2)$ or $\alpha(2)\beta(1)$. Because we cannot tell which electron is α and which is β, in the last case it is appropriate to express the spin states as the (normalized) linear combinations

$$\sigma_+(1,2)=(1/2^{1/2})\{\alpha(1)\beta(2)+\beta(1)\alpha(2)\} \tag{19.2a}$$

$$\sigma_-(1,2)=(1/2^{1/2})\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\} \tag{19.2b}$$

because these combinations allow one spin to be α and the other β with equal probability. A stronger justification for taking these two linear combinations is that they correspond to eigenfunctions of the total spin operators S^2 and S_z, with $S=1$, $M_s=0$ for σ_+ and $S=0$, $M_S=0$ for σ_-. A crucial point is that the latter combination, with zero net spin angular momentum, corresponds to the two electrons being paired (↑↓).

The total wavefunction of the system is the product of the orbital part and one of the four spin states:

$$\psi(1)\psi(2)\alpha(1)\alpha(2) \qquad \psi(1)\psi(2)\beta(1)\beta(2)$$
$$\psi(1)\psi(2)\sigma_+(1,2) \qquad \psi(1)\psi(2)\sigma_-(1,2)$$

The Pauli principle implies that for a total wavefunction to be acceptable (for electrons), it must change sign when the electrons are exchanged. In each case, exchanging the labels 1 and 2 converts the factor $\psi(1)\psi(2)$ into $\psi(2)\psi(1)$, which is the same, because the order of multiplying the functions does not change the value of the product. The same is true of $\alpha(1)\alpha(2)$ and $\beta(1)\beta(2)$. Therefore, the first two overall products (of the four listed above) are not allowed, because they do not change sign. The combination $\sigma_+(1,2)$ changes to

$$\sigma_+(2,1)=(1/2^{1/2})\{\alpha(2)\beta(1)+\beta(2)\alpha(1)\}=\sigma_+(1,2)$$

because it is simply the original function written in a different order. The third overall product is therefore also disallowed. All the terms in grey are therefore disallowed. Finally, consider $\sigma_-(1,2)$:

$$\begin{aligned}\sigma_-(2,1)&=(1/2^{1/2})\{\alpha(2)\beta(1)-\beta(2)\alpha(1)\}\\ &=-(1/2^{1/2})\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\}=-\sigma_-(1,2)\end{aligned}$$

This combination does change sign (it is 'antisymmetric'). Therefore the (blue) product $\psi(1)\psi(2)\sigma_-(1,2)$ also changes sign under particle exchange and is acceptable.

Now we see that only one of the four possible states is allowed by the Pauli principle, and the one that survives has paired α and β spins. This is the content of the Pauli exclusion principle. The exclusion principle is irrelevant when the orbitals occupied by the electrons are different, and both electrons may then have (but need not have) the same spin state. Nevertheless, even then the overall wavefunction must still be antisymmetric, and must still satisfy the more general Pauli principle itself.

Brief illustration 19.3 The Pauli principle

An excited state of He has the configuration $1s^12s^1$. One acceptable overall wavefunction that acknowledges that we cannot know which electron is in which orbital is $\{\psi_{1s}(1)\psi_{2s}(2)+\psi_{1s}(2)\psi_{2s}(1)\}\sigma_-(1,2)$, which is antisymmetric with respect to interchange of the two electrons. This wavefunction corresponds to the two electrons being paired and is a so-called 'singlet state' of the atom. The Self-test explores the possibilities of the electrons having parallel spins.

Self-test 19.3 Show that the $1s^12s^1$ configuration may also give rise to a 'triplet' state in which the spins are parallel.

Answer: $\psi_{1s}(1)\psi_{2s}(2)-\psi_{1s}(2)\psi_{2s}(1)$, which is antisymmetric, also acknowledges that we cannot know which electron is in which orbital, and it may be combined with $\alpha(1)\alpha(2)$, $\beta(1)\beta(2)$, or $\sigma_+(1,2)$

Now we can return to lithium. In Li ($Z=3$), the third electron cannot enter the 1s orbital because that orbital is already full: we say the K shell is **complete** and that the two electrons form a **closed shell**. Because a similar closed shell is characteristic of the He atom, we denote it [He]. The third electron is excluded from the K shell and must occupy the next available orbital, which is one with $n=2$ and hence belonging to the L shell. However, we now have to decide whether the next available orbital is the 2s orbital or a 2p orbital, and therefore whether the lowest energy configuration of the atom is $[\mathrm{He}]2s^1$ or $[\mathrm{He}]2p^1$.

(c) Penetration and shielding

In hydrogenic atoms all orbitals of a given shell are degenerate. In many-electron atoms, although orbitals of a given subshell remain degenerate, the subshells themselves have different energies. The difference can be traced to the fact that an electron in a many-electron atom experiences a Coulombic repulsion from all the other electrons present. If it is at a distance r from the nucleus, it experiences an average repulsion that can be represented by a point negative charge located at the nucleus and equal in magnitude to the total charge of the electrons

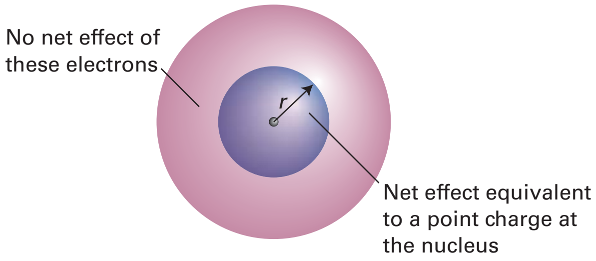

Figure 19.3 An electron at a distance *r* from the nucleus experiences a Coulombic repulsion from all the electrons within a sphere of radius *r* and which is equivalent to a point negative charge located on the nucleus. The negative charge reduces the effective nuclear charge of the nucleus from Ze to $Z_{\mathrm{eff}}e$.

within a sphere of radius r (Fig. 19.3). The effect of this point negative charge, when averaged over all the locations of the electron, is to reduce the full charge of the nucleus from Ze to $Z_{\mathrm{eff}}e$, the **effective nuclear charge**. In everyday parlance, Z_{eff} itself is commonly referred to as the 'effective nuclear charge'. We say that the electron experiences a **shielded** nuclear charge, and the difference between Z and Z_{eff} is called the **shielding constant**, σ:

$$Z_{\mathrm{eff}} = Z - \sigma \qquad \text{Effective nuclear charge} \qquad (19.3)$$

The electrons do not actually 'block' the full Coulombic attraction of the nucleus: the shielding constant is simply a way of expressing the net outcome of the nuclear attraction and the electronic repulsions in terms of a single equivalent charge at the centre of the atom.

The shielding constant is different for s and p electrons because they have different radial distribution functions (Fig. 19.4; also see Fig. 18.10). An s electron has a greater **penetration** through inner shells than a p electron, in the sense that it is more likely to be found close to the nucleus than a p electron of the same shell (the wavefunction of a p orbital, remember, is zero at the nucleus). Because only electrons inside the sphere defined by the location of the electron contribute to shielding, an s electron experiences less shielding than a p electron. Consequently, by the combined effects of penetration and shielding, an s electron is more tightly bound than a p electron of the same shell. Similarly, a d electron penetrates less than a p electron of the same shell (recall that the wavefunctions of orbitals are proportional to r^l close to the nucleus and therefore that a d orbital varies as r^2 close to the nucleus, whereas a p orbital varies as r), and therefore experiences more shielding. The consequence of penetration and shielding is that the energies of subshells of a shell in a many-electron atom in general lie in the order s < p < d < f.

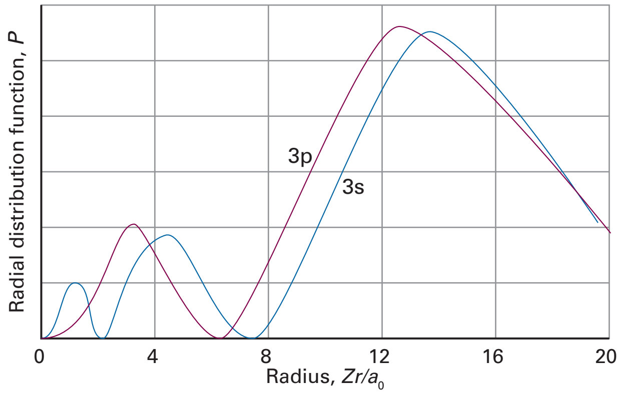

Figure 19.4 An electron in an s orbital (here a 3s orbital) is more likely to be found close to the nucleus than an electron in a p orbital of the same shell (note the closeness of the innermost peak of the 3s orbital to the nucleus at $r=0$). Hence an s electron experiences less shielding and is more tightly bound than a p electron.

Example 19.1 Analysing the extent of penetration

Although hydrogenic orbitals are only approximations to the orbitals of many-electron atoms, their properties give some insight into the extent of penetration. Explore the probability of finding an electron at a distance R from the nucleus for 3s, 3p, and 3d orbitals.

Method Use the radial distribution function (Topic 18) to calculate the total probability of finding the electron within a sphere of radius R by integration from $r=0$ to R. The radial wavefunctions are given in Table 17.1.

Answer The radial distribution function is $P_{nl}(r)=r^2R_{nl}(r)^2$, so we need to evaluate the total probability, $\bar{P}_{nl}(R)$, of being in a sphere of radius R:

$$\bar{P}_{nl}(R)=\int_0^R r^2R_{nl}^2(r)\mathrm{d}r$$

for the various radial wavefunctions. For instance, the 3s radial wavefunction is

$$R_{3,0}(r)=\frac{1}{243^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6-\frac{4Zr}{a_0}+\frac{4Z^2r^2}{9a_0^2}\right)\mathrm{e}^{-Zr/3a_0}$$

In each case the integral is best evaluated by using mathematical software, although hand integration is feasible (but tiresome). The results are plotted in Fig. 19.5. If, arbitrarily, we ask for the probability of finding the electron within a sphere of radius a_0/Z, we find

	3s ($l=0$)	3p ($l=1$)	3d ($l=2$)
$\bar{P}_{nl}(a_0/Z)$	0.0098	0.0013	0.000 006

These figures show that an electron in a 3s orbital is much more likely to be found close to the nucleus than one in a 3p orbital, which in turn is much more likely to be found close to the nucleus than one in a 3d orbital.

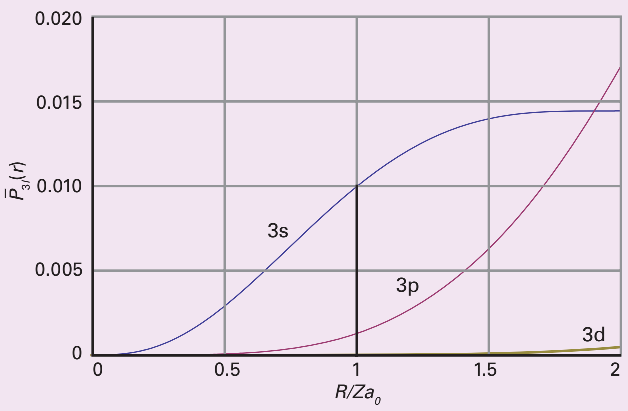

Figure 19.5 The results obtained in Example 19.1. The graphs show the total probability of an electron being inside a sphere of radius *R* when it occupies a 3s, 3p, and 3d orbital of a hydrogenic atom of atomic number *Z*.

Self-test 19.4 Repeat the analysis for orbitals of the L shell ($n=2$).

Answer: $\bar{P}_{2s}(a_0/Z)=0.0343$, $\bar{P}_{2p}(a_0/Z)=0.0036$

Shielding constants for different types of electrons in atoms have been calculated from their wavefunctions obtained by numerical solution of the Schrödinger equation (Table 19.1). We see that, in general, valence-shell s electrons do experience higher effective nuclear charges than p electrons, although there are some discrepancies which are considered in Topic 20.

We can now complete the Li story. Because the shell with $n=2$ consists of two non-degenerate subshells, with the 2s orbital lower in energy than the three 2p orbitals, the third electron occupies the 2s orbital. This occupation results in the ground-state configuration $1s^2 2s^1$, with the central nucleus surrounded by a complete helium-like shell of two 1s electrons, and around that a more diffuse 2s electron. The electrons in the outermost shell of an atom in its ground state are called the **valence electrons** because they are largely responsible for the chemical bonds that the atom forms. Thus, the valence electron in Li is a 2s electron and its other two electrons belong to its **core**, the inner electrons of the atoms.

Table 19.1* Effective nuclear charge, $Z_{\text{eff}}=Z-\sigma$

Element	Z	Orbital	Z_{eff}
He	2	1s	1.6875
C	6	1s	5.6727
		2s	3.2166
		2p	3.1358

*More values are given in the *Resource section*.

19.3 Self-consistent field calculations

The treatment we have given to the electronic configuration of many-electron species is only approximate because it is hopeless to expect to find exact solutions of a Schrödinger equation that takes into account the interaction of all the electrons with one another. However, computational techniques are available that give very detailed and reliable approximate solutions for the wavefunctions and energies. The techniques were originally introduced by D.R. Hartree (before computers were available) and then modified by V. Fock to take into account the Pauli principle correctly. These techniques are of great interest to chemists when applied to molecules, and are explained in detail in Topic 27; however, we should be aware of the general principles at this stage too. In broad outline, the **Hartree–Fock self-consistent field** (HF-SCF) procedure is as follows.

Imagine that we have an approximate idea of the structure of the atom. In the Ne atom, for instance, the orbital approximation suggests the configuration $1s^2 2s^2 2p^6$ with the orbitals approximated by hydrogenic atomic orbitals. Now consider one of the 2p electrons. A Schrödinger equation can be written for this electron by ascribing to it a potential energy due to the nuclear attraction and the repulsion from the other electrons. Although the equation is for the 2p orbital, it depends on the wavefunctions of all the other occupied orbitals in the atom. To solve the equation, we guess an approximate form of the wavefunctions of all the orbitals except 2p and then solve the Schrödinger equation for the 2p orbital. The procedure is then repeated for the 1s and 2s orbitals. This sequence of calculations gives the form of the 2p, 2s, and 1s orbitals, and in general they will differ from the set used initially to start the calculation. These improved orbitals can be used in another cycle of calculation, and a second improved set of orbitals and a better energy are obtained. The recycling continues until the orbitals and energies obtained are insignificantly different from those used at the start of the current cycle. The solutions are then self-consistent and accepted as solutions of the problem.

Figure 19.6 shows plots of some of the HF-SCF radial distribution functions for sodium. They show the grouping of electron density into shells, as was anticipated by the early chemists, and the differences of penetration as discussed above. These SCF calculations therefore support the qualitative discussions that are used to explain chemical periodicity (Topic 20). They also considerably extend that discussion by providing detailed wavefunctions and precise energies.

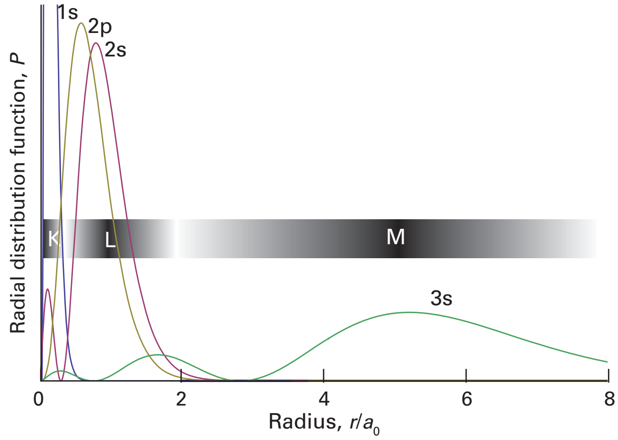

Figure 19.6 The radial distribution functions for the orbitals of Na based on SCF calculations. Note the shell-like structure, with the 3s orbital outside the inner concentric K and L shells.

Checklist of concepts

☐ 1. In the **orbital approximation** it is supposed that each electron occupies its 'own' orbital.

☐ 2. The **configuration** of an atom is the list of occupied orbitals.

☐ 3. The **Pauli exclusion principle** states that no more than two electrons may occupy any given orbital, and if two do occupy one orbital, then their spins must be paired.

☐ 4. A **fermion** is a particle with half-integral spin quantum number; a **boson** is a particle with integral spin quantum number.

☐ 5. An electron is a fermion with $s=\frac{1}{2}$.

☐ 6. The **Pauli principle** states that when the labels of any two identical fermions are exchanged, the total wavefunction changes sign; when the labels of any two identical bosons are exchanged, the total wavefunction retains the same sign.

☐ 7. The **effective nuclear charge,** $Z_{\text{eff}}e$, is the net charge experienced by an electron allowing for electron–electron repulsions.

☐ 8. **Shielding** is the effective reduction in charge of a nucleus by surrounding electrons.

☐ 9. **Penetration** is the ability of an electron to be found inside inner shells and close to the nucleus.

☐ 10. The outermost electrons of an atom are called its **valence electrons**; its inner electrons form the atom's **core**.

☐ 11. In the **Hartree–Fock self-consistent field** (HF-SCF) procedure the Schrödinger equation is solved numerically and iteratively until the solutions no longer change (to within certain criteria).

Checklist of equations

Property	Equation	Comment	Equation number
Orbital approximation	$\psi(r_1,r_2,\ldots)=\psi(r_1)\psi(r_2)\ldots$	Valid if electron–electron interactions ignored	19.1
Effective nuclear charge	$Z_{\text{eff}}=Z-\sigma$	Charge is actually $Z_{\text{eff}}e$	19.3

TOPIC 20

Periodicity

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➤ Why do you need to know this material?

The periodic table lies at the heart of chemistry, and it is essential for a chemist to understand the origins of the periodicity of the properties of the elements that the table summarizes.

➤ What is the key idea?

The periodic repetition of analogous configurations as electrons are added to nuclei accounts for the periodicity of the properties of the elements and the structure of the periodic table.

➤ What do you need to know already?

You need to be familiar with the concepts developed in Topic 19 concerning the features that govern the occupation of atomic orbitals.

Topic 19 introduces the considerations that allow us to predict the ground-state electron configurations of atoms. That Topic takes the story as far as lithium. This Topic extends the discussion to all the remaining elements. It also shows how certain chemically important atomic properties, such as atomic radii and ionization energies, reflect the configurations and vary periodically with increasing atomic number.

20.1 The building-up principle

The extension of the argument presented for lithium is called the **building-up principle**, or the *Aufbau principle*, from the German word for building up. We presume that it is familiar from introductory courses. In brief, we imagine the bare nucleus of atomic number Z, and then feed into the orbitals Z electrons in succession. The order of occupation, which reflects the consequences of shielding and penetration as explained in Topic 19, is

$$1s \quad 2s \quad 2p \quad 3s \quad 3p \quad 4s \quad 3d \quad 4p \quad 5s \quad 4d \quad 5p \quad 6s$$

According to the Pauli exclusion principle (Topic 19), each orbital may accommodate up to two electrons.

Brief illustration 20.1 The building-up principle

Consider the carbon atom, for which $Z=6$ and there are six electrons to accommodate. Two electrons enter and fill the 1s orbital, two enter and fill the 2s orbital, leaving two electrons to occupy the orbitals of the 2p subshell. Hence the ground-state configuration of C is $1s^22s^22p^2$, or more succinctly $[He]2s^22p^2$, with [He] the helium-like $1s^2$ core.

Self-test 20.1 Identify the ground-state configuration of a silicon atom.

Answer: $[Ne]3s^23p^2$ with $[Ne]=[He]2s^22p^6=1s^22s^22p^6$

We can be more precise than merely specifying the subshell: we can expect the last two electrons of carbon, as treated in *Brief illustration* 20.1, to occupy different 2p orbitals because they will then be further apart on average and repel each other less than if they were in the same orbital. Thus, one electron can be thought of as occupying the $2p_x$ orbital and the other the

$2p_y$ orbital (the x, y, z designation is arbitrary, and it would be equally valid to use the complex forms of these orbitals), and the lowest energy configuration of the atom is $[\mathrm{He}]2s^2 2p_x^1 2p_y^1$. The same rule applies whenever degenerate orbitals of a subshell are available for occupation. Thus, another rule of the building-up principle is:

> Electrons occupy different orbitals of a given subshell before doubly occupying any one of them.

For instance, nitrogen ($Z=7$) has the configuration $[\mathrm{He}]2s^2 2p_x^1 2p_y^1 2p_z^1$, and only when we get to oxygen ($Z=8$) is a 2p orbital doubly occupied, giving $[\mathrm{He}]2s^2 2p_x^2 2p_y^1 2p_z^1$. When electrons occupy orbitals singly we invoke **Hund's maximum multiplicity rule**:

> An atom in its ground state adopts a configuration with the greatest number of electrons with unpaired spins.

The explanation of Hund's rule is subtle, but it reflects the quantum mechanical property of **spin correlation**, that electrons with parallel spins behave as if they have a tendency to stay well apart (see the following *Justification*), and hence repel each other less. In essence, the effect of spin correlation is to allow the atom to shrink slightly, so the electron–nucleus interaction is improved when the spins are parallel. We can now conclude that in the ground state of the carbon atom, the two 2p electrons have the same spin, that all three 2p electrons in the N atom have the same spin, and that the two 2p electrons in different orbitals in the O atom have the same spin (the two in the $2p_x$ orbital are necessarily paired).

Justification 20.1 Spin correlation

Suppose electron 1 is described by a spatial wavefunction $\psi_a(\boldsymbol{r}_1)$ and electron 2 is described by a wavefunction $\psi_b(\boldsymbol{r}_2)$; then, in the orbital approximation, the joint wavefunction of the electrons is the product $\psi=\psi_a(\boldsymbol{r}_1)\psi_b(\boldsymbol{r}_2)$. However, this wavefunction is not acceptable, because it suggests that we know which electron is in which orbital, whereas we cannot keep track of electrons. According to quantum mechanics, the correct description is either of the two following wavefunctions:

$$\psi_{\pm}=(1/2)^{1/2}\{\psi_a(\boldsymbol{r}_1)\psi_b(\boldsymbol{r}_2)\pm\psi_b(\boldsymbol{r}_1)\psi_a(\boldsymbol{r}_2)\}$$

According to the Pauli principle, because ψ_+ is symmetrical under particle interchange, it must be multiplied by an antisymmetric spin function (the one denoted σ_- in eqn 19.2b). That combination corresponds to a spin-paired state. Conversely, ψ_- is antisymmetric, so it must be multiplied by one of the three symmetric spin states($\alpha(1)\alpha(2)$, $\beta(1)\beta(2)$, or $\sigma_+(1,2)$). These three symmetric states correspond to electrons with parallel spins (they correspond to eigenfunctions of the total spin operator $\hat{S}^2$ with $S=1$ as mentioned in Topic 19 and as more fully discussed in Topic 21).

Now consider the values of the two combinations $\psi_\pm$ when one electron approaches another, and eventually $\boldsymbol{r}_1=\boldsymbol{r}_2$. We see that ψ_- vanishes, which means that there is zero probability of finding the two electrons at the same point in space when they have parallel spins. The decreasing probability that the electrons approach one another in the state ψ_- is called a **Fermi hole**. The other combination does not vanish when the two electrons are at the same point in space. Because the two electrons have different relative spatial distributions depending on whether their spins are parallel or not, it follows that their Coulombic interaction is different, and hence that the two states have different energies, with the state corresponding to parallel spins being lower in energy.

However, we have to be cautious with this explanation, for it supposes that the original wavefunctions are unchanged. Detailed numerical calculations have shown that in the specific case of a helium atom electrons with parallel spins are actually closer together than those with antiparallel spins. The explanation in this case is that spin correlation between electrons with parallel spins allows the entire atom to shrink. Therefore, although the average separation is reduced, the electrons are found closer to the nucleus, which lowers their potential energy.

20.2 The configurations of the elements

Neon, with $Z=10$, has the configuration $[\mathrm{He}]2s^2 2p^6$, which completes the L shell. This closed-shell configuration is denoted [Ne], and acts as a core for subsequent elements. The next electron must enter the 3s orbital and begin a new shell, so an Na atom, with $Z=11$, has the configuration $[\mathrm{Ne}]3s^1$. Like lithium with the configuration $[\mathrm{He}]2s^1$, sodium has a single s electron outside a complete core. This analysis has brought us to the origin of chemical periodicity. The L shell is completed by eight electrons, so the element with $Z=3$ (Li) should have similar properties to the element with $Z=11$ (Na). Likewise, Be ($Z=4$) should be similar to $Z=12$ (Mg), and so on, up to the noble gases He ($Z=2$), Ne ($Z=10$), and Ar ($Z=18$).

Ten electrons can be accommodated in the five 3d orbitals, which accounts for the electron configurations of scandium to zinc. Calculations of the type discussed in Topic 27 show that for these atoms the energies of the 3d orbitals are always lower than the energy of the 4s orbital. However, spectroscopic results show that Sc has the ground-state configuration $[\mathrm{Ar}]3d^1 4s^2$, instead of $[\mathrm{Ar}]3d^3$ or $[\mathrm{Ar}]3d^2 4s^1$. To understand this observation, we have to consider the nature of electron–electron repulsions in 3d and 4s orbitals, where the effects are particularly

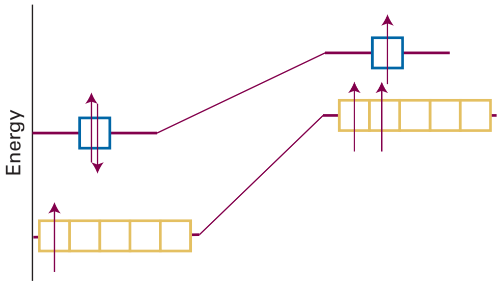

Figure 20.1 Strong electron–electron repulsions in the 3d orbitals are minimized in the ground state of Sc if the atom has the configuration $[Ar]3d^14s^2$ (shown on the left) instead of $[Ar]3d^24s^1$ (shown on the right). The total energy of the atom is lower when it has the $[Ar]3d^14s^2$ configuration despite the cost of populating the high energy 4s orbital.

finely balanced because there is only a small difference in energy between the orbitals. The most probable distance of a 3d electron (with no radial nodes) from the nucleus is less than that for a 4s electron (with three radial nodes), so two 3d electrons repel each other more strongly than two 4s electrons. As a result, Sc has the configuration $[Ar]3d^14s^2$ rather than the two alternatives, for then the strong electron–electron repulsions in the 3d orbitals are minimized. The total energy of the atom is least despite the cost of allowing electrons to populate the high energy 4s orbital (Fig. 20.1).

The effect just described is generally true for scandium through zinc, so their electron configurations are of the form $[Ar]3d^n4s^2$, where $n=1$ for scandium and $n=10$ for zinc. Two notable exceptions, which are observed experimentally, are Cr, with electron configuration $[Ar]3d^54s^1$, and Cu, with electron configuration $[Ar]3d^{10}4s^1$. The theoretical basis of the exceptions represented by Cr and Cu is the additional energy lowering characteristic of half-filled and completely filled d subshells.

At gallium, the building-up principle is used in the same way as in preceding periods. Now the 4s and 4p subshells constitute the valence shell, and the period terminates with krypton. Because 18 electrons have intervened since argon, this period is the first 'long period' of the periodic table. The existence of the d-block elements (the 'transition metals') reflects the stepwise occupation of the 3d orbitals, and the subtle shades of energy differences and effects of electron–electron repulsion along this series gives rise to the rich complexity of inorganic d-metal chemistry. A similar intrusion of the f orbitals in Periods 6 and 7 accounts for the existence of the f block of the periodic table (the lanthanoids and actinoids).

We derive the configurations of cations of elements in the s, p, and d blocks of the periodic table by removing electrons from the ground-state configuration of the neutral atom in a specific order. First, we remove valence p electrons, then valence s electrons, and then as many d electrons as are necessary to achieve the specified charge. The configurations of anions of the p-block elements are derived by continuing the building-up procedure and adding electrons to the neutral atom until the configuration of the next noble gas has been reached.

Brief illustration 20.2 The configurations of ions

Because the configuration of V is $[Ar]3d^34s^2$, the V^{2+} cation has the configuration $[Ar]3d^3$. It is reasonable that we remove the more energetic 4s electrons in order to form the cation, but it is not obvious why the $[Ar]3d^3$ configuration is preferred in V^{2+} over the $[Ar]3d^14s^2$ configuration, which is found in the isoelectronic Sc atom. Calculations show that the energy difference between $[Ar]3d^3$ and $[Ar]3d^14s^2$ depends on Z_{eff}. As Z_{eff} increases, transfer of a 4s electron to a 3d orbital becomes more favourable because the electron–electron repulsions are compensated by attractive interactions between the nucleus and the electrons in the spatially compact 3d orbital (see the 3d radial distribution function in Fig. 18.10). Indeed, calculations reveal that for a sufficiently large Z_{eff}, $[Ar]3d^3$ is lower in energy than $[Ar]3d^14s^2$. This conclusion explains why V^{2+} has an $[Ar]3d^3$ configuration and also accounts for the observed $[Ar]4s^03d^n$ configurations of the M^{2+} cations of Sc through Zn.

Self-test 20.2 Identify the configuration of the O^{2-} ion.

Answer: $[He]2s^22p^6=[Ne]$

20.3 The periodicity of atomic properties

Three atomic properties are of considerable importance for determining the chemical properties of the elements, namely atomic radii, ionization energies, and electron affinities. All three show periodic variation with increasing atomic number.

(a) Atomic radii

An atom does not have a precise radius because far from the nucleus the electron density falls off only exponentially (but sharply). However, we can expect atoms with numerous electrons to be larger, in some sense, than atoms that have only a few electrons. The **atomic radius** of an element is defined as half the distance of neighboring atoms in a solid (such as Cu) or, for non-metals, in a homonuclear molecule (such as H_2 or S_8). The data in Table 20.1 show that *atomic radii increase down a group*, and that they *decrease from left to right across a period*. These trends are readily interpreted in terms of the electronic structure of the atoms. On descending a group, the valence electrons are found in orbitals of successively higher principal quantum number. The atoms within the group have a greater

Table 20.1 Atomic radii of main-group elements, r/pm

Li 157	Be 112	B 88	C 77	N 74	O 66	F 64
Na 191	Mg 160	Al 143	Si 118	P 110	S 104	Cl 99
K 235	Ca 197	Ga 153	Ge 122	As 121	Se 117	Br 114
Rb 250	Sr 215	In 167	Sn 158	Sb 141	Te 137	I 133
Cs 272	Ba 224	Tl 171	Pb 175	Bi 182	Po 167	

number of completed shells of electrons in successive periods and hence their radii increase down the group. Across a period, the valence electrons enter orbitals of the same shell; however, the increase in effective nuclear charge across the period draws in the electrons and results in progressively more compact atoms. The general increase in radius down a group and decrease across a period should be remembered as they correlate well with trends in many chemical properties.

Period 6 shows an interesting and important modification to these otherwise general trends. The metallic radii in the third row of the d block are very similar to those in the second row, and not significantly larger as might be expected given their considerably greater numbers of electrons. For example, the atomic radii of Mo ($Z=42$) and W ($Z=74$) are 140 and 141 pm, respectively, despite the latter having many more electrons. The reduction of radius below that expected on the basis of a simple extrapolation down the group is called the **lanthanide contraction**. The name points to the origin of the effect. The elements in the third row of the d block (Period 6) are preceded by the elements of the first row of the f block, the lanthanoids, in which the 4f orbitals are being occupied. These orbitals have poor shielding properties and so the valence electrons experience more attraction from the nuclear charge than might be expected. The repulsions between electrons being added on crossing the f block fail to compensate for the increasing nuclear charge, so Z_{eff} increases from left to right across a period. The dominating effect of the latter is to draw in all the electrons and hence to result in a more compact atom. A similar contraction is found in the elements that follow the d block for the same reasons. For example, although there is a substantial increase in atomic radius between C and Si (77 and 118 pm, respectively), the atomic radius of Ge (122 pm) is only slightly greater than that of Si.

All monatomic anions are larger than their parent atoms and all monatomic cations are smaller than their parent atoms (in some cases, markedly so). The increase in radius of an atom on anion formation is a result of the greater electron–electron repulsions that occur when an additional electron is added to form an anion. There is also an associated decrease in the value of Z_{eff}. The smaller radius of a cation compared with its parent atom is a consequence not only of the reduction in electron–electron repulsions that follows electron loss but also of the fact that cation formation typically results in the loss of the valence electrons and an increase in Z_{eff}. That loss often leaves behind only the much more compact closed shells of electrons. Once these gross differences are taken into account, the variation in ionic radii through the periodic table mirrors that of the atoms.

(b) Ionization energies

The minimum energy necessary to remove an electron from a many-electron atom in the gas phase is the **first ionization energy**, I_1, of the element. The **second ionization energy**, I_2, is the minimum energy needed to remove a second electron (from the singly charged cation). Some numerical values are given in Table 20.2.

As will be familiar from introductory chemistry, ionization energies show periodicities (Fig. 20.2). Lithium has a low first ionization energy because its outermost electron is well shielded from the nucleus by the core electrons ($Z_{eff}=1.3$, compared with $Z=3$). The ionization energy of beryllium ($Z=4$) is greater but that of boron is lower because in the latter the outermost electron occupies a 2p orbital and is less strongly bound than if it had been a 2s electron.

The ionization energy increases from boron to nitrogen on account of the increasing nuclear charge. However, the ionization energy of oxygen is less than would be expected by simple extrapolation. The explanation is that at oxygen a 2p orbital must become doubly occupied, and the electron–electron

Table 20.2* First and second ionization energies

Element	I_1/(kJ mol^{-1})	I_2/(kJ mol^{-1})
H	1312	
He	2372	5250
Mg	738	1451
Na	496	4562

*More values are given in the *Resource section*.

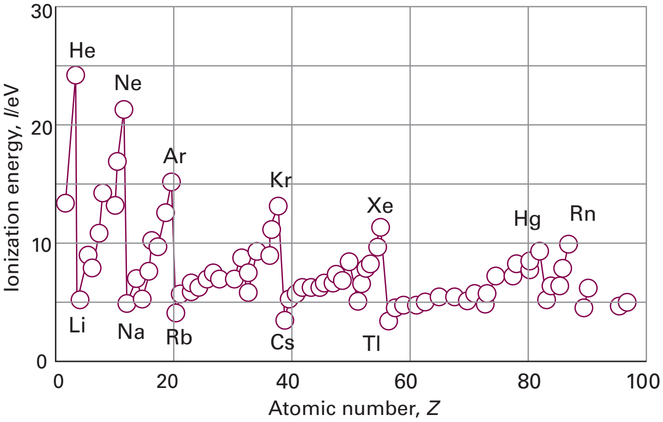

Figure 20.2 The first ionization energies of the elements plotted against atomic number.

repulsions are increased above what would be expected by simple extrapolation along the row. In addition, the loss of a 2p electron results in a configuration with a half-filled subshell (like that of N), which is an arrangement of low energy, so the energy of $O^+ + e^-$ is lower than might be expected, and the ionization energy is correspondingly low too. (The kink is less pronounced in the next row, between phosphorus and sulfur because their orbitals are more diffuse.) The values for oxygen, fluorine, and neon fall roughly on the same line, the increase of their ionization energies reflecting the increasing attraction of the more highly charged nuclei for the outermost electrons.

The outermost electron in sodium is 3s. It is far from the nucleus, and the latter's charge is shielded by the compact, complete neon-like core. As a result, the ionization energy of sodium is substantially lower than that of neon. The periodic cycle starts again along this row, and the variation of the ionization energy can be traced to similar reasons.

(c) Electron affinities

The **electron affinity**, E_{ea}, is the energy released when an electron attaches to a gas-phase atom (Table 20.3). In a common, logical, but not universal convention (which we adopt), the electron affinity is positive if energy is released when the electron attaches to the atom.

Electron affinities are greatest close to fluorine, for the incoming electron enters a vacancy in a compact valence shell and can interact strongly with the nucleus. The attachment of an electron to an anion (as in the formation of O^{2-} from O^-) invariably requires the absorption of energy, so E_{ea} is negative. The incoming electron is repelled by the charge already present. Electron affinities are also small, and may be negative, when an electron enters an orbital that is far from the nucleus (as in the heavier alkali metal atoms) or is forced by the Pauli principle to occupy a new shell (as in the noble gas atoms).

Table 20.3* **Electron** affinities, $E_{ea}/(\text{kJ mol}^{-1})$

Cl	349		
F	322		
H	73		
O	141	O^-	−844

*More values are given in the *Resource section*.

The values of ionization energies and electron affinities can help us to understand a great deal of chemistry and, through chemistry, biology. We can now begin to see why carbon is an essential building block of complex biological structures. Among the elements in Period 2, carbon has intermediate values of the ionization energy and electron affinity, so it can share electrons (that is, form covalent bonds) with many other elements, such as hydrogen, nitrogen, oxygen, sulfur, and, more importantly, other carbon atoms. As a consequence, such networks as long carbon–carbon chains (as in lipids) and chains of peptide links can form readily. Because the ionization energy and electron affinity of carbon are neither too high nor too low, the bonds in these covalent networks are neither too strong nor too weak. As a result, biological molecules are sufficiently stable to form viable organisms but are still susceptible to dissociation and rearrangement.

Checklist of concepts

☐ 1. The **building-up** (*Aufbau*) **principle** is the procedure for filling atomic orbitals that leads to the ground-state configuration of an atom.

☐ 2. **Hund's maximum multiplicity rule** states that an atom in its ground state adopts a configuration with the greatest number of electrons with unpaired spins.

☐ 3. Atomic radii typically decrease across a period and increase down a group.

☐ 4. The **lanthanide contraction** is the reduction in atomic radius of elements following the lanthanoids.

☐ 5. The **ionization energy** is the minimum energy necessary to remove an electron from an atom in the gas phase.

☐ 6. The **electron affinity** is the energy released when an electron attaches to an atom in the gas phase.

TOPIC 21

Atomic spectroscopy

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➤ Why do you need to know this material?

Atomic spectroscopy not only inspired the development of quantum mechanics but provides detailed information about the energies of electrons in atoms. The labels that specify atomic states, and their molecular counterparts, play a crucial role in spectroscopy, in the discussion of magnetic properties, in photochemistry, and in the description of the operation of lasers.

➤ What is the key idea?

Transitions take place between allowed energy states subject to selection rules that stem from the angular momentum of the photon and the conservation of angular momentum.

➤ What do you need to know already?

You need to be aware of the discussion of the energy levels of hydrogenic atoms (Topic 17) and how that discussion is extended to account for the structures of many-electron atoms (Topic 19). The discussion of selection rules makes use of the discussion of transitions (Topic 16).

The general idea behind atomic spectroscopy is straightforward: lines in the spectrum (in either emission or absorption) occur when the atom undergoes a transition with a change of energy $|\Delta E|$, and emits or absorbs a photon of frequency $\nu = |\Delta E|/h$ and wavenumber $\tilde{\nu} = |\Delta E|/hc$. Hence, we can expect the spectrum to give information about the energies of electrons in atoms. However, in many-electron atoms the actual energy levels are not given solely by the energies of the orbitals, because the electrons interact with one another in various ways, and it is necessary to consider contributions to the energy beyond those of the orbital approximation.

21.1 The spectrum of hydrogen

When an electric discharge is passed through gaseous hydrogen, the H_2 molecules are dissociated and the energetically excited H atoms that are generated emit light of discrete frequencies, producing a spectrum of a series of 'lines' (Fig. 21.1).

(a) The spectral series

The Swedish spectroscopist Johannes Rydberg noted (in 1890) that all the lines are described by the expression

$$\tilde{\nu} = \tilde{R}_{\mathrm{H}}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \tilde{R}_{\mathrm{H}} = 109\,677\,\mathrm{cm}^{-1} \qquad \text{Rydberg expression} \qquad (21.1)$$

with $n_1 = 1$ (the *Lyman series*), 2 (the *Balmer series*), 3 (the *Paschen series*), and 4 (the *Brackett series*), and that in each case $n_2 = n_1 + 1, n_1 + 2, \ldots$. The constant $\tilde{R}_{\mathrm{H}}$ is now called the **Rydberg constant** for the hydrogen atom (Topic 17).

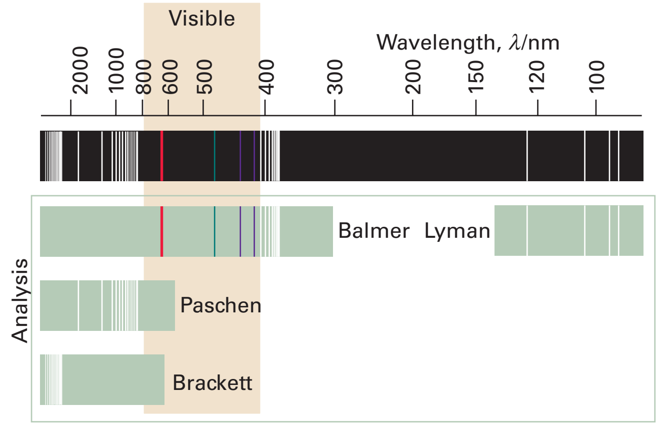

Figure 21.1 The spectrum of atomic hydrogen. Both the observed spectrum and its resolution into overlapping series are shown. Note that the Balmer series lies in the visible region.

The form of eqn 21.1 strongly suggests that each spectral line arises from a **transition**, a jump from one state to another, each with an energy proportional to $\tilde{R}_H/n^2$, with the difference in energy discarded as electromagnetic radiation of frequency (and wavenumber) given by the Bohr frequency condition ($\Delta E = h\nu$). As is shown in Topic 17, this is precisely the form of the energy levels of a hydrogen atom, and its explanation was an early triumph of quantum mechanics.

Example 21.1 Calculating the shortest and longest wavelength lines in a series

Determine the shortest and longest wavelength lines in the Balmer series.

Method Identify the value of n_1 for the Balmer series. The shortest-wavelength line corresponds to the largest wavenumber; from eqn 21.1, recognize that this line will arise from $n_2 = \infty$. The longest wavelength corresponds to the smallest wavenumber, which will arise from $n_2 = n_1 + 1$.

Answer The Balmer series corresponds to $n_1 = 2$. The largest wavenumber (use $n_2 = \infty$), calculated from eqn 21.1, is 27 419 cm^{-1}, which corresponds to a wavelength of 365 nm. The smallest wavenumber (use $n_2 = 3$) is 15 233 cm^{-1}, which corresponds to a wavelength of 656 nm.

Self-test 21.1 Calculate the shortest and longest wavelength lines in the Paschen series.

Answer: 821 nm, 1876 nm

(b) Selection rules

Although Topic 17 establishes the allowed energy levels of a hydrogenic atom as $-Z^2hc\tilde{R}_H/n^2$, not all conceivable transitions are allowed. As explained in Topic 16, it is necessary to identify and apply the selection rules. For hydrogenic atoms, the selection rules are derived by identifying the transitions that conserve angular momentum when a photon (a boson of spin 1) is emitted or absorbed:

$$\Delta l = \pm 1 \quad \Delta m_l = 0, \ \pm 1 \qquad \text{Hydrogenic atoms} \quad \text{Selection rules} \qquad (21.2)$$

The principal quantum number n can change by any amount consistent with the Δl for the transition, because it does not relate directly to the angular momentum. The mathematical basis of the selection rules is developed in the following *Justification*.

Brief illustration 21.1 Selection rules

To identify the orbitals to which a 4d electron may make radiative transitions, we first identify the value of l and then apply the selection rule for this quantum number. Because $l = 2$, the final orbital must have $l = 1$ or 3. Thus, an electron may make a transition from a 4d orbital to any np orbital (subject to $\Delta m_l = 0, \pm 1$) and to any nf orbital (subject to the same rule). However, it cannot undergo a transition to any other orbital, so a transition to any ns orbital or to another nd orbital is forbidden.

Self-test 21.2 To what orbitals may an electron in a 4s orbital make electric-dipole allowed radiative transitions?

Answer: to np orbitals only

Justification 21.1 The identification of selection rules

To determine the selection rules for atoms, we need to identify the conditions for which the transition dipole moment, μ_{fi}, (Topic 16) connecting the final state ψ_f and the initial state ψ_i is nonzero:

$$\mu_{q,n0} = \int \psi_n^* \hat{\mu}_q \psi_0 \mathrm{d}\tau \quad q = x, y, z$$

where $\hat{\mu}_q = -eq$. We consider each component in turn. To evaluate the integral, we note from Table 14.1 that $z = (4\pi/3)^{1/2} rY_{1,0}$, so

$$\int \psi_n^* \hat{\mu}_z \psi_0 \mathrm{d}\tau = \int_0^\infty \int_0^\pi \int_0^{2\pi} \overbrace{R_{n_f l_f} Y_{l_f m_{l,f}}^*}^{\psi_f^*} \overbrace{\left(\frac{4\pi}{3}\right)^{1/2} rY_{1,0}}^{z} \overbrace{R_{n_i l_i} Y_{l_i m_{l,i}}}^{\psi_i} \overbrace{r^2 \mathrm{d}r \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi}^{\mathrm{d}\tau}$$

This multiple integral is the product of three factors, an integral over r and two integrals over the angles, so the factor on the right can be grouped as follows:

$$\int \psi_f^* \mu_z \psi_i \mathrm{d}\tau = \left(\frac{4\pi}{3}\right)^{1/2} \int_0^\infty R_{n_f l_f} r R_{n_i l_i} r^2 \mathrm{d}r \int_0^\pi \int_0^{2\pi} Y_{l_f m_{l,f}}^* Y_{1,0} Y_{l_i m_{l,i}} \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi$$

We now use the property of spherical harmonics that

$$\int_0^{\pi}\int_0^{2\pi} Y_{l''m_l''}(\theta,\phi)^{*}\,Y_{l'm_l'}(\theta,\phi)Y_{lm_l}(\theta,\phi)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi=0$$

unless l, l', and l'' are integers denoting lengths of lines that can form the sides of a triangle (such as 1, 2, and 3, or 1, 1, and 1, but not 1, 2, and 4) and $m_l+m_l'+m_l''=0$. It follows that the angular integral (blue) is zero unless $l_\mathrm{f}=l_\mathrm{i}\pm 1$ and $m_{l,\mathrm{f}}=m_{l,\mathrm{i}}+m$. Because $m=0$ in the present case, the angular integral, and hence the z-component of the transition dipole moment, is zero unless $\Delta l=\pm 1$ and $\Delta m_l=0$, which is a part of the set of selection rules. The same procedure, but considering the x- and y-components (Problem 21.7), results in the complete set of rules.

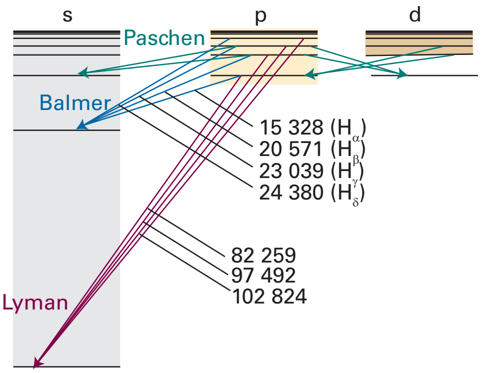

Figure 21.2 A Grotrian diagram that summarizes the appearance and analysis of the spectrum of atomic hydrogen. The thicker the line, the more intense the transition. The wavenumbers of the transitions (in cm^{-1}) are indicated.

The selection rules and the atomic energy levels jointly account for the structure of a **Grotrian diagram** (Fig. 21.2), which summarizes the energies of the states and the transitions between them. In some versions, lines of various thicknesses are used to denote their relative intensities in the spectrum obtained by evaluating the transition dipole moments.

21.2 Term symbols

The spectra of many-electron atoms are considerably richer than those of hydrogenic atoms. Although Topic 19 explains how to account for the ground-state configurations of atoms, to understand their spectra we need to examine their states in more detail, especially their excited states, and to consider the transitions between them. A complication we immediately encounter is that a single configuration of an atom, such as the excited configuration of He, $1s^1 2s^1$ for instance, or the ground state of C, $[He]2s^2 2p^2$, can give rise to a number of different individual states with various energies. Our first task is to identify these states and find a way to label them with a **term symbol**, a symbol that specifies the state.

The key to identifying the various states that can arise from a configuration and attaching a term symbol is the angular momentum of the electrons: that includes their orbital angular momentum, their spin, and their total angular momentum. Our first job is to identify the allowed values of these angular momenta for atoms with more than one electron.

(a) The total orbital angular momentum

Consider an atom with two electrons outside a closed core, so there are two sources of orbital angular momentum. We suppose that the orbital angular momentum quantum numbers of the two electrons are l_1 and l_2. If the electron configuration of the atoms we are considering is p^2, both electrons are in p orbitals and $l_1=l_2=1$. The total angular momenta that can arise from a configuration depends on the magnitudes and the relative orientation of these individual momenta, and is described by the **total orbital angular momentum quantum number**, L, a non-negative integer obtained by using the **Clebsch–Gordan series**:

$$L=l_1+l_2,\,l_1+l_2-1,\,\ldots,\,|l_1-l_2| \qquad \text{Clebsch–Gordan series} \qquad (21.3)$$

For instance, if $l_1=l_2=1$, then $L=2$, 1, and 0. Once we know the value of the L we can calculate the magnitude of the total orbital angular momentum from $\{L(L+1)\}^{1/2}\hbar$. As for any angular momentum, the total orbital angular momentum has $2L+1$ orientations, distinguished by the quantum number M_L, which can take the values L, $L-1$, …, $-L$.

Just as we use lowercase letters to tell us the value of l, so we use an uppercase letter to tell us the value of L. The code for converting the value of L into a letter is the same as for the s, p, d, f,… designation of orbitals, but uses uppercase letters:

L:	0	1	2	3	4	5	6…
	S	P	D	F	G	H	I…

Thus a p^2 configuration can give rise to D, P, and S terms. A closed shell has zero orbital angular momentum because all the individual orbital angular momenta sum to zero. Therefore, when working out term symbols, we need consider only the electrons of the unfilled shell. In the case of a single electron outside a closed shell, the value of L is the same as the value of l; so the configuration $[Ne]3s^1$ has only an S term.

Example 21.2 Deriving the total orbital angular momentum of a configuration

Find the terms that can arise from the configurations (a) d^2, (b) p^3.

Method Use the Clebsch–Gordan series and begin by finding the minimum value of L (so that we know where the series terminates). When there are more than two electrons to couple together, use two series in succession: first couple two electrons, and then couple the third to each combined state, and so on.

Answer (a) The minimum value is $|l_1 - l_2| = |2 - 2| = 0$. Therefore,

$$L = 2+2,\ 2+2-1, \ldots, 0 = 4,\ 3,\ 2,\ 1,\ 0$$

corresponding to G, F, D, P, S terms, respectively. (b) Coupling two electrons gives a minimum value of $|1 - 1| = 0$. Therefore,

$$L' = 1+1,\ 1+1-1, \ldots, 0 = 2,\ 1,\ 0$$

Now couple $l_3 = 1$ with $L' = 2$, to give $L = 3, 2, 1$; with $L' = 1$, to give $L = 2, 1, 0$; and with $L' = 0$, to give $L = 1$. The overall result is

$$L = 3,\ 2,\ 2,\ 1,\ 1,\ 1,\ 0$$

giving one F, two D, three P, and one S term.

Self-test 21.3 Repeat the question for the configurations (a) f^1d^1 and (b) d^3.

Answer: (a) H, G, F, D, P; (b) I, 2H, 3G, 4F, 5D, 3P, S

The terms that arise from a given configuration differ in energy due to the Coulombic interaction between the electrons. For example, to achieve a D ($L = 2$) term from a $2p^13p^1$ configuration, both electrons need to be circulating in the same direction around the nucleus, but to achieve an S ($L = 0$) term, they would need to be circulating in opposite directions. In the former arrangement, they do not meet; in the latter they do. On the basis of this classical picture, we can suspect that the repulsion between them will be higher if they meet, and therefore that the S term will lie higher in energy than the D term. The quantum mechanical analysis of the problem supports this interpretation.

(b) The total spin angular momentum

The energy of a term also depends on the relative orientation of the electron spins. Topic 20 provides a hint of this dependence, where it explains that spin correlation results in states with parallel spins having a lower energy than states with antiparallel spins. Parallel (unpaired) and antiparallel (paired) spins differ in their overall spin angular momentum. In the paired case, the two spin momenta cancel each other, and there is zero net spin (as is depicted in Fig. 19.2), and so once again we are brought to a correlation between an angular momentum, in this case spin, and an energy.

When there are several electrons to be taken into account, we must assess their **total spin angular momentum quantum number**, S (a non-negative integer or half integer). To do so, we use the Clebsch–Gordan series, this time in the form

$$S = s_1 + s_2,\ s_1 + s_2 - 1, \ldots, |s_1 - s_2| \qquad (21.4)$$

noting that each electron has $s = \frac{1}{2}$, which gives $S = 1, 0$ for two electrons (Fig. 21.3). If there are three electrons, the total spin angular momentum is obtained by coupling the third spin to each of the values of S for the first two spins, which results in $S = \frac{3}{2}$ and $S = \frac{1}{2}$.

The value of S for a term is expressed by giving the **multiplicity** of a term, the value of $2S+1$, as a left-superscript on the term symbol. Thus, ^{1}P is a 'singlet' term ($S = 0$, $2S+1 = 1$) and ^{3}P is a 'triplet' term ($S = 1$, $2S+1 = 3$). The multiplicity actually tells us the number of permitted values of $M_S = S, S-1, \ldots, -S$ for the given value of S, and hence the number of orientations in space that the total spin can adopt. We shall see the importance of this information shortly.

A note on good practice Throughout our discussion of atomic spectroscopy, distinguish italic S, the total spin quantum number, from Roman S, the term label. Thus, ^{3}S is a triplet term with $S = 1$ (and $L = 0$). All state symbols are upright; all quantum numbers and physical observables are oblique (sloping).

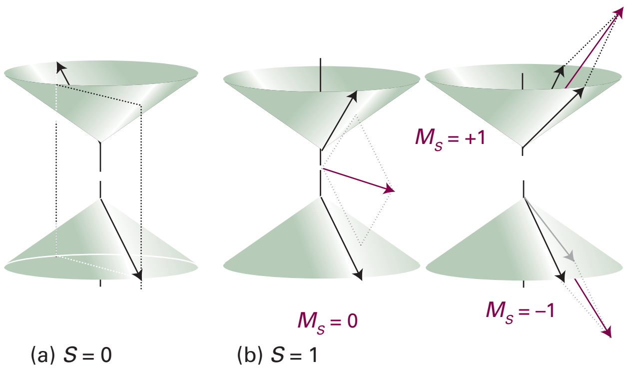

Figure 21.3 (a) Electrons with paired spins have zero resultant spin angular momentum ($S = 0$). They can be represented by two vectors that lie at an indeterminate position on the cones shown here, but wherever one lies on its cone, the other points in the opposite direction; their resultant is zero. (b) When two electrons have parallel spins, they have a nonzero total spin angular momentum ($S = 1$). There are three ways of achieving this resultant, which are shown by these vector representations. Note that, whereas two paired spins are precisely antiparallel, two 'parallel' spins are not strictly parallel.

Brief illustration 21.2 The multiplicities of terms

When $S=0$ (as for a closed shell, like $1s^2$), $M_S=0$, the electron spins are all paired, and there is no net spin: this arrangement gives a singlet term, ^1S. A single electron has $S=s=\frac{1}{2}$ ($M_S=m_s=\pm\frac{1}{2}$), so a configuration such as $[Ne]3s^1$ can give rise to a doublet term, ^2S. Likewise, the configuration $[Ne]3p^1$ is a doublet, ^2P. When there are two electrons with unpaired spins, $S=1$ ($M_S=\pm1, 0$), so $2S+1=3$, giving a triplet term, such as ^3D.

Self-test 21.4 What terms can arise from scandium in the excited configuration $[Ar]3s^23p^14p^1$?

Answer: $^{1,3}D, ^{1,3}P, ^{1,3}S$

It is explained in Topic 20 that the energies of two states, one with paired spins and one with unpaired spins, differ on account of the different effects of spin correlation. The fact that the parallel arrangement of spins, as in the $1s^12s^1$ configuration of the He atom, lies lower in energy than the antiparallel arrangement can now be expressed by saying that the triplet state of the $1s^12s^1$ configuration of He lies lower in energy than the singlet state. This is a general conclusion that applies to other atoms (and molecules), and *for states arising from the same configuration, the triplet state generally lies lower in energy than the singlet state*. The latter is an example of Hund's rule of maximum multiplicity (Topic 20) which can be restated as:

> For a given configuration, the term of greatest multiplicity lies lowest in energy.

Because the Coulombic interaction between electrons in an atom is strong, the difference in energies between singlet and triplet states of the same configuration can be large. The triplet and singlet terms of $He1s^12s^1$, for instance, differ by $6421\,\text{cm}^{-1}$ (corresponding to 0.80 eV).

Hund's rule of maximum multiplicity is the first of three rules devised by Friedrich Hund to identify the lowest energy term of a configuration with the minimum of calculation. The second rule is

> For a given multiplicity, the term with the highest value of L lies lowest in energy.

Therefore, as discussed above, a D term is expected to lie lower in energy than an S term of the same multiplicity. The third rule is introduced below after a discussion of spin–orbit coupling. The three rules are reliable only for the ground-state configuration of an atom.

(c) The total angular momentum

When there is a net orbital angular momentum and a net spin angular momentum in an atom, we can expect to be able to combine these angular momenta into a total angular momentum and—perhaps—for the energy of the atom to depend on its value. The **total angular momentum quantum number**, J (a non-negative integer or half integer), takes the values

$$J=L+S,\ L+S-1,\ \ldots,\ |L-S| \qquad \text{Total angular momentum} \qquad (21.5)$$

and, as usual, we can calculate the magnitude of the total angular momentum from $\{J(J+1)\}^{1/2}\hbar$. The specific value of J is given as a right-subscript on the term symbol; for example, a ^3P term with $J=2$ is fully dressed as $^3P_2$.

If $S\leq L$, there are $2S+1$ values of J for a given L, so the number of values of J is the same as the multiplicity of the term. Each possible value of J designates a **level** of a term, so provided $S\leq L$, the multiplicity tells us the number of levels. For example, the $[Ne]3p^1$ configuration of sodium (an excited state) has $L=1$ and $S=\frac{1}{2}$ and a multiplicity of 2; the two levels are $J=\frac{3}{2}$ and $\frac{1}{2}$ and the ^2P term therefore has two levels, $^2P_{3/2}$ and $^2P_{1/2}$.

Before moving on, we should note that there is a hidden assumption in eqn 21.5. We have assumed that the orbital angular momenta of the electrons all combine to give a total orbital angular momentum, that their spins all combine to give a total spin, and that only then do these two totals combine to give the overall total angular momentum of the atom. This procedure is called **Russell–Saunders coupling**. An alternative is that the orbital and spin angular momenta of each electron combine separately into a resultant for each one (with quantum number j), and then those resultants combine to give an overall total. We shall not deal with this so-called ***jj*-coupling** case: Russell–Saunders coupling turns out to be reasonably accurate for light atoms.

Example 21.3 Deriving term symbols

Write the term symbols arising from the ground-state configurations of (a) Na and (b) F, and (c) the excited-state configuration $1s^22s^22p^13p^1$ of C.

Method Begin by writing the configurations, but ignore inner closed shells. Then couple the orbital momenta to find L and the spins to find S. Next, couple L and S to find J. Finally, express the term as $^{2S+1}\{L\}_J$, where $\{L\}$ is the appropriate letter. For F, for which the valence configuration is $2p^5$, treat the single gap in the closed-shell $2p^6$ configuration as a single particle.

Answer (a) For Na, the configuration is $[Ne]3s^1$, and we consider the single 3s electron. Because $L=l=0$ and $S=s=\frac{1}{2}$, it is possible for $J=j=s=\frac{1}{2}$ only. Hence the term symbol is $^2S_{1/2}$. (b) For F, the configuration is $[He]2s^22p^5$, which we can treat as $[Ne]2p^{-1}$ (where the notation $2p^{-1}$ signifies the absence of a 2p electron). Hence $L=1$, and $S=s=\frac{1}{2}$. Two values of $J=j$ are allowed: $J=\frac{3}{2}, \frac{1}{2}$. Hence, the term symbols for the two levels are ${}^2P_{3/2}$, ${}^2P_{1/2}$. (c) We are treating an excited configuration of carbon because, in the ground configuration, 2p^2, the Pauli principle (Topic 19) forbids some terms, and deciding which survive (${}^1D$, ${}^3P$, ${}^1S$, in fact) is quite complicated.[1] That is, there is a distinction between 'equivalent electrons', which are electrons that occupy the same orbitals, and 'inequivalent electrons', which are electrons that occupy different orbitals; we consider only the latter here. The excited configuration of C under consideration is effectively 2p^{1}3p^1. This is a two-electron problem, and $l_1 = l_2 = 1$, $s_1 = s_2 = \frac{1}{2}$. It follows that $L = 2, 1, 0$ and $S = 1, 0$. The terms are therefore ${}^3D$ and ${}^1D$, ${}^3P$ and ${}^1P$, and ${}^3S$ and ${}^1S$. For ${}^3D$, $L = 2$ and $S = 1$; hence $J = 3, 2, 1$ and the levels are ${}^3D_3$, ${}^3D_2$, and ${}^3D_1$. For ${}^1D$, $L = 2$ and $S = 0$, so the single level is ${}^1D_2$. The triplet of levels of ${}^3P$ is ${}^3P_2$, ${}^3P_1$, and ${}^3P_0$, and the singlet is ${}^1P_1$. For the ${}^3S$ term there is only one level, ${}^3S_1$ (because $J = 1$ only), and the singlet term is ${}^1S_0$.

Self-test 21.5 Write down the terms arising from the configurations (a) 2s^{1}2p^1, (b) 2p^{1}3d^1.

Answer: (a) ${}^3P_2$, ${}^3P_1$, ${}^3P_0$, ${}^1P_1$;
(b) ${}^3F_4$, ${}^3F_3$, ${}^3F_2$, ${}^1F_3$, ${}^3D_3$, ${}^3D_2$, ${}^3D_1$, ${}^1D_2$, ${}^3P_2$, ${}^3P_1$, ${}^3P_0$, ${}^1P_1$

(d) Spin–orbit coupling

The different levels of a term, such as ${}^2P_{1/2}$ and ${}^2P_{3/2}$, have different energies due to **spin–orbit coupling**, a magnetic interaction between angular momenta. To see the origin of this coupling, we need to note that a circulating current gives rise to a magnetic moment (Fig. 21.4). The spin of an electron is one source of magnetic moment and its orbital angular momentum is another. Two magnetic dipole moments close to each other interact to an extent that depends on their relative orientation.

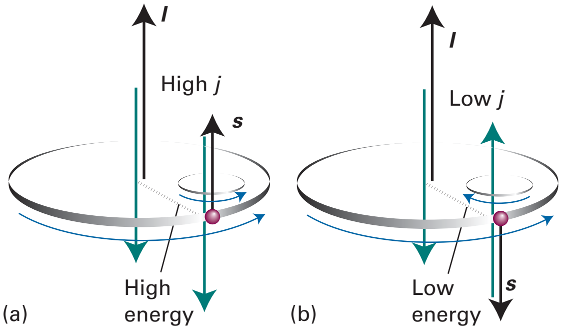

Figure 21.4 Spin–orbit coupling is a magnetic interaction between spin and orbital magnetic moments. When the angular momenta are parallel, as in (a), the magnetic moments are aligned unfavourably; when they are opposed, as in (b), the interaction is favourable. This magnetic coupling is the cause of the splitting of a configuration into levels.

However, the relative orientation of the two momenta also determines the electron's total angular momentum, so there is a correlation between the energy of interaction and the value of J. Magnetic dipole moments that are antiparallel (that is, lie in opposite directions) are lower in energy than when they are parallel; therefore, a lower energy is achieved when the orbital and spin angular momenta are antiparallel, corresponding to a lower value of J. In the case of the ${}^2P$ term, we predict that the ${}^2P_{1/2}$ level is lower in energy than the ${}^2P_{3/2}$ level. For a system with many electrons, a detailed analysis yields the following general statement, which is the third of Hund's rules:

Type of configuration	Order of levels
Less than half-full shell	Lowest value of J lies lowest in energy
More than half-full shell	Highest value of J lies lowest in energy

For a quantitative treatment of spin–orbit coupling, we need to include in the hamiltonian a term that depends on the relative orientation of the vectors that represent the spin and orbital angular momenta. The simplest procedure is to write the contribution as

$$\hat{H}_{\mathrm{so}} = \lambda \boldsymbol{L}\cdot\boldsymbol{S} \qquad \lambda = hc\tilde{A}/\hbar^2 \tag{21.6}$$

Spin–orbit coupling

where λ is a measure of the strength of the coupling, and for practical purposes best expressed as a wavenumber by introducing the parameter $\tilde{A}$. The quantity $\boldsymbol{L}\cdot\boldsymbol{S}$ is the scalar product of the vectors $\boldsymbol{L}$ and $\boldsymbol{S}$ (as we see in *Mathematical background* 4, $\boldsymbol{L}\cdot\boldsymbol{S}$ is proportional to cos θ, where θ is the angle between the two vectors, so the expression models the fact that the energy of interaction depends on the relative orientation of the two magnetic moments). To use this expression, we note that the total angular momentum is $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$, so

$$\boldsymbol{J}\cdot\boldsymbol{J} = (\boldsymbol{L}+\boldsymbol{S})\cdot(\boldsymbol{L}+\boldsymbol{S}) = L^2 + S^2 + 2\boldsymbol{L}\cdot\boldsymbol{S}$$

and therefore (because $\boldsymbol{J}\cdot\boldsymbol{J} = J^2$)

$$\lambda \boldsymbol{L}\cdot\boldsymbol{S} = \tfrac{1}{2}\lambda(J^2 - L^2 - S^2)$$

We now treat the J^2, L^2, and S^2 as operators with eigenvalues $J(J+1)\hbar^2$, $L(L+1)\hbar^2$, and $S(S+1)\hbar^2$, respectively. It then follows that the eigenvalues of $\hat{H}_{\mathrm{so}}$ are

$$E_{\mathrm{so}} = \tfrac{1}{2}hc\tilde{A}\{J(J+1) - L(L+1) - S(S+1)\} \tag{21.7}$$

Spin–orbit coupling energy

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[1] For details, see our *Inorganic chemistry*, Oxford University Press and W. H. Freeman & Co. (2014).

Brief illustration 21.3 Spin–orbit coupling energy

When $L=1$ and $S=\frac{1}{2}$, as in a ^{2}P term,

$$E_{\rm so}=\tfrac{1}{2}hc\tilde{A}\left\{J(J+1)-2-\tfrac{3}{4}\right\}=\tfrac{1}{2}hc\tilde{A}\left\{J(J+1)-\tfrac{11}{4}\right\}$$

Therefore, for a level with $J=\frac{3}{2}$, $E_{\rm so}=\frac{1}{2}hc\tilde{A}$, and for a level with $J=\frac{1}{2}$ from the same configuration, $E_{\rm so}=-hc\tilde{A}$. The separation of the two levels is therefore $\Delta E_{\rm so}=\frac{3}{2}hc\tilde{A}$.

Self-test 21.6 Confirm that the spin–orbit interaction leaves the mean energy of the ^{2}P term unchanged. *Hint*: Take account of the degeneracies of the two levels.

Answer: $4(\frac{1}{2}hc\tilde{A})+2(-hc\tilde{A})=0$

The strength of the spin–orbit coupling as measured by $\tilde{A}$ depends on the nuclear charge. To understand why this is so, imagine riding on the orbiting electron and seeing a charged nucleus apparently orbiting around us (like the Sun rising and setting). As a result, we find ourselves at the centre of a ring of current. The greater the nuclear charge, the greater this current, and therefore the stronger the magnetic field we detect. Because the spin magnetic moment of the electron interacts with this orbital magnetic field, it follows that the greater the nuclear charge, the stronger the spin–orbit interaction. The coupling increases sharply with atomic number (as Z^4 in hydrogenic atoms). Whereas it is only small in H (giving rise to shifts of energy levels of no more than about 0.4 cm^{-1}), in heavy atoms like Pb it is very large (giving shifts of the order of thousands of reciprocal centimetres).

Two spectral lines are observed when the p electron of an electronically excited alkali metal atom undergoes a transition and falls into a lower s orbital. The higher-frequency line is due to a transition starting in a ^{2}P$_{3/2}$ level and the other line is due to a transition starting in the ^{2}P$_{1/2}$ level of the same configuration. The presence of these two lines is an example of **fine structure**, the structure in a spectrum due to spin–orbit coupling.

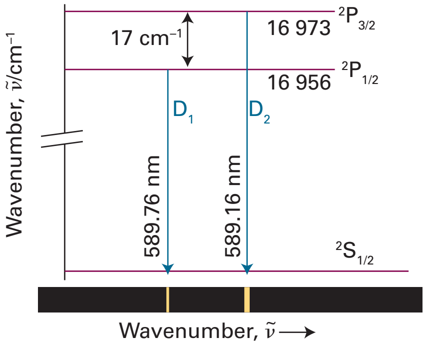

Figure 21.5 The energy–level diagram for the formation of the sodium D lines. The splitting of the spectral lines (by 17 cm^{-1}) reflects the splitting of the levels of the ^{2}P term.

Brief illustration 21.4 Fine structure

Fine structure can be seen in the emission spectrum from sodium vapour excited by an electric discharge (for example, in one kind of street lighting). The yellow line at 589 nm (close to 17 000 cm^{-1}) is actually a doublet composed of one line at 589.76 nm (16 956.2 cm^{-1}) and another at 589.16 nm (16 973.4 cm^{-1}); the components of this doublet are the 'D lines' of the spectrum (Fig. 21.5). Therefore, in Na, the spin–orbit coupling affects the energies by about 17 cm^{-1}.

Self-test 21.7 In the emission spectrum of potassium lines are observed at 766.70 nm and 770.11 nm. What is the spin–orbit coupling constant of potassium?

Answer: 57.75 cm^{-1}

21.3 Selection rules of many-electron atoms

Any state of the atom, and any spectral transition, can be specified by using term symbols. For example, the transitions giving rise to the yellow sodium doublet (which were shown in Fig. 21.5) are

$$3{\rm p}^1\ {}^2{\rm P}_{3/2}\rightarrow 3{\rm s}^1\ {}^2{\rm S}_{1/2}\qquad 3{\rm p}^1\ {}^2{\rm P}_{1/2}\rightarrow 3{\rm s}^1\ {}^2{\rm S}_{1/2}$$

By convention, the upper term precedes the lower. The corresponding absorptions are therefore denoted $^2{\rm P}_{3/2}\leftarrow{}^2{\rm S}_{1/2}$ and $^2{\rm P}_{1/2}\leftarrow{}^2{\rm S}_{1/2}$ (the configurations have been omitted).

We have seen (in *Justification* 21.1) that selection rules arise from the conservation of angular momentum during a transition and from the fact that a photon has a spin of 1. They can therefore be expressed in terms of the term symbols, because the latter carry information about angular momentum. A detailed analysis leads to the following rules:

$$\begin{gathered}\Delta S=0\quad \Delta L=0,\pm1\quad \Delta l=\pm1\\ \Delta J=0,\pm1,\ \text{but}\ J=0\leftarrow\!\!|\!\!\rightarrow J=0\end{gathered}\qquad \textit{Many-electron atoms}\quad \text{Selection rules}\tag{21.8}$$

where the symbol $\leftarrow\!|\!\rightarrow$ denotes a forbidden transition. The rule about ΔS (no change of overall spin) stems from the fact that the light does not affect the spin directly. The rules about ΔL and Δl express the fact that the orbital angular momentum of an individual electron must change (so $\Delta l=\pm1$), but whether or not this results in an overall change of orbital momentum depends on the coupling.

Brief illustration 21.5 Selection rules

If we were presented with the following possible transitions in the emission spectrum of a many-electron atom, namely $^3D_2 \rightarrow {}^3P_1$, $^3P_2 \rightarrow {}^1S_0$, and $^3F_4 \rightarrow {}^3D_3$ we could decide which are allowed by constructing the following table and referring to the rules in eqn 21.8. Forbidden values are in red.

	ΔS	ΔL	ΔJ	
$^3D_2 \rightarrow {}^3P_1$	0	−1	−1	Allowed
$^3P_2 \rightarrow {}^1S_0$	−1	−1	−2	Forbidden
$^3F_4 \rightarrow {}^3D_3$	0	−1	−1	Allowed

Self-test 21.8 Which of the transitions (a) $^2P_{3/2} \rightarrow {}^2S_{1/2}$, (b) $^3P_0 \rightarrow {}^3S_1$, (c) $^3D_3 \rightarrow {}^1P_1$ are allowed?

Answer: (a), (b)

The selection rules given above apply when Russell–Saunders coupling is valid (in light atoms). If we insist on labelling the terms of heavy atoms with symbols like ^3D, then we shall find that the selection rules progressively fail as the atomic number increases because the quantum numbers S and L become ill defined as *jj*-coupling becomes more appropriate. As explained above, Russell–Saunders term symbols are only a convenient way of labelling the terms of heavy atoms: they do not bear any direct relation to the actual angular momenta of the electrons in a heavy atom. For this reason, transitions between singlet and triplet states (for which $\Delta S = \pm 1$), while forbidden in light atoms, are allowed in heavy atoms.

Checklist of concepts

☐ 1. The **Lyman, Balmer, and Paschen series** in the spectrum of atomic hydrogen arise, respectively, from the transitions $n \rightarrow 1$, $n \rightarrow 2$, and $n \rightarrow 3$.

☐ 2. The wavenumbers of all the spectral lines of a hydrogen atom can be expressed in terms of transitions between allowed energy levels.

☐ 3. A **Grotrian diagram** summarizes the energies of the states and the transitions between them.

☐ 4. A **level** is a group of states with a common value of J.

☐ 5. The **multiplicity** of a term is the value of $2S+1$; provided $L \geq S$, the multiplicity is the number of levels of the term.

☐ 6. A **term symbol** is a symbolic specification of the state of an atom, $^{2S+1}\{L\}_J$.

☐ 7. **Hund's rules**, which allow the identification of the lowest energy term of a configuration, can be expressed as:

- The term with the maximum multiplicity lies lowest in energy.
- For a given multiplicity, the term with the highest value of L lies lowest in energy.
- For atoms with less than half-filled shells, the level with the lowest value of J lies lowest in energy; for more than half-filled shells, the highest value of J.

☐ 8. The allowed values of the total orbital angular momentum L of a configuration are obtained by using the **Clebsch–Gordan series** $L = l_1 + l_2, l_1 + l_2 - 1, \ldots, |l_1 - l_2|$.

☐ 9. The allowed values of the total spin angular momentum S are obtained by using the Clebsch–Gordan series $S = s_1 + s_2, s_1 + s_2 - 1, \ldots, |s_1 - s_2|$.

☐ 10. **Spin–orbit coupling** is the interaction of the spin magnetic moment with the magnetic field arising from the orbital angular momentum.

☐ 11. **Russell–Saunders coupling** is a coupling scheme based on the view that if spin–orbit coupling is weak, then it is effective only when all the orbital momenta are operating cooperatively.

☐ 12. The **total angular momentum** J, in the Russell–Saunders coupling scheme, has possible values $J = L + S$, $L + S - 1, \ldots, |L - S|$.

☐ 13. **Fine structure** is the structure in a spectrum due to spin–orbit coupling.

☐ 14. The **selection rules** for spectroscopic transitions in polyelectronic atoms are set out in the Checklist of equations below. They apply when Russell–Saunders coupling is valid.

Checklist of equations

Property	Equation	Comment	Equation number
Rydberg formula	$\tilde{\nu}=\tilde{R}_{\mathrm{H}}(1/n_1^2-1/n_2^2)$	$n_2=n_1+1, n_1+2, \ldots$	21.1
Selection rules	$\Delta l=\pm 1, \Delta m_l=0, \pm 1$	Hydrogenic atoms	21.2
Clebsch–Gordan series	$J=j_1+j_2, j_1+j_2-1, \ldots, \lvert j_1-j_2\rvert$	j an angular momentum quantum number	21.3
Spin–orbit coupling energy	$E_{\mathrm{so}}=\frac{1}{2}hc\tilde{A}\{J(J+1)-L(L+1)-S(S+1)\}$	Russell–Saunders coupling	21.7
Selection rules	$\Delta S=0$, $\Delta L=0, \pm 1$, $\Delta l=\pm 1$, $\Delta J=0, \pm 1$, but $J=0 \leftarrow\!\mid\!\rightarrow J=0$	Many-electron atoms and Russell–Saunders coupling	21.8

Focus 5 on Atomic structure and spectra

Topic 17 Hydrogenic atoms

Discussion questions

17.1 Discuss the separation of variables procedure as it is applied to simplify the description of a hydrogenic atom free to move through space.

17.2 List and discuss the significance of the quantum numbers needed to specify the internal state of a hydrogenic atom.

Exercises

17.1(a) Compute the ionization energy of the He^+ ion.
17.1(b) Compute the ionization energy of the Li^{2+} ion.

17.2(a) When ultraviolet radiation of wavelength 58.4 nm from a helium lamp is directed on to a sample of krypton, electrons are ejected with a speed of $1.59\times10^6\,m\,s^{-1}$. Calculate the ionization energy of krypton.
17.2(b) When ultraviolet radiation of wavelength 58.4 nm from a helium lamp is directed on to a sample of xenon, electrons are ejected with a speed of $1.79\times10^6\,m\,s^{-1}$. Calculate the ionization energy of xenon.

17.3(a) The wavefunction for the ground state of a hydrogen atom is Ne^{-r/a_0}. Determine the normalization constant N.
17.3(b) The wavefunction for the 2s orbital of a hydrogen atom is $N(2-r/a_0)e^{-r/2a_0}$. Determine the normalization constant N.

17.4(a) By differentiation of the 2s radial wavefunction, show that it has two extrema in its amplitude and locate them.
17.4(b) By differentiation of the 3s radial wavefunction, show that it has three extrema in its amplitude and locate them.

17.5(a) Locate the radial nodes in the 3p orbital of an H atom.
17.5(b) Locate the radial nodes in the 3d orbital of an H atom.

Problems

17.1 The *Humphreys series* is a group of lines in the spectrum of atomic hydrogen. It begins at 12 368 nm and has been traced to 3281.4 nm. What are the transitions involved? What are the wavelengths of the intermediate transitions?

17.2 A series of lines in the spectrum of atomic hydrogen lies at 656.46 nm, 486.27 nm, 434.17 nm, and 410.29 nm. What is the wavelength of the next line in the series? What is the ionization energy of the atom when it is in the lower state of the transitions?

17.3 Atomic units of length and energy may be based on the properties of a particular atom. The usual choice is that of a hydrogen atom, with the unit of length being the Bohr radius, a_0, and the unit of energy being the (negative of the) energy of the 1s orbital. If the positronium atom (e^+,e^-) were used instead, with analogous definitions of units of length and energy, what would be the relation between these two sets of atomic units?

17.4 Show that the radial wave equation (eqn 17.5) can be written in the form of eqn 17.6 by introducing the function $u=rR$.

17.5 Hydrogen is the most abundant element in all stars. However, neither absorption nor emission lines due to neutral hydrogen are found in the spectra of stars with effective temperatures higher than 25 000 K. Account for this observation.

17.6 The initial value of the principal quantum number n was not specified in Example 17.3. Show that the correct value of n can be determined by making several choices and selecting the one that leads to a straight line.

Topic 18 Hydrogenic atomic orbitals

Discussion questions

18.1 Describe how the presence of orbital angular momentum affects the shape of the atomic orbital.

18.2 Discuss the significance of (a) a boundary surface and (b) the radial distribution function for hydrogenic orbitals.

Exercises

18.1(a) What is the orbital angular momentum of an electron in the orbitals (a) 2s, (b) 3p, (c) 5f? Give the numbers of angular and radial nodes in each case.
18.1(b) What is the orbital angular momentum of an electron in the orbitals (a) 3d, (b) 4f, (c) 3s? Give the numbers of angular and radial nodes in each case.

18.2(a) What is the degeneracy of an energy level in the L shell of a hydrogenic atom?
18.2(b) What is the degeneracy of an energy level in the N shell of a hydrogenic atom?

18.3(a) State the orbital degeneracy of the levels in a hydrogen atom that have energy: (a) $-hc\tilde{R}_{\mathrm{H}}$; (b) $-\frac{1}{4}hc\tilde{R}_{\mathrm{H}}$; (c) $-\frac{1}{16}hc\tilde{R}_{\mathrm{H}}$.
18.3(b) State the orbital degeneracy of the levels in a hydrogenic atom (Z in parentheses) that have energy: (a) $-hc\tilde{R}_{\mathrm{atom}}$ (2); (b) $-\frac{1}{4}hc\tilde{R}_{\mathrm{atom}}$ (4); (c) $-\frac{25}{16}hc\tilde{R}_{\mathrm{atom}}$ (5).

18.4(a) Calculate the average kinetic and potential energies of an electron in the ground state of a He^+ ion.
18.4(b) Calculate the average kinetic and potential energies of a 3s electron in an H atom.

18.5(a) Compute the mean radius and the most probable radius for a 2s electron in a hydrogenic atom of atomic number Z.
18.5(b) Compute the mean radius and the most probable radius for a 2p electron in a hydrogenic atom of atomic number Z.

18.6(a) Write down the expression for the radial distribution function of a 3s electron in a hydrogenic atom and determine the radius at which the electron is most likely to be found.
18.6(b) Write down the expression for the radial distribution function of a 3p electron in a hydrogenic atom and determine the radius at which the electron is most likely to be found.

18.7(a) Locate the angular nodes and nodal planes of each of the 2p orbitals of a hydrogenic atom of atomic number Z. To locate the angular nodes, give the angle that the plane makes with the z-axis.
18.7(b) Locate the angular nodes and nodal planes of each of the 3d orbitals of a hydrogenic atom of atomic number Z. To locate the angular nodes, give the angle that the plane makes with the z-axis.

Problems

18.1 In 1976 it was mistakenly believed that the first of the 'superheavy' elements had been discovered in a sample of mica. Its atomic number was believed to be 126. What is the most probable distance of the innermost electrons from the nucleus of an atom of this element? (In such elements, relativistic effects are very important, but ignore them here.)

18.2 (a) Calculate the probability of the electron being found anywhere within a sphere of radius 53 pm for a hydrogenic atom. (b) If the radius of the atom is defined as the radius of the sphere inside which there is a 90 per cent probability of finding the electron, what is the atom's radius?

18.3 At what point in the hydrogen atom is there maximum probability of finding a (a) $2p_z$ electron, (b) $3p_z$ electron? How do these most probable points compare to the most probable radii for the locations of $2p_z$ and $3p_z$ electrons?

18.4 Show by explicit integration that hydrogenic (a) 1s and 2s orbitals are mutually orthogonal, (b) $2p_x$ and $2p_z$ orbitals are mutually orthogonal.

18.5‡ Explicit expressions for hydrogenic orbitals are given in Table 18.1. (a) Verify that the $3p_x$ orbital is normalized and that $3p_x$ and $3d_{xy}$ are mutually orthogonal. (b) Determine the positions of both the radial nodes and nodal planes of the 3s, $3p_x$, and $3d_{xy}$ orbitals. (c) Determine the mean radius of the 3s orbital. (d) Draw a graph of the radial distribution function for the three orbitals (of part (b)) and discuss the significance of the graphs for interpreting the properties of many-electron atoms. (e) Create both xy-plane polar plots and boundary-surface plots for these orbitals. Construct the boundary plots so that the distance from the origin to the surface is the absolute value of the angular part of the wavefunction. Compare the s, p, and d boundary surface plots with that of an f orbital; for example, $\psi_{\mathrm{f}} \propto x(5z^2-r^2) \propto \sin\theta(5\cos^2\theta-1)\cos\phi$.

18.6 Show that d orbitals with opposite values of m_l may be combined in pairs to give real standing waves with boundary surfaces, as shown in Fig. 18.7, and with forms that are given in Table 18.1.

18.7 As in Problem 18.2, the 'size' of an atom is sometimes considered to be measured by the radius of a sphere that contains 90 per cent of the probability density of the electrons in the outermost occupied orbital. Explore how the 'size' of a ground-state hydrogenic atom varies as the definition is changed to other percentages, and plot your conclusion.

18.8 A quantity important in some branches of spectroscopy is the probability density of an electron being found at the same location as the nucleus. Evaluate this probability density for an electron in the 1s, 2s, and 3s orbitals of a hydrogenic atom. What happens to the probability density when an orbital other than s is considered?

18.9 Some atomic properties depend on the average value of $1/r$ rather than the average value of r itself. Evaluate the expectation value of $1/r$ for (a) a hydrogen 1s orbital, (b) a hydrogenic 2s orbital, (c) a hydrogenic 2p orbital.

Topic 19 Many-electron atoms

Discussion questions

19.1 Distinguish between a fermion and a boson. Provide examples of each type of particle.

19.2 Describe the orbital approximation for the wavefunction of a many-electron atom. What are the limitations of the approximation?

19.3 Compare and contrast the properties of spin angular momentum and the properties of angular momentum arising from rotational motion in two and three dimensions.

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‡ These problems were supplied by Charles Trapp and Carmen Giunta.

Exercises

19.1(a) The classical picture of an electron is that of a sphere of radius $r_e = 2.82$ fm. On the basis of this model, how fast is a point on the equator of the electron moving? Is this answer plausible?

19.1(b) A proton has a spin angular momentum with $I = \frac{1}{2}$. Suppose it is a sphere of radius 1 fm. On the basis of this model, how fast is a point on the equator of the proton moving?

Problems

19.1 Derive an expression in terms of l and m_l for the half-angle of the apex of the cone used to represent an angular momentum according to the vector model. Evaluate the expression for an α spin. Show that the minimum possible angle approaches 0 as $l \to \infty$.

19.2‡ Stern–Gerlach splittings of atomic beams are small and require either large magnetic field gradients or long magnets for their observation. For a beam of atoms with zero orbital angular momentum, such as H or Ag, the deflection is given by $x = \pm(\mu_B L^2/4E_k)\mathrm{d}\mathcal{B}/\mathrm{d}z$, where $\mu_B = e\hbar/2m_e = 9.274 \times 10^{-24}$ J T^{-1} is known as the Bohr magneton (see inside front cover), L is the length of the magnet, E_k is the average kinetic energy of the atoms in the beam, and $\mathrm{d}\mathcal{B}/\mathrm{d}z$ is the magnetic field gradient across the beam. (a) Given that the average translational kinetic energy of the atoms emerging as a beam from a pinhole in an oven at temperature T is $\frac{1}{2}kT$, calculate the magnetic field gradient required to produce a splitting of 2.00 mm in a beam of Ag atoms from an oven at 1200 K with a magnet of length 80 cm.

Topic 20 Periodicity

Discussion questions

20.1 Discuss the relationship between the location of a many-electron atom in the periodic table and its electron configuration.

20.2 Describe and account for the variation of first ionization energies along Period 2 of the periodic table. Would you expect the same variation in Period 3?

Exercises

20.1(a) What are the values of the quantum numbers n, l, m_l, s, and m_s for each of the valence electrons in the ground state of a carbon atom?
20.1(b) What are the values of the quantum numbers n, l, m_l, s, and m_s for each of the valence electrons in the ground state of a nitrogen atom?

20.2(a) Write the ground-state electron configurations of the d metals from scandium to zinc.
20.2(b) Write the ground-state electron configurations of the d metals from yttrium to cadmium.

Problems

20.1 The d metals iron, copper, and manganese form cations with different oxidation states. For this reason, they are found in many oxidoreductases and in several proteins of oxidative phosphorylation and photosynthesis. Explain why many d metals form cations with different oxidation states.

20.2 Thallium, a neurotoxin, is the heaviest member of Group 13 of the periodic table and is found most usually in the +1 oxidation state. Aluminium, which causes anaemia and dementia, is also a member of the group but its chemical properties are dominated by the +3 oxidation state. Examine this issue by plotting the first, second, and third ionization energies for the Group 13 elements against atomic number. Explain the trends you observe. *Hint*: The third ionization energy, I_3, is the minimum energy needed to remove an electron from the doubly charged cation: $\mathrm{E}^{2+}(\mathrm{g}) \to \mathrm{E}^{3+}(\mathrm{g}) + \mathrm{e}^-(\mathrm{g})$, $I_3 = E(\mathrm{E}^{3+}) - E(\mathrm{E}^{2+})$. Consult the printed or online literature for sources of data.

Topic 21 Atomic spectroscopy

Discussion questions

21.1 Discuss the origin of the series of lines in the emission spectra of hydrogen. What region of the electromagnetic spectrum is associated with each of the series shown in Fig. 21.1?

21.2 Specify and account for the selection rules for transitions in hydrogenic atoms. Are they strictly valid?

21.3 Explain the origin of spin–orbit coupling and how it affects the appearance of a spectrum.

Exercises

21.1(a) Determine the shortest-and longest-wavelength lines in the Lyman series.

21.1(b) The Pfund series has $n_1 = 5$. Determine the shortest-and longest-wavelength lines in the Pfund series.

21.2(a) Compute the wavelength, frequency, and wavenumber of the $n = 2 \rightarrow n = 1$ transition in He^+.

21.2(b) Compute the wavelength, frequency, and wavenumber of the $n = 5 \rightarrow n = 4$ transition in Li^{+2}.

21.3(a) Which of the following transitions are allowed in the normal electronic emission spectrum of an atom: (a) 3s → 1s, (b) 3p → 2s, (c) 5d → 2p?

21.3(b) Which of the following transitions are allowed in the normal electronic emission spectrum of an atom: (a) 5d → 3s, (b) 5s → 3p, (c) 6f → 4p?

21.4(a) (i) Write the electron configuration of the Pd^{2+} ion. (ii) What are the possible values of the total spin quantum numbers S and M_S for this ion?

21.4(b) (i) Write the electron configuration of the Nb^{2+} ion. (ii) What are the possible values of the total spin quantum numbers S and M_S for this ion?

21.5(a) Calculate the permitted values of j for (a) a d electron, (b) an f electron.

21.5(b) Calculate the permitted values of j for (a) a p electron, (b) an h electron.

21.6(a) An electron in two different states of an atom is known to have $j = \frac{5}{2}$ and $\frac{1}{2}$. What is its orbital angular momentum quantum number in each case?

21.6(b) An electron in two different states of an atom is known to have $j = \frac{7}{2}$ and $\frac{3}{2}$. What is its orbital angular momentum quantum number in each case?

21.7(a) What are the allowed total angular momentum quantum numbers of a composite system in which $j_1 = 1$ and $j_2 = 2$?

21.7(b) What are the allowed total angular momentum quantum numbers of a composite system in which $j_1 = 4$ and $j_2 = 2$?

21.8(a) What information does the term symbol $^3P_2$ provide about the angular momentum of an atom?

21.8(b) What information does the term symbol $^2D_{3/2}$ provide about the angular momentum of an atom?

21.9(a) Suppose that an atom has (a) 2, (b) 3 electrons in different orbitals. What are the possible values of the total spin quantum number S? What is the multiplicity in each case?

21.9(b) Suppose that an atom has (a) 4, (b) 5, electrons in different orbitals. What are the possible values of the total spin quantum number S? What is the multiplicity in each case?

21.10(a) What atomic terms are possible for the electron configuration $n\text{s}^1 n\text{d}^1$? Which term is likely to lie lowest in energy?

21.10(b) What atomic terms are possible for the electron configuration $n\text{p}^1 n\text{d}^1$? Which term is likely to lie lowest in energy?

21.11(a) What values of J may occur in the terms (a) ^3S, (b) ^2D, (c) ^1P? How many states (distinguished by the quantum number M_J) belong to each level?

21.11(b) What values of J may occur in the terms (a) ^3F, (b) ^4G, (c) ^2P? How many states (distinguished by the quantum number M_J) belong to each level?

21.12(a) Give the possible term symbols for (a) Na [Ne]$3s^1$, (b) K [Ar]$3d^1$.

21.12(b) Give the possible term symbols for (a) Y [Kr]$4d^1 5s^2$, (b) I [Kr]$4d^{10} 5s^2 5p^5$.

Problems

21.1 The Li^{2+} ion is hydrogenic and has a Lyman series at 740 747 cm^{-1}, 877 924 cm^{-1}, 925 933 cm^{-1}, and beyond. Show that the energy levels are of the form $-hc\tilde{R}/n^2$ and find the value of $\tilde{R}$ for this ion. Go on to predict the wavenumbers of the two longest-wavelength transitions of the Balmer series of the ion and find the ionization energy of the ion.

21.2 A series of lines in the spectrum of neutral Li atoms rise from combinations of $1s^2 2p^1$ ^2P with $1s^2 n\text{d}^1$ ^2D and occur at 610.36 nm, 460.29 nm, and 413.23 nm. The d orbitals are hydrogenic. It is known that the ^2P term lies at 670.78 nm above the ground state, which is $1s^2 2s^1$ ^2S. Calculate the ionization energy of the ground-state atom.

21.3‡ Wijesundera, et al. (*Phys. Rev.* A **51**, 278 (1995)) attempted to determine the electron configuration of the ground state of lawrencium, element 103. The two contending configurations are [Rn]$5f^{14} 7s^2 7p^1$ and [Rn]$5f^{14} 6d^1 7s^2$. Write down the term symbols for each of these configurations, and identify the lowest level within each configuration. Which level would be lowest according to a simple estimate of spin–orbit coupling?

21.4 The characteristic emission from K atoms when heated is purple and lies at 770 nm. On close inspection, the line is found to have two closely spaced components, one at 766.70 nm and the other at 770.11 nm. Account for this observation, and deduce what information you can.

21.5 Calculate the mass of the deuteron given that the first line in the Lyman series of H lies at 82 259.098 cm^{-1} whereas that of D lies at 82 281.476 cm^{-1}. Calculate the ratio of the ionization energies of H and D.

21.6 Positronium consists of an electron and a positron (same mass, opposite charge) orbiting round their common centre of mass. The broad features of the spectrum are therefore expected to be hydrogen-like, the differences arising largely from the mass differences. Predict the wavenumbers of the first three lines of the Balmer series of positronium. What is the binding energy of the ground state of positronium?

21.7 Some of the selection rules for hydrogenic atoms were derived in *Justification* 21.1. Complete the derivation by considering the x- and y-components of the electric dipole moment operator.

21.8 The distribution of isotopes of an element may yield clues about the nuclear reactions that occur in the interior of a star. Show that it is possible to use spectroscopy to confirm the presence of both $^4He^+$ and $^3He^+$ in a star by calculating the wavenumbers of the $n = 3 \rightarrow n = 2$ and of the $n = 2 \rightarrow n = 1$ transitions for each isotope.

Integrated activities

F5.1 The *Zeeman effect* is the modification of an atomic spectrum by the application of a strong magnetic field. It arises from the interaction between applied magnetic fields and the magnetic moments due to orbital and spin angular momenta (recall the evidence provided for electron spin by the

Stern–Gerlach experiment). To gain some appreciation for the so-called *normal Zeeman effect*, which is observed in transitions involving singlet states, consider a p electron, with $l=1$ and $m_l=0, \pm 1$. In the absence of a magnetic field, these three states are degenerate. When a field of magnitude $\mathcal{B}$ is present, the degeneracy is removed and it is observed that the state with $m_l=+1$ moves up in energy by $\mu_B\mathcal{B}$, the state with $m_l=0$ is unchanged, and the state with $m_l=-1$ moves down in energy by $\mu_B\mathcal{B}$, where $\mu_B = e\hbar/2m_e = 9.274\times 10^{-24}$ J T^{-1} is known as the Bohr magneton. Therefore, a transition between a $^1S_0$ term and a $^1P_1$ term consists of three spectral lines in the presence of a magnetic field where, in the absence of the magnetic field, there is only one. (a) Calculate the splitting in reciprocal centimetres between the three spectral lines of a transition between a $^1S_0$ term and a $^1P_1$ term in the presence of a magnetic field of 2 T (where 1 T = 1 kg s^{-2} A^{-1}). (b) Compare the value you calculated in (a) with typical optical transition wavenumbers, such as those for the Balmer series of the H atom. Is the line splitting caused by the normal Zeeman effect relatively small or relatively large?

F5.2 An electron in the ground-state He$^+$ ion undergoes a transition to a state described by the wavefunction $R_{4,1}(r)Y_{1,1}(\theta,\phi)$(a) Describe the transition using term symbols. (b) Compute the wavelength, frequency, and wavenumber of the transition. (c) By how much does the mean radius of the electron change due to the transition?

F5.3 The electron in a Li^{2+} ion is prepared in a state that is the following superposition of hydrogenic atomic orbitals:

$$\psi(r,\theta,\phi) = -\left(\tfrac{1}{3}\right)^{1/2} R_{4,2}(r)Y_{2,-1}(\theta,\phi) + \tfrac{2}{3}\,\mathrm{i}R_{3,2}(r)Y_{2,1}(\theta,\phi) - \left(\tfrac{2}{9}\right)^{1/2} R_{1,0}(r)Y_{0,0}(\theta,\phi)$$

(a) If the total energy of different Li^{2+} ions in this state is measured, what values will be found? If more than one value is found, what is the probability of obtaining each result and what is the average value?
(b) After the energy is measured, the electron is in a state described by an eigenfunction of the hamiltonian. Are transitions to the ground state of Li^{2+} allowed and, if so, what are the frequency and wavenumber of the transition(s)?

F5.4‡ Highly excited atoms have electrons with large principal quantum numbers. Such *Rydberg atoms* have unique properties and are of interest to astrophysicists. Derive a relation for the separation of energy levels for hydrogen atoms with large n. Calculate this separation for $n=100$; also calculate the average radius, the geometric cross-section, and the ionization energy. Could a thermal collision with another hydrogen atom ionize this Rydberg atom? What minimum velocity of the second atom is required? Could a normal sized neutral H atom simply pass through the Rydberg atom leaving it undisturbed? What might the radial wavefunction for a 100s orbital be like?

F5.5 Use mathematical software, a spreadsheet, or the *Living graphs* (labelled $^{\mathrm{LG}}$) on the website of this book for the following exercises:

(a)$^{\mathrm{LG}}$ Plot the effective potential energy of an electron in the hydrogen atom against r for several nonzero values of the orbital angular momentum l. How does the location of the minimum in the effective potential energy vary with l?
(b) Find the locations of the radial nodes in hydrogenic wavefunctions with n up to 3.
(c) Plot the boundary surfaces of the real parts of the spherical harmonics $Y_{l,m_l}(\theta,\phi)$ for $l=1$. The resulting plots are not strictly the p orbital boundary surfaces, but sufficiently close to be reasonable representations of the shapes of hydrogenic orbitals.
(d) To gain insight into the shapes of the f orbitals, plot the boundary surfaces of the real parts of the spherical harmonics $Y_{l,m_l}(\theta,\phi)$ for $l=3$.
(e) Calculate and plot the radial distribution functions for the hydrogenic 4s, 4p, 4d, and 4f orbitals. How does the degree of shielding experienced by an electron vary with l?

Mathematical background 4 Vectors

A **scalar physical property** (such as temperature) in general varies through space and is represented by a single value at each point of space. A **vector physical property** (such as the electric field strength) also varies through space, but in general has a different direction as well as a different magnitude at each point.

MB4.1 Definitions

A **vector** $\boldsymbol{v}$ has the general form (in three dimensions):

$$\boldsymbol{v}=v_x\boldsymbol{i}+v_y\boldsymbol{j}+v_z\boldsymbol{k} \qquad \text{(MB4.1)}$$

where $\boldsymbol{i}$, $\boldsymbol{j}$, and $\boldsymbol{k}$ are **unit vectors**, vectors of magnitude 1, pointing along the positive directions on the x, y, and z axes and v_x, v_y, and v_z are the **components** of the vector on each axis (Fig. MB4.1). The **magnitude** of the vector is denoted v or $|\boldsymbol{v}|$ and is given by

$$v=(v_x^2+v_y^2+v_z^2)^{1/2} \qquad \text{Magnitude} \qquad \text{(MB4.2)}$$

The vector makes an angle θ with the z–axis and an angle ϕ to the x-axis in the xy-plane. It follows that

$$v_x=v\sin\theta\cos\phi \quad v_y=v\sin\theta\sin\phi \qquad \text{Orientation} \qquad \text{(MB4.3a)}$$
$$v_z=v\cos\theta$$

and therefore that

$$\theta=\arccos(v_z/v) \quad \phi=\arctan(v_y/v_x) \qquad \text{(MB4.3b)}$$

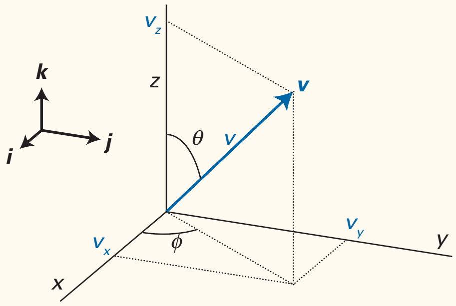

Figure MB4.1 The vector $\boldsymbol{v}$ has components v_x, v_y, and v_z on the x, y, and z axes, respectively. It has a magnitude v and makes an angle θ with the z-axis and an angle ϕ to the x-axis in the xy-plane.

Brief illustration MB4.1 Vector orientation

The vector $\boldsymbol{v}=2\boldsymbol{i}+3\boldsymbol{j}-\boldsymbol{k}$ has magnitude

$$v=\{2^2+3^2+(-1)^2\}^{1/2}=14^{1/2}=3.74$$

Its direction is given by

$$\theta=\arccos(-1/14^{1/2})=105.5^\circ \quad \phi=\arctan(3/2)=56.3^\circ$$

MB4.2 Operations

Consider the two vectors

$$\boldsymbol{u}=u_x\boldsymbol{i}+u_y\boldsymbol{j}+u_z\boldsymbol{k} \qquad \boldsymbol{v}=v_x\boldsymbol{i}+v_y\boldsymbol{j}+v_z\boldsymbol{k}$$

The operations of addition, subtraction, and multiplication are as follows:

1. *Addition*:

$$\boldsymbol{v}+\boldsymbol{u}=(v_x+u_x)\boldsymbol{i}+(v_y+u_y)\boldsymbol{j}+(v_z+u_z)\boldsymbol{k} \qquad \text{(MB4.4a)}$$

2. *Subtraction*:

$$\boldsymbol{v}-\boldsymbol{u}=(v_x-u_x)\boldsymbol{i}+(v_y-u_y)\boldsymbol{j}+(v_z-u_z)\boldsymbol{k} \qquad \text{(MB4.4b)}$$

Brief illustration MB4.2 Addition and subtraction

Consider the vectors $\boldsymbol{u}=\boldsymbol{i}-4\boldsymbol{j}+\boldsymbol{k}$ (of magnitude 4.24) and $\boldsymbol{v}=-4\boldsymbol{i}+2\boldsymbol{j}+3\boldsymbol{k}$ (of magnitude 5.39). Their sum is

$$\boldsymbol{u}+\boldsymbol{v}=(1-4)\boldsymbol{i}+(-4+2)\boldsymbol{j}+(1+3)\boldsymbol{k}=-3\boldsymbol{i}-2\boldsymbol{j}+4\boldsymbol{k}$$

The magnitude of the resultant vector is $29^{1/2}=5.39$. The difference of the two vectors is

$$\boldsymbol{u}-\boldsymbol{v}=(1+4)\boldsymbol{i}+(-4-2)\boldsymbol{j}+(1-3)\boldsymbol{k}=5\boldsymbol{i}-6\boldsymbol{j}-2\boldsymbol{k}$$

The magnitude of this resultant is 8.06. Note that in this case the difference is longer than either individual vector.

3. *Multiplication*:
   (a) The **scalar product**, or *dot product*, of the two vectors $\boldsymbol{u}$ and $\boldsymbol{v}$ is

$$\boldsymbol{u}\cdot\boldsymbol{v}=u_xv_x+u_yv_y+u_zv_z \qquad \text{Scalar product} \qquad \text{(MB4.4c)}$$

and is itself a scalar quantity. We can always choose a new coordinate system—we shall write it X, Y, Z—in which the Z-axis lies parallel to $\boldsymbol{u}$, so $\boldsymbol{u}=u\boldsymbol{K}$, where $\boldsymbol{K}$ is the unit vector parallel to $\boldsymbol{u}$. It then follows from eqn MB4.4c that $\boldsymbol{u}\cdot\boldsymbol{v}=uv_Z$. Then, with $v_Z=v\cos\theta$, where θ is the angle between $\boldsymbol{u}$ and $\boldsymbol{v}$, we find

$$\boldsymbol{u}\cdot\boldsymbol{v}=uv\cos\theta \tag{MB4.4d}$$

Scalar product

(b) The **vector product,** or *cross product,* of two vectors is

$$\begin{aligned}\boldsymbol{u}\times\boldsymbol{v}&=\begin{vmatrix}\boldsymbol{i} & \boldsymbol{j} & \boldsymbol{k}\\ u_x & u_y & u_z\\ v_x & v_y & v_z\end{vmatrix}\\ &=(u_yv_z-u_zv_y)\boldsymbol{i}-(u_xv_z-u_zv_x)\boldsymbol{j}\\ &\quad+(u_xv_y-u_yv_x)\boldsymbol{k}\end{aligned} \tag{MB4.4e}$$

Vector product

(Determinants are discussed in *Mathematical background* 5.) Once again, choosing the coordinate system so that $\boldsymbol{u}=u\boldsymbol{K}$ leads to the simple expression

$$\boldsymbol{u}\times\boldsymbol{v}=(uv\sin\theta)\boldsymbol{l} \tag{MB4.4f}$$

Vector product

where θ is the angle between the two vectors and $\boldsymbol{l}$ is a unit vector perpendicular to both $\boldsymbol{u}$ and $\boldsymbol{v}$, with a direction determined by the 'right-hand rule' as in Fig. MB4.2. A special case is when each vector is a unit vector, for then

$$\boldsymbol{i}\times\boldsymbol{j}=\boldsymbol{k}\quad \boldsymbol{j}\times\boldsymbol{k}=\boldsymbol{i}\quad \boldsymbol{k}\times\boldsymbol{i}=\boldsymbol{j} \tag{MB4.5}$$

It is important to note that the order of vector multiplication is important and that $\boldsymbol{u}\times\boldsymbol{v}=-\boldsymbol{v}\times\boldsymbol{u}$.

Brief illustration MB4.3 Scalar and vector products

The scalar and vector products of the two vectors in *Brief illustration* MB4.2, $\boldsymbol{u}=\boldsymbol{i}-4\boldsymbol{j}+\boldsymbol{k}$ (of magnitude 4.24) and $\boldsymbol{v}=-4\boldsymbol{i}+2\boldsymbol{j}+3\boldsymbol{k}$ (of magnitude 5.39) are

$$\boldsymbol{u}\cdot\boldsymbol{v}=\{1\times(-4)\}+\{(-4)\times 2\}+\{1\times 3\}=-9$$

$$\begin{aligned}\boldsymbol{u}\times\boldsymbol{v}&=\begin{vmatrix}\boldsymbol{i} & \boldsymbol{j} & \boldsymbol{k}\\ 1 & -4 & 1\\ -4 & 2 & 3\end{vmatrix}\\ &=\{(-4)(3)-(1)(2)\}\boldsymbol{i}-\{(1)(3)-(1)(-4)\}\boldsymbol{j}\\ &\quad+\{(1)(2)-(-4)(-4)\}\boldsymbol{k}\\ &=-14\boldsymbol{i}-7\boldsymbol{j}-14\boldsymbol{k}\end{aligned}$$

The vector product is a vector of magnitude 21.00 pointing in a direction perpendicular to the plane defined by the two individual vectors.

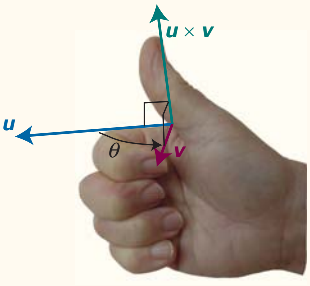

Figure MB4.2 A depiction of the 'right-hand rule'. When the fingers of the right hand rotate $\boldsymbol{u}$ into $\boldsymbol{v}$, the thumb points in the direction of $\boldsymbol{u}\times\boldsymbol{v}$.

MB4.3 The graphical representation of vector operations

Consider two vectors $\boldsymbol{v}$ and $\boldsymbol{u}$ making an angle θ (Fig. MB4.3). The first step in the addition of $\boldsymbol{u}$ to $\boldsymbol{v}$ consists of joining the tip (the 'head') of $\boldsymbol{u}$ to the starting point (the 'tail') of $\boldsymbol{v}$. In the second step, we draw a vector $\boldsymbol{v}_{\text{res}}$, the **resultant vector**, originating from the tail of $\boldsymbol{u}$ to the head of $\boldsymbol{v}$. Reversing the order of addition leads to the same result; that is, we obtain the same $\boldsymbol{v}_{\text{res}}$ whether we add $\boldsymbol{u}$ to $\boldsymbol{v}$ or $\boldsymbol{v}$ to $\boldsymbol{u}$. To calculate the magnitude of $\boldsymbol{v}_{\text{res}}$, we note that

$$v_{\text{res}}^2=(\boldsymbol{u}+\boldsymbol{v})\cdot(\boldsymbol{u}+\boldsymbol{v})=\boldsymbol{u}\cdot\boldsymbol{u}+\boldsymbol{v}\cdot\boldsymbol{v}+2\boldsymbol{u}\cdot\boldsymbol{v}=u^2+v^2+2uv\cos\theta$$

where θ is the angle between $\boldsymbol{u}$ and $\boldsymbol{v}$. In terms of the angle $\theta'=\pi-\theta$ shown in the figure, and $\cos(\pi-\theta)=-\cos\theta$, we obtain the **law of cosines**:

$$v_{\text{res}}^2=u^2+v^2-2uv\cos\theta' \tag{MB4.6}$$

Law of cosines

for the relation between the lengths of the sides of a triangle.

Subtraction of $\boldsymbol{v}$ from $\boldsymbol{u}$ amounts to addition of $-\boldsymbol{v}$ to $\boldsymbol{u}$. It follows that in the first step of subtraction we draw $-\boldsymbol{v}$ by reversing

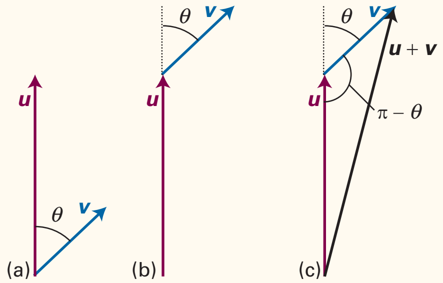

Figure MB4.3 (a) The vectors $\boldsymbol{v}$ and $\boldsymbol{u}$ make an angle θ. (b) To add $\boldsymbol{u}$ to $\boldsymbol{v}$, we first join the head of $\boldsymbol{u}$ to the tail of $\boldsymbol{v}$, making sure that the angle θ between the vectors remains unchanged. (c) To finish the process, we draw the resultant vector by joining the tail of $\boldsymbol{u}$ to the head of $\boldsymbol{v}$.

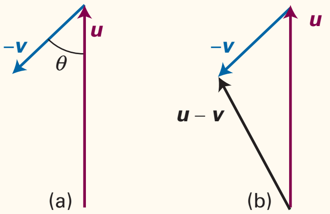

Figure MB4.4 The graphical method for subtraction of the vector $\boldsymbol{v}$ from the vector $\boldsymbol{u}$ (shown in Fig. MB4.3a) consists of two steps: (a) reversing the direction of $\boldsymbol{v}$ to form $-\boldsymbol{v}$, and (b) adding $-\boldsymbol{v}$ to $\boldsymbol{u}$.

the direction of $\boldsymbol{v}$ (Fig. MB4.4). Then, the second step consists of adding $-\boldsymbol{v}$ to $\boldsymbol{u}$ by using the strategy shown in the figure: we draw a resultant vector $\boldsymbol{v}_{\text{res}}$ originating from the tail of $\boldsymbol{u}$ to the head of $-\boldsymbol{v}$.

Vector multiplication is represented graphically by drawing a vector (using the right-hand rule) perpendicular to the plane defined by the vectors $\boldsymbol{u}$ and $\boldsymbol{v}$, as shown in Fig. MB4.5. Its length is equal to $uv \sin\theta$, where θ is the angle between $\boldsymbol{u}$ and $\boldsymbol{v}$.

MB4.4 Vector differentiation

The derivative $\mathrm{d}\boldsymbol{v}/\mathrm{d}t$, where the components v_x, v_y, and v_z are themselves functions of t, is

$$\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t}=\left(\frac{\mathrm{d}v_x}{\mathrm{d}t}\right)\boldsymbol{i}+\left(\frac{\mathrm{d}v_y}{\mathrm{d}t}\right)\boldsymbol{j}+\left(\frac{\mathrm{d}v_z}{\mathrm{d}t}\right)\boldsymbol{k} \qquad \text{(MB4.7)}$$

Derivative

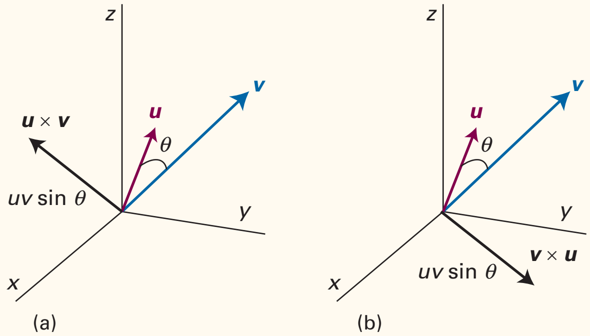

Figure MB4.5 The direction of the cross products of two vectors $\boldsymbol{u}$ and $\boldsymbol{v}$ with an angle θ between them: (a) $\boldsymbol{u}\times\boldsymbol{v}$ and (b) $\boldsymbol{v}\times\boldsymbol{u}$. Note that the cross product, and the unit vector l of eqn MB4.4f, are perpendicular to both $\boldsymbol{u}$ and $\boldsymbol{v}$ but the direction depends on the order in which the product is taken. The magnitude of the cross product, in either case, is $uv \sin\theta$.

The derivatives of scalar and vector products are obtained using the rules of differentiating a product:

$$\frac{\mathrm{d}\boldsymbol{u}\cdot\boldsymbol{v}}{\mathrm{d}t}=\left(\frac{\mathrm{d}\boldsymbol{u}}{\mathrm{d}t}\right)\cdot\boldsymbol{v}+\boldsymbol{u}\cdot\left(\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t}\right) \qquad \text{(MB4.8a)}$$

$$\frac{\mathrm{d}\boldsymbol{u}\times\boldsymbol{v}}{\mathrm{d}t}=\left(\frac{\mathrm{d}\boldsymbol{u}}{\mathrm{d}t}\right)\times\boldsymbol{v}+\boldsymbol{u}\times\left(\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t}\right) \qquad \text{(MB4.8b)}$$

In the latter, note the importance of preserving the order of vectors.

The **gradient** of a scalar function $f(x,y,z)$, denoted grad f or ∇f, is

$$\nabla f=\left(\frac{\partial f}{\partial x}\right)\boldsymbol{i}+\left(\frac{\partial f}{\partial y}\right)\boldsymbol{j}+\left(\frac{\partial f}{\partial z}\right)\boldsymbol{k} \qquad \text{(MB4.9)}$$

Gradient

where partial derivatives are mentioned in *Mathematical background* 1 and are treated at length in *Mathematical background* 8. Note that the gradient of a scalar function is a vector. We can treat ∇ as a vector operator (in the sense that it operates on a function and results in a vector), and write

$$\nabla=\boldsymbol{i}\frac{\partial}{\partial x}+\boldsymbol{j}\frac{\partial}{\partial y}+\boldsymbol{k}\frac{\partial}{\partial z} \qquad \text{(MB4.10)}$$

The scalar product of ∇ and ∇f, using eqns MB4.9 and MB4.10, is

$$\begin{aligned}\nabla\cdot\nabla f&=\left(\boldsymbol{i}\frac{\partial}{\partial x}+\boldsymbol{j}\frac{\partial}{\partial y}+\boldsymbol{k}\frac{\partial}{\partial z}\right)\cdot\left(\boldsymbol{i}\frac{\partial}{\partial x}+\boldsymbol{j}\frac{\partial}{\partial y}+\boldsymbol{k}\frac{\partial}{\partial z}\right)f\\&=\frac{\partial^2 f}{\partial x^2}+\frac{\partial^2 f}{\partial y^2}+\frac{\partial^2 f}{\partial z^2}\end{aligned} \qquad \text{(MB4.11)}$$

Laplacian

Equation MB4.11 defines the **laplacian** ($\nabla^2=\nabla\cdot\nabla$) of a function.

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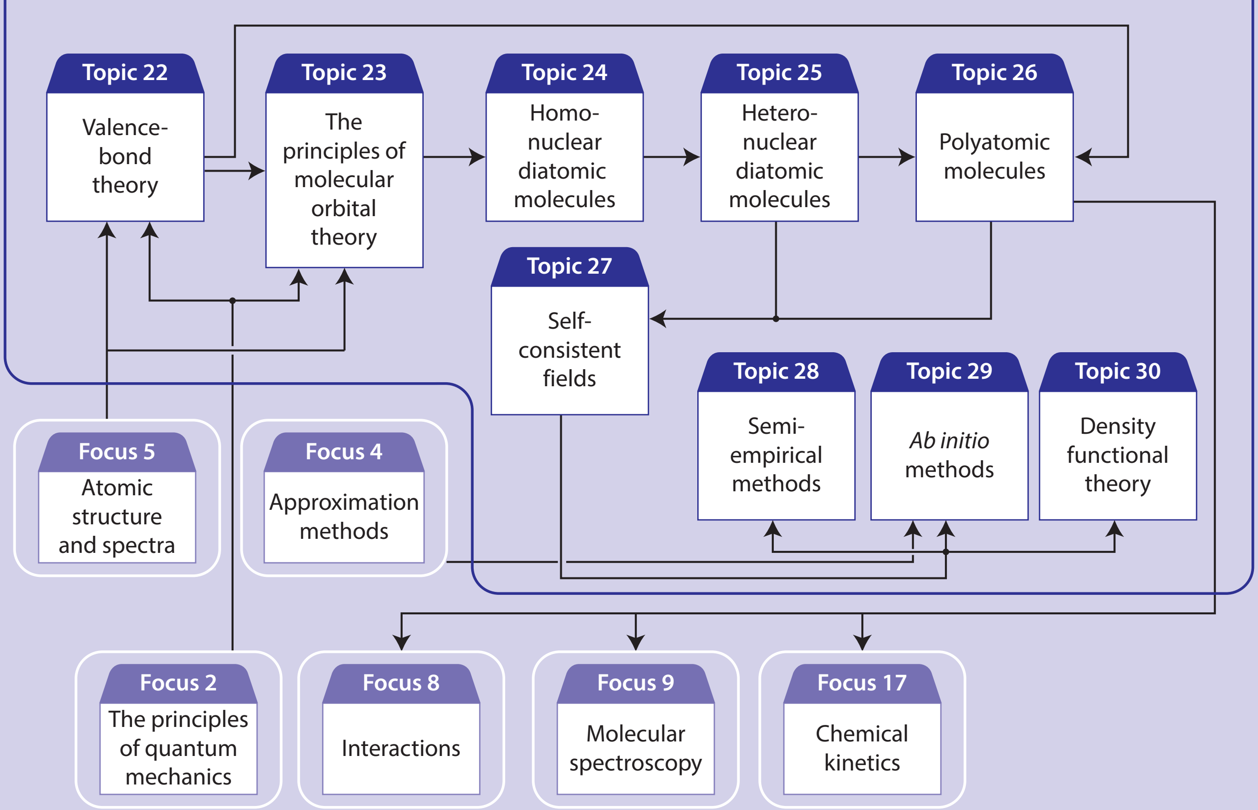
FOCUS 6 ON Molecular structure



Molecular structure lies at the heart of chemistry and is a hugely important aspect of the subject, as it underlies the discussion of the properties of materials and the reactions they undergo. Primitive versions of bonding theories emerged at the beginning of the twentieth century when G.N. Lewis identified the crucial role of the electron pair. That role was clarified by the quantum mechanical descriptions of bonding that are now pervasive in chemistry. All the descriptions can be regarded as extensions of the quantum mechanical discussion of *Atomic structure and spectra*.

One of the earliest applications of *The principles of quantum mechanics* to the description of the chemical bond was 'valence-bond theory' (**Topic 22**). It focused on the role of the electron pair and introduced many widely used concepts into chemistry, such as hybridization.

At about the same time, 'molecular orbital theory' was introduced (**Topic 23**), and has become the description of choice for quantitative computation. Molecular orbital theory extends the concept of atomic orbital to wavefunctions that are delocalized over the entire molecule. It introduces the concepts of bonding and antibonding orbital. We introduce the concepts of molecular orbital theory with the simplest of all molecules, H_2, and then progressively extend the discussion to homonuclear diatomic molecules (**Topic 24**), heteronuclear diatomic molecules (**Topic 25**), and—the ultimate target of this group of Topics—polyatomic molecules (**Topic 26**).

All those Topics are essentially qualitative. In the remaining Topics of this group we show how molecular orbital theory is used in computational chemistry, the computation of electron wavefunctions and their energies. All spring from the numerical procedure called the 'self-consistent field' method (**Topic 27**). Three versions of this method are commonly encountered. In one, the 'semi-empirical method', the integrals that appear in the calculation are replaced by parameters that lead to good agreement with certain experimentally determined properties (**Topic 28**). In another, the '*ab initio* method', attempts are made to evaluate the integrals from first principles (**Topic 29**); one *ab initio* method has its foundations in perturbation theory described in *Approximation methods*. A third and currently very popular procedure, 'density functional theory', takes a different route: it seeks to calculate the electron density itself rather than the wavefunction (**Topic 30**).

TOPIC 22

Valence-bond theory

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➤ Why do you need to know this material?

Valence-bond theory was the first quantum mechanical theory of bonding to be developed. The language it introduced, which includes concepts such as spin pairing, σ and π bonds, and hybridization, is widely used throughout chemistry, especially in the description of the properties and reactions of organic compounds.

➤ What is the key idea?

A bond forms when an electron in an atomic orbital on one atom pairs its spin with that of an electron in an atomic orbital on another atom.

➤ What do you need to know already?

You need to know about atomic orbitals (Topic 18) and the concepts of normalization (Topic 5) and orthogonality (Topic 7). This Topic also makes use of the Pauli principle (Topic 19).

Here we summarize essential topics of **valence-bond theory** (VB theory) that should be familiar from introductory chemistry and set the stage for the development of molecular orbital theory (Topic 23). However, there is an important preliminary point. All theories of molecular structure make the same simplification at the outset. Whereas the Schrödinger equation for a hydrogen atom can be solved exactly, an exact solution is not possible for any molecule because even the simplest molecule consists of three particles (two nuclei and one electron). We therefore adopt the **Born–Oppenheimer approximation** in which it is supposed that the nuclei, being so much heavier than an electron, move relatively slowly and may be treated as stationary while the electrons move in their field. That is, we think of the nuclei as fixed at arbitrary locations, and then solve the Schrödinger equation for the wavefunction of the electrons alone. The approximation is quite good for ground-state molecules, for calculations suggest that the nuclei in H_2 move through only about 1 pm while the electron speeds through 1000 pm.

The Born–Oppenheimer approximation allows us to select an internuclear separation in a diatomic molecule and then to solve the Schrödinger equation for the electrons at that nuclear separation. Then we choose a different separation and repeat the calculation, and so on. In this way we can explore how the energy of the molecule varies with bond length and obtain a **molecular potential energy curve** (Fig. 22.1). It is called a *potential* energy curve because the kinetic energy of the stationary nuclei is zero. Once the curve has been calculated or determined experimentally (by using the spectroscopic techniques described in Topics 40–46), we can identify the **equilibrium bond length**, R_e, the internuclear separation at the minimum of the curve, and the **bond dissociation energy**, D_0, which is closely related to the depth, D_e, of the minimum below the energy of the infinitely widely separated and stationary atoms. When more than one molecular parameter is changed in a polyatomic molecule, such as its various bond lengths and angles, we obtain a potential energy *surface*; the overall equilibrium shape of the molecule corresponds to the global minimum of the surface.

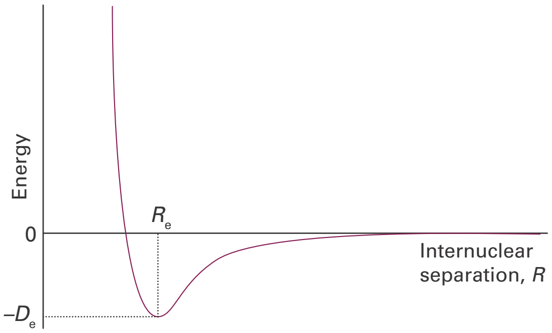


Figure 22.1 A molecular potential energy curve. The equilibrium bond length corresponds to the energy minimum.

22.1 Diatomic molecules

We begin the account of VB theory by considering the simplest possible chemical bond, the one in molecular hydrogen, H_2.

(a) The basic formalism

The spatial wavefunction for an electron on each of two widely separated H atoms is

$$\psi = \chi_{\mathrm{H1s_A}}(\boldsymbol{r}_1)\chi_{\mathrm{H1s_B}}(\boldsymbol{r}_2) \tag{22.1}$$

if electron 1 is on atom A and electron 2 is on atom B; in this Topic, and as is common in the chemical literature, we use χ (chi) to denote atomic orbitals. For simplicity, we shall write this wavefunction as $\psi = A(1)B(2)$. When the atoms are close, it is not possible to know whether it is electron 1 or electron 2 that is on A. An equally valid description is therefore $\psi = A(2)B(1)$, in which electron 2 is on A and electron 1 is on B. When two outcomes are equally probable, quantum mechanics instructs us to describe the true state of the system as a superposition of the wavefunctions for each possibility (Topic 7), so a better description of the molecule than either wavefunction alone is one of the (unnormalized) linear combinations $\psi = A(1)B(2) \pm A(2)B(1)$. The combination with lower energy is the one with a + sign, so the valence-bond wavefunction of the electrons in an H_2 molecule is

$$\psi = A(1)B(2) + A(2)B(1) \quad \text{A valence-bond wavefunction} \tag{22.2}$$

The reason why this linear combination has a lower energy than either the separate atoms or the linear combination with a negative sign can be traced to the constructive interference between the wave patterns represented by the terms $A(1)B(2)$ and $A(2)B(1)$, and the resulting enhancement of the probability density of the electrons in the internuclear region (Fig. 22.2).

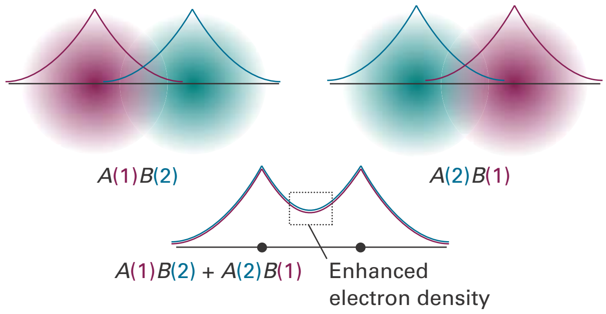


Figure 22.2 It is very difficult to represent valence-bond wavefunctions because they refer to two electrons simultaneously. However, this illustration is an attempt. The atomic orbital for electron 1 is represented by the purple shading, and that of electron 2 is represented by the green shading. The left illustration represents *A*(1)*B*(2), and the right illustration represents the contribution *A*(2)*B*(1). When the two contributions are superimposed, there is interference between the purple contributions and between the green contributions, resulting in an enhanced (two-electron) density in the internuclear region.

Brief illustration 22.1 A valence-bond wavefunction

The wavefunction in eqn 22.2 might look abstract, but in fact it can be expressed in terms of simple exponential functions. Thus, if we use the wavefunction for an H1s orbital ($Z=1$) given in Topic 18, then, with the radii measured from their respective nuclei,

$$\begin{aligned}\psi &= \overbrace{\frac{1}{(\pi a_0^3)^{1/2}}\mathrm{e}^{-r_{\mathrm{A}1}/a_0}}^{A(1)} \times \overbrace{\frac{1}{(\pi a_0^3)^{1/2}}\mathrm{e}^{-r_{\mathrm{B}2}/a_0}}^{B(2)} + \overbrace{\frac{1}{(\pi a_0^3)^{1/2}}\mathrm{e}^{-r_{\mathrm{A}2}/a_0}}^{A(2)}\\ &\quad \times \overbrace{\frac{1}{(\pi a_0^3)^{1/2}}\mathrm{e}^{-r_{\mathrm{B}1}/a_0}}^{B(1)}\\ &= \frac{1}{\pi a_0^3}\{\mathrm{e}^{-(r_{\mathrm{A}1}+r_{\mathrm{B}2})/a_0} + \mathrm{e}^{-(r_{\mathrm{A}2}+r_{\mathrm{B}1})/a_0}\}\end{aligned}$$

Self-test 22.1 Express this wavefunction in terms of the Cartesian coordinates of each electron given that the internuclear separation (along the *z*-axis) is *R*.

Answer: $r_{\mathrm{A}i} = (x_i^2 + y_i^2 + z_i^2)^{1/2}$, $r_{\mathrm{B}i} = (x_i^2 + y_i^2 + (z_i - R)^2)^{1/2}$

The electron distribution described by the wavefunction in eqn 22.2 is called a **σ bond**. A σ bond has cylindrical symmetry around the internuclear axis, and is so called because, when viewed along the internuclear axis, it resembles a pair of electrons in an s orbital (and σ is the Greek equivalent of s).

A chemist's picture of a covalent bond is one in which the spins of two electrons pair as the atomic orbitals overlap. The origin of the role of spin, as we show in the following *Justification*, is that the wavefunction in eqn 22.2 can be formed only by a pair of spin-paired electrons. Spin pairing is not an end in itself: it is a means of achieving a wavefunction and the probability distribution it implies that corresponds to a low energy.

Justification 22.1 Electron pairing in VB theory

The Pauli principle requires the overall wavefunction of two electrons, the wavefunction including spin, to change sign when the labels of the electrons are interchanged (Topic 19). The overall VB wavefunction for two electrons is

$$\psi(1,2)=\{A(1)B(2)+A(2)B(1)\}\sigma(1,2)$$

where σ represents the spin component of the wavefunction. When the labels 1 and 2 are interchanged, this wavefunction becomes

$$\begin{aligned}\psi(2,1)&=\{A(2)B(1)+A(1)B(2)\}\sigma(2,1)\\&=\{A(1)B(2)+A(2)B(1)\}\sigma(2,1)\end{aligned}$$

The Pauli principle requires that $\psi(2,1)=-\psi(1,2)$, which is satisfied only if $\sigma(2,1)=-\sigma(1,2)$. The combination of two spins that has this property is

$$\sigma_-(1,2)=(1/2^{1/2})\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\}$$

which corresponds to paired electron spins (Topic 19). Therefore, we conclude that the state of lower energy (and hence the formation of a chemical bond) is achieved if the electron spins are paired.

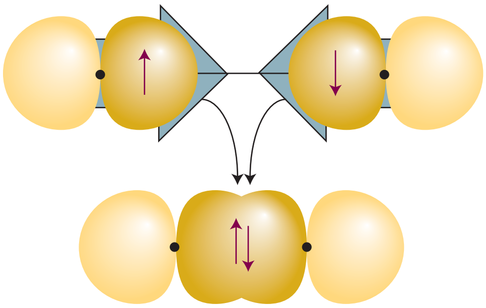


Figure 22.3 The orbital overlap and spin pairing between electrons in two collinear p orbitals that results in the formation of a σ bond.

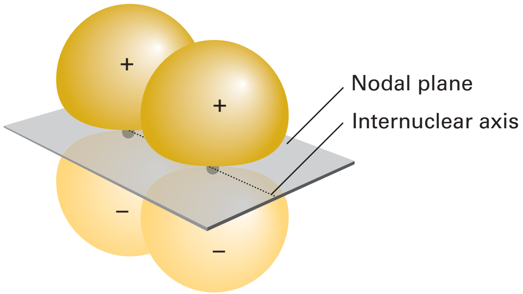


Figure 22.4 A π bond results from orbital overlap and spin pairing between electrons in p orbitals with their axes perpendicular to the internuclear axis. The bond has two lobes of electron density separated by a nodal plane.

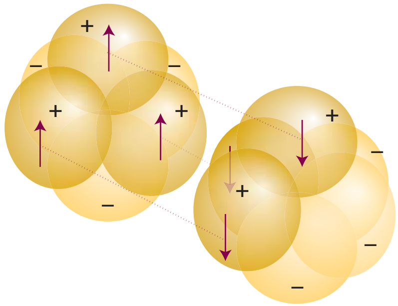


Figure 22.5 The structure of bonds in a nitrogen molecule, with one σ bond and two π bonds.

The VB description of H_2 can be applied to other homonuclear diatomic molecules. For N_2, for instance, we consider the valence electron configuration of each atom, which is $2s^2 2p_x^1 2p_y^1 2p_z^1$. It is conventional to take the z-axis to be the internuclear axis, so we can imagine each atom as having a $2p_z$ orbital pointing towards a $2p_z$ orbital on the other atom (Fig. 22.3), with the $2p_x$ and $2p_y$ orbitals perpendicular to the axis. A σ bond is then formed by spin pairing between the two electrons in the two $2p_z$ orbitals. Its spatial wavefunction is given by eqn 22.2, but now A and B stand for the two $2p_z$ orbitals.

The remaining N2p orbitals cannot merge to give σ bonds as they do not have cylindrical symmetry around the internuclear axis. Instead, they merge to form two π bonds. A **π bond** arises from the spin pairing of electrons in two p orbitals that approach side-by-side (Fig. 22.4). It is so called because, viewed along the internuclear axis, a π bond resembles a pair of electrons in a p orbital (and π is the Greek equivalent of p).

There are two π bonds in N_2, one formed by spin pairing in two neighbouring $2p_x$ orbitals and the other by spin pairing in two neighbouring $2p_y$ orbitals. The overall bonding pattern in N_2 is therefore a σ bond plus two π bonds (Fig. 22.5), which is consistent with the Lewis structure :N≡N: for nitrogen.

(b) Resonance

Another term introduced into chemistry by VB theory is **resonance**, the superposition of the wavefunctions representing different electron distributions *in the same nuclear framework*. To understand what this means, consider the VB description of a purely covalently bonded HCl molecule, which could be written as $\psi=A(1)B(2)+A(2)B(1)$, with A now a H1s orbital and B a Cl2p orbital. However, there is something wrong with this description: it allows electron 1 to be on the H atom when electron 2 is on the Cl atom, and vice versa, but it does not allow for the possibility that both electrons are on the Cl atom ($\psi = B(1)B(2)$, representing H^+Cl^-) or even on the H atom ($\psi = A(1)A(2)$, representing the much less likely H^-Cl^+). A better description of the wavefunction for the molecule is as a superposition of the covalent and ionic descriptions, and we write (with a slightly simplified notation, and ignoring the less likely $H^-\,Cl^+$ possibility) $\psi_{\text{HCl}} = \psi_{\text{H–Cl}} + \lambda\psi_{\text{H}^+\text{Cl}^-}$ with λ (lambda) some numerical coefficient. In general, we write

$$\psi = \psi_{\text{covalent}} + \lambda\psi_{\text{ionic}} \tag{22.3}$$

where ψ_{covalent} is the wavefunction for the purely covalent form of the bond and ψ_{ionic} is the wavefunction for the ionic form of the bond. The approach summarized by eqn 22.3 is an example of resonance. In this case, where one structure is pure covalent and the other pure ionic, it is called **ionic–covalent resonance**. The interpretation of the wavefunction, which is called a **resonance hybrid**, is that if we were to inspect the molecule, then the probability that it would be found with an ionic structure is proportional to λ^2. If λ^2 is very small, the covalent description is dominant. If λ^2 is very large, the ionic description is dominant. Resonance is not a flickering between the contributing states: it is a blending of their characteristics, much as a mule is a blend of a horse and a donkey. It is only a mathematical device for achieving a closer approximation to the true wavefunction of the molecule than that represented by any single contributing structure alone.

A systematic way of calculating the value of λ is provided by the **variation principle** which is proved in Topic 25:

> If an arbitrary wavefunction is used to calculate the energy, then the value calculated is never less than the true energy.

Variation principle

The arbitrary wavefunction is called the **trial wavefunction**. The principle implies that, if we vary the parameter λ in the trial wavefunction until the lowest energy is achieved (by evaluating the expectation value of the hamiltonian for the wavefunction), then that value of λ will be the best and through λ^2 represents the appropriate contribution of the ionic wavefunction to the resonance hybrid.

Brief illustration 22.2 Resonance hybrids

Consider a bond described by eqn 22.3. We might find that the lowest energy is reached when $\lambda = 0.1$, so the best description of the bond in the molecule is a resonance structure described by the wavefunction $\psi = \psi_{\text{covalent}} + 0.1\psi_{\text{ionic}}$. This wavefunction implies that the probabilities of finding the molecule in its covalent and ionic forms are in the ratio 100:1 (because $0.1^2 = 0.01$).

Self-test 22.2 If a normalized wavefunction has the form $\psi = 0.889\psi_{\text{covalent}} + 0.458\psi_{\text{ionic}}$, what is the percentage probability of finding both electrons of the bond on one atom?

Answer: 21.0 per cent

22.2 Polyatomic molecules

Each σ bond in a polyatomic molecule is formed by the spin pairing of electrons in atomic orbitals with cylindrical symmetry around the relevant internuclear axis. Likewise, π bonds are formed by pairing electrons that occupy atomic orbitals of the appropriate symmetry.

Brief illustration 22.3 A polyatomic molecule

The VB description of H_2O will make this approach clear. The valence-electron configuration of an O atom is $2s^2 2p_x^2 2p_y^1 2p_z^1$. The two unpaired electrons in the O2p orbitals can each pair with an electron in an H1s orbital, and each combination results in the formation of a σ bond (each bond has cylindrical symmetry about the respective O—H internuclear axis). Because the $2p_y$ and $2p_z$ orbitals lie at 90° to each other, the two σ bonds also lie at 90° to each other (Fig. 22.6). We predict, therefore, that H_2O should be an angular molecule, which it is. However, the theory predicts a bond angle of 90°, whereas the actual bond angle is 104.5°.

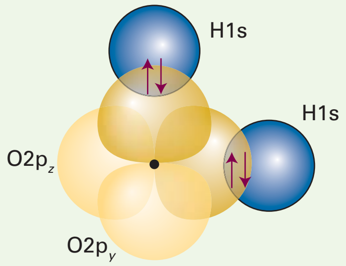
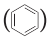


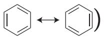
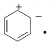
Figure 22.6 In a primitive view of the structure of an H_2O molecule, each bond is formed by the overlap and spin pairing of an H1s electron and an O2p electron.

Self-test 22.3 Use VB theory to suggest a shape for the ammonia molecule, NH_3.

Answer: Trigonal pyramidal with HNH bond angle 90°; experimental: 107°

Resonance plays an important role in the valence-bond description of polyatomic molecules. One of the most famous examples of resonance is in the VB description of benzene, where the wavefunction of the molecule is written as a superposition of the wavefunctions of the two covalent Kekulé structures:

$\psi = \psi($  $) + \psi($  $)$ (22.4)

The two contributing structures have identical energies, so they contribute equally to the superposition. The effect of resonance (which is represented by a double-headed arrow, ) in this case is to distribute double-bond character around the ring and to make the lengths and strengths of all the carbon–carbon bonds identical. The wavefunction is improved by allowing resonance because it allows for a more accurate description of the location of the electrons, and in particular the distribution can adjust into a state of lower energy. This lowering is called the **resonance stabilization** of the molecule and, in the context of VB theory, is largely responsible for the unusual stability of aromatic rings. Resonance always lowers the energy, and the lowering is greatest when the contributing structures have similar energies. The wavefunction of benzene is improved still further, and the calculated energy of the molecule is lowered further still, if we allow ionic–covalent resonance too, by allowing a small admixture of structures such as .

(a) Promotion

Another deficiency of this initial formulation of VB theory is its inability to account for carbon's tetravalence (its ability to form four bonds). The ground-state configuration of C is $2s^2 2p_x^1 2p_y^1$, which suggests that a carbon atom should be capable of forming only two bonds, not four.

This deficiency is overcome by allowing for **promotion**, the excitation of an electron to an orbital of higher energy. In carbon, for example, the promotion of a 2s electron to a 2p orbital can be thought of as leading to the configuration $2s^1 2p_x^1 2p_y^1 2p_z^1$, with four unpaired electrons in separate orbitals. These electrons may pair with four electrons in orbitals provided by four other atoms (such as four H1s orbitals if the molecule is CH_4), and hence form four σ bonds. Although energy was required to promote the electron, it is more than recovered by the promoted atom's ability to form four bonds in place of the two bonds of the unpromoted atom.

Promotion, and the formation of four bonds, is a characteristic feature of carbon because the promotion energy is quite small: the promoted electron leaves a doubly occupied 2s orbital and enters a vacant 2p orbital, hence significantly relieving the electron–electron repulsion it experiences in the former. However, it is important to remember that promotion is not a 'real' process in which an atom somehow becomes excited and then forms bonds: it is a notional contribution to the overall energy change that occurs when bonds form.

Brief illustration 22.4 Promotion

Sulfur can form six bonds (an 'expanded octet'), as in the molecule SF_6. Because the ground-state electron configuration of sulfur is $[Ne]3s^2 3p^4$, this bonding pattern requires the promotion of a 3s electron and a 3p electron to two different 3d orbitals, which are nearby in energy, to produce the notional configuration $[Ne]3s^1 3p^3 3d^2$ with all six of the valence electrons in different orbitals and capable of bond formation with six electrons provided by six F atoms.

Self-test 22.4 Account for the ability of phosphorus to form five bonds, as in PF_5.

Answer: Promotion of a 3s electron from $[Ne]3s^2 3p^3$ to $[Ne]3s^1 3p^3 3d^1$

(b) Hybridization

The description of the bonding in CH_4 (and other alkanes) is still incomplete because it implies the presence of three σ bonds of one type (formed from H1s and C2p orbitals) and a fourth σ bond of a distinctly different character (formed from H1s and C2s). This problem is overcome by realizing that the electron density distribution in the promoted atom is equivalent to the electron density in which each electron occupies a **hybrid orbital** formed by interference between the C2s and C2p orbitals of the same atom. The origin of the hybridization can be appreciated by thinking of the four atomic orbitals centred on a nucleus as waves that interfere destructively and constructively in different regions, and give rise to four new shapes.

As we show in the following *Justification*, the specific linear combinations that give rise to four equivalent hybrid orbitals are

$$\begin{aligned} h_1 &= s + p_x + p_y + p_z \quad & h_2 &= s - p_x - p_y + p_z \\ h_3 &= s - p_x + p_y - p_z \quad & h_4 &= s + p_x - p_y - p_z \end{aligned} \qquad \text{sp}^3\text{ hybrid orbitals} \tag{22.5}$$

As a result of the interference between the component orbitals, each hybrid orbital consists of a large lobe pointing in the direction of one corner of a regular tetrahedron (Fig. 22.7). The angle between the axes of the hybrid orbitals is the tetrahedral angle, $\arccos(-\frac{1}{3}) = 109.47°$. Because each hybrid is built from one s orbital and three p orbitals, it is called an **sp³ hybrid orbital**.

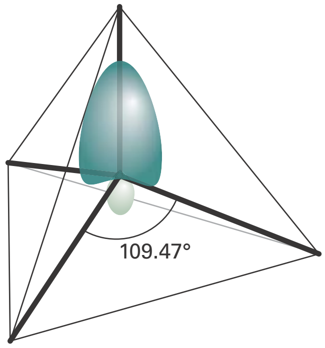


Figure 22.7 An sp³ hybrid orbital formed from the superposition of s and p orbitals on the same atom. There are four such hybrids: each one points towards the corner of a regular tetrahedron. The overall electron density remains spherically symmetrical.

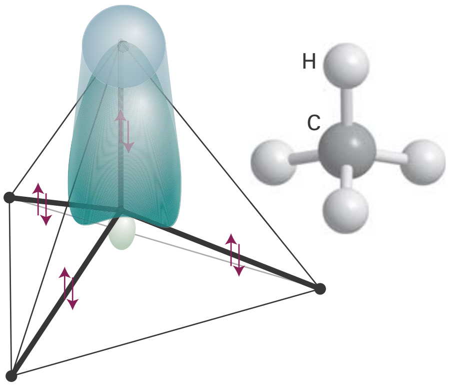


Figure 22.8 Each sp³ hybrid orbital forms a σ bond by overlap with an H1s orbital located at the corner of the tetrahedron. This model accounts for the equivalence of the four bonds in CH_4.

Justification 22.2 Determining the form of tetrahedral hybrid orbitals

We begin by supposing that each hybrid can be written in the form $h = as + b_x p_x + b_y p_y + b_z p_z$. The hybrid h_1 that points to the (1,1,1) corner of a cube must have equal contributions from all three p orbitals, so we can set the three b coefficients equal to each other and write $h_1 = as + b(p_x + p_y + p_z)$. The other three hybrids have the same composition (they are equivalent, apart from their direction in space), but are orthogonal to h_1. This orthogonality is achieved by choosing different signs for the p orbitals but the same overall composition. For instance, we might choose $h_2 = as + b(-p_x - p_y + p_z)$, in which case the orthogonality condition is

$$\int h_1 h_2 \mathrm{d}\tau = \int \{as + b(p_x + p_y + p_z)\}\{as + b(-p_x - p_y + p_z)\}\mathrm{d}\tau$$
$$= a^2 \overbrace{\int s^2 \mathrm{d}\tau}^{1} - b^2 \overbrace{\int p_x^2 \mathrm{d}\tau}^{1} - \cdots - ab \overbrace{\int s p_x \mathrm{d}\tau}^{0} - \cdots$$
$$- b^2 \overbrace{\int p_x p_y \mathrm{d}\tau}^{0} + \cdots = a^2 - b^2 - b^2 + b^2 = a^2 - b^2 = 0$$

We conclude that a solution is $a = b$ (the alternative solution, $a = -b$, simply corresponds to choosing different absolute phases for the p orbitals) and the two hybrid orbitals are the h_1 and h_2 in eqn 22.5. A similar argument but with $h_3 = as + b(-p_x + p_y - p_z)$ or $h_4 = as + b(p_x - p_y - p_z)$ leads to the other two hybrids in eqn 22.5.

It is now easy to see how the valence-bond description of the CH_4 molecule leads to a tetrahedral molecule containing four equivalent C—H bonds. Each hybrid orbital of the promoted C atom contains a single unpaired electron; an H1s electron can pair with each one, giving rise to a σ bond pointing in a tetrahedral direction (Fig. 22.8). For example, the (unnormalized) wavefunction for the bond formed by the hybrid orbital h_1 and the $1s_A$ orbital (with wavefunction that we shall denote A) is

$$\psi = h_1(1)A(2) + h_1(2)A(1) \qquad (22.6)$$

As for H_2, to achieve this wavefunction, the two electrons it describes must be paired. Because each sp³ hybrid orbital has the same composition, all four σ bonds are identical apart from their orientation in space.

A hybrid orbital has enhanced amplitude in the internuclear region, which arises from the constructive interference between the s orbital and the positive lobes of the p orbitals. As a result, the bond strength is greater than for a bond formed from an s or p orbital alone. This increased bond strength is another factor that helps to repay the promotion energy.

Hybridization is used to describe the structure of an ethene molecule, $H_2C{=}CH_2$, and the torsional rigidity of double bonds. An ethene molecule is planar, with HCH and HCC bond angles close to 120°. To reproduce the σ bonding structure, each C atom is regarded as promoted to a $2s^12p^3$ configuration. However, instead of using all four orbitals to form hybrids, we form **sp² hybrid orbitals**:

$$\begin{aligned} h_1 &= s + 2^{1/2} p_y \\ h_2 &= s + (\tfrac{3}{2})^{1/2} p_x - (\tfrac{1}{2})^{1/2} p_y \\ h_3 &= s - (\tfrac{3}{2})^{1/2} p_x - (\tfrac{1}{2})^{1/2} p_y \end{aligned} \qquad \text{sp}^2 \text{ hybrid orbitals} \qquad (22.7)$$

These hybrids lie in a plane and point towards the corners of an equilateral triangle at 120° to each other (Fig. 22.9 and Problem 22.2). The third 2p orbital ($2p_z$) is not included in the hybridization; its axis is perpendicular to the plane in which the hybrids lie. The different signs of the coefficients, as well as ensuring that the hybrids are mutually orthogonal, also ensure that constructive interference takes place in different regions of space,

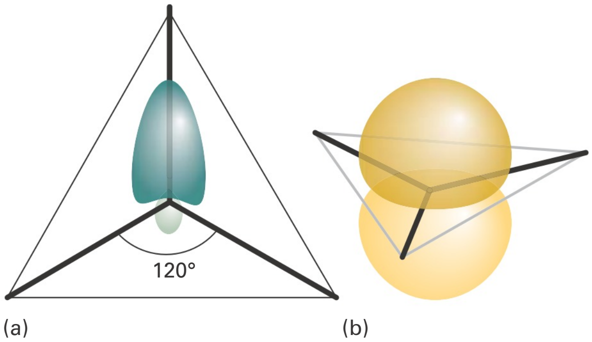


Figure 22.9 (a) An s orbital and two p orbitals can be hybridized to form three equivalent orbitals that point towards the corners of an equilateral triangle. (b) The remaining, unhybridized p orbital is perpendicular to the plane.

so giving the patterns in the illustration. The sp^2-hybridized C atoms each form three σ bonds by spin pairing with either the h_1 hybrid of the other C atom or with H1s orbitals. The σ framework therefore consists of C—H and C—C σ bonds at 120° to each other. When the two CH_2 groups lie in the same plane, the two electrons in the unhybridized p orbitals can pair and form a π bond (Fig. 22.10). The formation of this π bond locks the framework into the planar arrangement, for any rotation of one CH_2 group relative to the other leads to a weakening of the π bond (and consequently an increase in energy of the molecule).

A similar description applies to ethyne, HC≡CH, a linear molecule. Now the C atoms are **sp hybridized**, and the σ bonds are formed using hybrid atomic orbitals of the form

$$h_1 = \mathrm{s} + \mathrm{p}_z \quad h_2 = \mathrm{s} - \mathrm{p}_z \qquad \text{sp hybrid orbitals} \qquad (22.8)$$

These two hybrids lie along the internuclear axis. The electrons in them pair either with an electron in the corresponding hybrid orbital on the other C atom or with an electron in one of the H1s orbitals. Electrons in the two remaining p orbitals on each atom, which are perpendicular to the molecular axis, pair to form two perpendicular π bonds (Fig. 22.11).

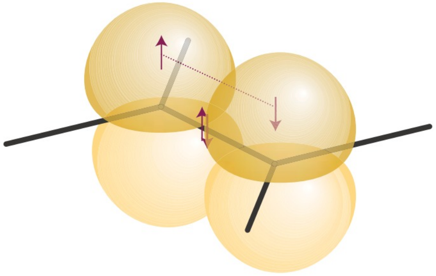


Figure 22.10 A representation of the structure of the double bond in ethene; only the π bond is shown explicitly.

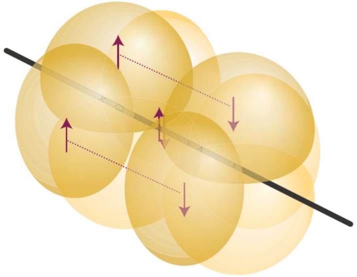


Figure 22.11 A representation of the structure of the triple bond in ethyne; only the π bonds are shown explicitly.

Table 22.1 Some hybridization schemes

Coordination number	Arrangement	Composition
2	Linear	sp, pd, sd
	Angular	sd
3	Trigonal planar	sp^2, p^2d
	Trigonal pyramidal	pd^2
4	Tetrahedral	sp^3, sd^3
	Square planar	p^2d^2, sp^2d
5	Trigonal bipyramidal	sp^3d, spd^3
	Pentagonal planar	p^2d^3
6	Octahedral	sp^3d^2

Other hybridization schemes, particularly those involving d orbitals, are often invoked in elementary descriptions of molecular structure to be consistent with other molecular geometries (Table 22.1). The hybridization of N atomic orbitals always results in the formation of N hybrid orbitals, which may either form bonds or contain lone pairs of electrons.

Brief illustration 22.5 Hybrid structures

For example, sp^3d^2 hybridization results in six equivalent hybrid orbitals pointing towards the corners of a regular octahedron; it is sometimes invoked to account for the structure of octahedral molecules, such as SF_6 (recall the promotion of sulfur's electrons in *Brief illustration* 22.4). Hybrid orbitals do not always form bonds: they may also contain lone pairs of electrons. For example, in the hydrogen peroxide molecule, H_2O_2, each O atom can be regarded as sp^3 hybridized. Two of the hybrid orbitals form bonds, one O—O bond and one O—H bond at approximately 109° (the experimental value is much less, at 94.8°). The remaining two hybrids on each atom accommodate lone pairs of electrons. Rotation around the O—O bond is possible, so the molecule is conformationally mobile.

Self-test 22.5 Account for the structure of methylamine, CH_3NH_2.

Answer: C, N both sp^3 hybridized; a lone pair on N

Checklist of concepts

- ☐ 1. The **Born–Oppenheimer approximation** treats the nuclei as stationary while the electrons move in their field.
- ☐ 2. A **molecular potential energy curve** depicts the variation of the energy of the molecule as a function of bond length.
- ☐ 3. The **equilibrium bond length** is the internuclear separation at the minimum of the curve.
- ☐ 4. The **bond dissociation energy** is the minimum energy needed to separate the two atoms of a molecule.
- ☐ 5. A bond forms when an electron in an atomic orbital on one atom pairs its spin with that of an electron in an atomic orbital on another atom.
- ☐ 6. **Resonance** refers to the superposition of the wavefunctions representing different electron distributions in the same nuclear framework. The wavefunction resulting from the superposition is called a **resonance hybrid.**
- ☐ 7. To accommodate the shapes of polyatomic molecules, VB theory introduces the concepts of **promotion** and **hybridization**.
- ☐ 8. A **σ bond** has cylindrical symmetry around the internuclear axis.
- ☐ 9. A **π bond** has symmetry like that of a p orbital perpendicular to the internuclear axis.

Checklist of equations

Property	Equation	Comment	Equation number
Valence-bond wavefunction	$\psi = A(1)B(2) + A(2)B(1)$	A,B are atomic orbitals	22.2
Hybridization	$h = \sum_i c_i \chi_i$	All atomic orbitals on the same atom; specific forms in the text	22.5 (sp^3) 22.7 (sp^2) 22.8 (sp)

TOPIC 23

The principles of molecular orbital theory

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➤ Why do you need to know this material?

Molecular orbital theory is the basis of almost all descriptions of chemical bonding, including that in individual molecules and of solids. It is the foundation of most computational techniques for the prediction and analysis of the properties of molecules.

➤ What is the key idea?

Molecular orbitals are wavefunctions that spread over all the atoms in a molecule.

➤ What do you need to know already?

You need to be familiar with the shapes of atomic orbitals (Topic 18) and how an energy and probability density are calculated from a wavefunction (Topics 5 and 7). The entire discussion is within the framework of the Born–Oppenheimer approximation (Topic 22).

In **molecular orbital theory** (MO theory), electrons do not belong to particular bonds but spread throughout the entire molecule. This theory has been more fully developed than VB theory (Topic 22) and provides the language that is widely used in modern discussions of bonding. To introduce it, we follow the same strategy as in Topic 19, where the one-electron H atom was taken as the fundamental species for discussing atomic structure and then developed into a description of many-electron atoms. In this Topic we use the simplest molecular species of all, the hydrogen molecule-ion, H_2^+, to introduce the essential features of bonding and then use it to describe the structures of more complex systems.

23.1 Linear combinations of atomic orbitals

The hamiltonian for the single electron in H_2^+ is

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 + V \qquad V = -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{A1}} + \frac{1}{r_{B1}} - \frac{1}{R}\right) \tag{23.1}$$

where r_{A1} and r_{B1} are the distances of the electron from the two nuclei A and B (**1**) and R is the distance between the two nuclei. In the expression for V, the first two terms in parentheses are the attractive contribution from the interaction between the electron and the nuclei; the remaining term is the repulsive interaction between the nuclei. The collection of fundamental constants $e^2/4\pi\varepsilon_0$ occurs widely throughout these Topics, and we shall denote it j_0. The one-electron wavefunctions obtained by solving the Schrödinger

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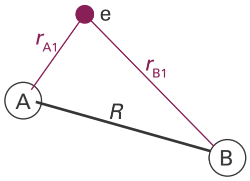


equation $\hat{H}\psi = E\psi$ with this hamiltonian and its analogues for other molecules are called **molecular orbitals** (MOs). A molecular orbital is like an atomic orbital, but spreads throughout the molecule. It gives, through the value of $|\psi|^2$, the probability distribution of the electron in the molecule.

(a) The construction of linear combinations

The Schrödinger equation can be solved analytically for H_2^+ (within the Born–Oppenheimer approximation, Topic 22), but the wavefunctions are very complicated functions; moreover, the solution cannot be extended to polyatomic systems. Therefore, we adopt a simpler procedure that, while more approximate, can be extended readily to other molecules.

If an electron can be found in an atomic orbital belonging to atom A and also in an atomic orbital belonging to atom B, then the overall wavefunction is a superposition of the two atomic orbitals:

$$\psi_\pm = N(A \pm B) \qquad \text{Linear combination of atomic orbitals} \qquad (23.2)$$

where, for H_2^+, A denotes an H1s atomic orbital on atom A, which we denote (as in Topic 22) $\chi_{\text{H1s}_\text{A}}$, B likewise denotes $\chi_{\text{H1s}_\text{B}}$, and N is a normalization factor. The technical term for the superposition in eqn 23.2 is a **linear combination of atomic orbitals** (LCAO). An approximate molecular orbital formed from a linear combination of atomic orbitals is called an **LCAO-MO**. A molecular orbital that has cylindrical symmetry around the internuclear axis, such as the one we are discussing, is called a **σ orbital** because it resembles an s orbital when viewed along the axis and, more precisely, because it has zero orbital angular momentum around the internuclear axis.

Example 23.1 Normalizing a molecular orbital

Normalize the molecular orbital ψ_+ in eqn 23.2.

Method We need to find the factor N such that $\int\psi^*\psi\,d\tau = 1$. To proceed, substitute the LCAO into this integral, and make use of the fact that the atomic orbitals are individually normalized.

Answer Substitution of the wavefunction gives

$$\int\psi^*\psi\,d\tau = N^2\left\{\overbrace{\int A^2 d\tau}^{1} + \overbrace{\int B^2 d\tau}^{1} + 2\overbrace{\int AB\,d\tau}^{S}\right\} = 2(1+S)N^2$$

where $S = \int AB\,d\tau$ and has a value that depends on the nuclear separation (this 'overlap integral' will play a significant role later). For the integral to be equal to 1, we require

$$N = \frac{1}{\{2(1+S)\}^{1/2}}$$

In H_2^+, $S \approx 0.59$, so $N = 0.56$.

Self-test 23.1 Normalize the orbital ψ_- in eqn 23.2.

Answer: $N = 1/\{2(1-S)\}^{1/2}$; if $S \approx 0.59$, then $N = 1.10$

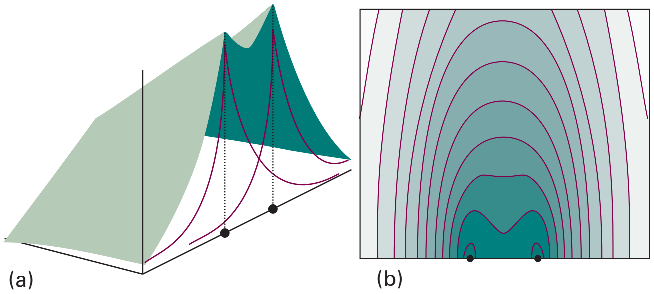


Figure 23.1 (a) The amplitude of the bonding molecular orbital in a hydrogen molecule-ion in a plane containing the two nuclei and (b) a contour representation of the amplitude.

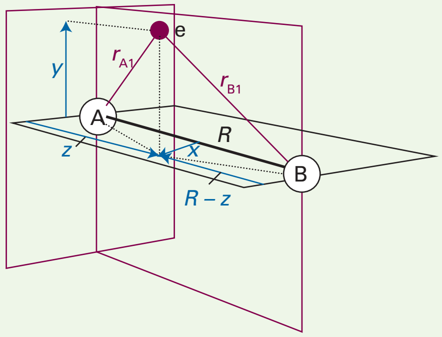
Figure 23.1 shows the contours of constant amplitude for the molecular orbital ψ_+ in eqn 23.2. Plots like these are readily obtained using commercially available software. The calculation is quite straightforward, because all we need do is feed in the mathematical forms of the two atomic orbitals and then let the program do the rest.

Brief illustration 23.1 A molecular orbital

We can use the following two H1s orbitals

$$A = \frac{1}{(\pi a_0^3)^{1/2}}e^{-r_{A1}/a_0} \qquad B = \frac{1}{(\pi a_0^3)^{1/2}}e^{-r_{B1}/a_0}$$

Note that r_{A1} and r_{B1} are not independent, but when expressed in Cartesian coordinates based on atom A (**2**) are related by $r_{A1} = \{x^2+y^2+z^2\}^{1/2}$ and $r_{B1} = \{x^2+y^2+(z-R)^2\}^{1/2}$, where R is the bond length.



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The resulting surfaces of constant amplitude are shown in Fig. 23.2.

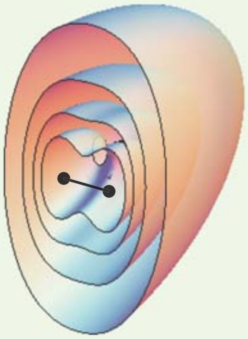

Figure 23.2 Surfaces of constant amplitude of the wavefunction ψ_+ of the hydrogen molecule-ion.

Self-test 23.2 Repeat the analysis for ψ_-.

Answer:

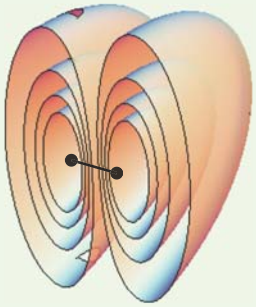

Figure 23.3 Surfaces of constant amplitude of the wavefunction ψ_- of the hydrogen molecule-ion.

(b) Bonding orbitals

According to the Born interpretation, the probability density of the electron at each point in H_2^+ is proportional to the square modulus of its wavefunction at that point. The probability density corresponding to the (real) wavefunction ψ_+ in eqn 23.2 is

$$\psi_+^2 = N^2(A^2 + B^2 + 2AB) \quad \text{Bonding probability density} \quad (23.3)$$

This probability density is plotted in Fig. 23.4. An important feature becomes apparent when we examine the internuclear region, where both atomic orbitals have similar amplitudes. According to eqn 23.3, the total probability density is proportional to the sum of

Physical interpretation

- A^2, the probability density if the electron were confined to the atomic orbital A;
- B^2, the probability density if the electron were confined to the atomic orbital B;
- $2AB$, an extra contribution to the density from both atomic orbitals.

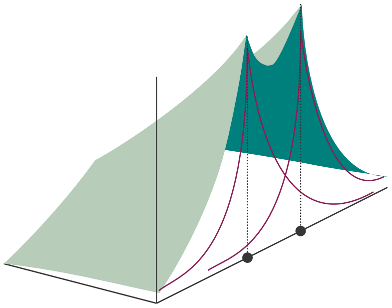

Figure 23.4 The electron density calculated by forming the square of the wavefunction used to construct Fig. 23.1. Note the accumulation of electron density in the internuclear region.

The last contribution, the **overlap density**, is crucial, because it represents an enhancement of the probability of finding the electron in the internuclear region. The enhancement can be traced to the constructive interference of the two atomic orbitals: each has a positive amplitude in the internuclear region, so the total amplitude is greater there than if the electron were confined to a single atomic orbital.

We shall frequently make use of the observation that *bonds form when electrons accumulate in regions where atomic orbitals overlap and interfere constructively*. The conventional explanation of this observation is based on the notion that accumulation of electron density between the nuclei puts the electron in a position where it interacts strongly with both nuclei. Hence, the energy of the molecule is lower than that of the separate atoms, where each electron can interact strongly with only one nucleus. This conventional explanation, however, has been called into question, because shifting an electron away from a nucleus into the internuclear region *raises* its potential energy. The modern (and still controversial) explanation does not emerge from the simple LCAO treatment given here. It seems that, at the same time as the electron shifts into the internuclear region, the atomic orbitals shrink. This orbital shrinkage improves the electron–nucleus attraction more than it is decreased by the migration to the internuclear region, so there is a net lowering of potential energy. The kinetic energy of the electron is also modified because the curvature of the wavefunction is changed, but the change in kinetic energy is dominated by the change in potential energy. Throughout the following discussion we ascribe the strength of chemical bonds to the accumulation of electron density in the internuclear region. We leave open the question whether in molecules more complicated than H_2^+ the true source of energy lowering is that accumulation itself or some indirect but related effect.

The σ orbital we have described is an example of a **bonding orbital**, an orbital which, if occupied, helps to bind two atoms together by lowering its energy below that of the separate atoms. Specifically, we label it 1σ as it is the σ orbital of lowest energy. An electron that occupies a σ orbital is called a **σ electron**, and if that is the only electron present in the molecule (as in the ground state of H_2^+), then we report the configuration of the molecule as $1\sigma^1$.

The energy $E_{1\sigma}$ of the 1σ orbital is (see Problem 23.3)

$$E_{1\sigma} = E_{\text{H1s}} + \frac{j_0}{R} - \frac{j+k}{1+S} \tag{23.4}$$

Energy of bonding orbital

where E_{H1s} is the energy of a H1s orbital, j_0/R is the potential energy of repulsion between the two nuclei (remember that j_0 is shorthand for $e^2/4\pi\varepsilon_0$), and

$$S = \int AB\,\mathrm{d}\tau = \left\{1 + \frac{R}{a_0} + \frac{1}{3}\left(\frac{R}{a_0}\right)^2\right\}\mathrm{e}^{-R/a_0} \tag{23.5a}$$

$$j = j_0 \int \frac{A^2}{r_{\mathrm{B}}}\,\mathrm{d}\tau = \frac{j_0}{R}\left\{1 - \left(1 + \frac{R}{a_0}\right)\mathrm{e}^{-2R/a_0}\right\} \tag{23.5b}$$

$$k = j_0 \int \frac{AB}{r_{\mathrm{B}}}\,\mathrm{d}\tau = \frac{j_0}{a_0}\left(1 + \frac{R}{a_0}\right)\mathrm{e}^{-R/a_0} \tag{23.5c}$$

The integrals are plotted in Fig. 23.5. We can interpret them as follows:

- All three integrals are positive and decline towards zero at large internuclear separations (S and k on account of the exponential term, j on account of the factor $1/R$). The integral S is discussed in more detail in Topic 24.
- The integral j is a measure of the interaction between a nucleus and electron density centred on the other nucleus.
- The integral k is a measure of the interaction between a nucleus and the excess electron density in the internuclear region arising from overlap.

Physical interpretation

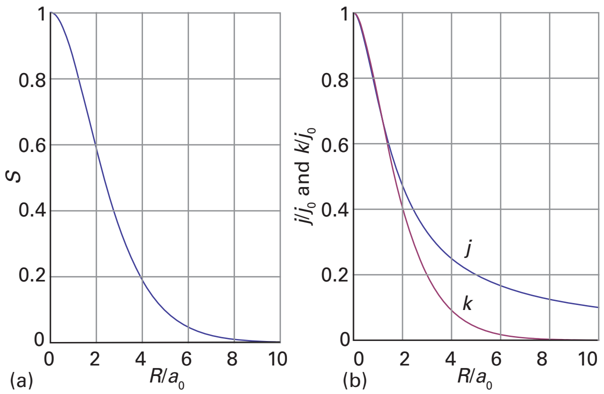

Figure 23.5 The integrals (a) S and (b) j and k calculated for H_2^+ as a function of internuclear distance.

Brief illustration 23.2 Molecular integrals

It turns out (see below) that the minimum value of $E_{1\sigma}$ occurs at $R = 2.45a_0$. At this separation

$$S = \left\{1 + 2.45 + \frac{2.45^2}{3}\right\}\mathrm{e}^{-2.45} = 0.47$$

$$j = \frac{j_0/a_0}{2.45}\left\{1 - 3.45\mathrm{e}^{-4.90}\right\} = 0.40\,j_0/a_0$$

$$k = \frac{j_0}{a_0}(1 + 2.45)\mathrm{e}^{-2.45} = 0.30\,j_0/a_0$$

To express $j_0/a_0 = e^2/4\pi\varepsilon_0 a_0$ in electronvolts, divide it by e, and then find

$$\frac{j_0}{ea_0} = \frac{e}{4\pi\varepsilon_0 a_0} = \frac{e}{4\pi\varepsilon_0} \times \frac{\pi m_e e^2}{\varepsilon_0 h^2} = \frac{m_e e^3}{4\varepsilon_0^2 h^2} = 27.211\ldots\,\mathrm{V}$$

(The value should be recognized as $2hc\tilde{R}_\infty/e$, Topic 17.) Therefore, $j = 11$ eV and $k = 8.2$ eV.

Self-test 23.3 Evaluate the integrals when the internuclear separation is twice its value at the minimum.

Answer: 0.10, 5.5 eV, 1.2 eV

Figure 23.6 shows a plot of $E_{1\sigma}$ against R relative to the energy of the separated atoms. The energy of the 1σ orbital decreases as the internuclear separation decreases from large values because electron density accumulates in the internuclear region as the constructive interference between the atomic orbitals increases (Fig. 23.7). However, at small separations there is too little space

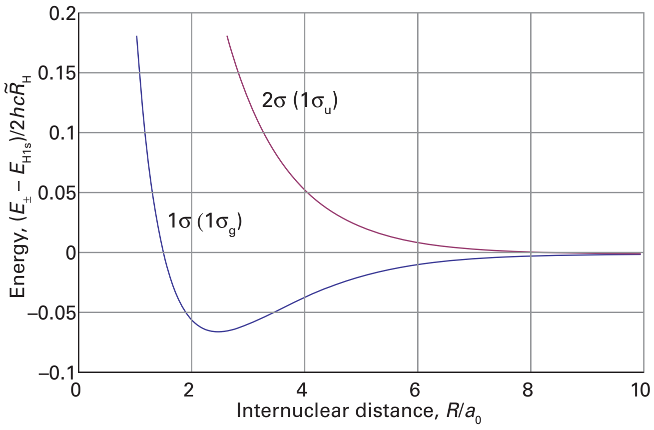

Figure 23.6 The calculated molecular potential energy curves for a hydrogen molecule-ion showing the variation of the energies of the bonding and antibonding orbitals as the bond length is changed. The alternative notation of the orbitals is explained later.

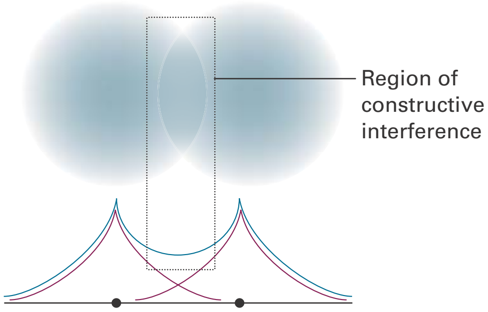

Figure 23.7 A representation of the constructive interference that occurs when two H1s orbitals overlap and form a bonding σ orbital.

between the nuclei for significant accumulation of electron density there. In addition, the nucleus–nucleus repulsion (which is proportional to $1/R$) becomes large. As a result, the energy of the molecule rises at short distances, and there is a minimum in the potential energy curve. Calculations on H_2^+ give $R_e = 130$ pm and $D_e = 1.76$ eV (171 kJ mol^{-1}); the experimental values are 106 pm and 2.6 eV, so this simple LCAO-MO description of the molecule, while inaccurate, is not absurdly wrong.

(c) Antibonding orbitals

The linear combination ψ_- in eqn 23.2 corresponds to a higher energy than that of ψ_+. Because it is also a σ orbital we label it 2σ. This orbital has an internuclear nodal plane where A and B cancel exactly (Figs 23.8 and 23.9; compare Fig. 23.1). The probability density is

$$\psi_-^2 = N^2(A^2 + B^2 - 2AB) \quad \text{Antibonding probability density} \qquad (23.6)$$

There is a reduction in probability density between the nuclei due to the $-2AB$ term (Fig. 23.10); in physical terms, there is destructive interference where the two atomic orbitals overlap. The 2σ orbital is an example of an **antibonding orbital**, an orbital that, if occupied, contributes to a reduction in the cohesion between two atoms and helps to raise the energy of the molecule relative to that of the separated atoms.

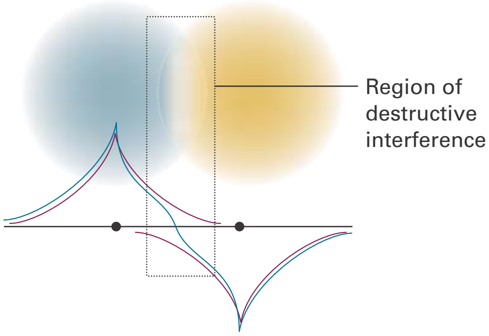

Figure 23.8 A representation of the destructive interference that occurs when two H1s orbitals overlap and form an antibonding 2σ orbital.

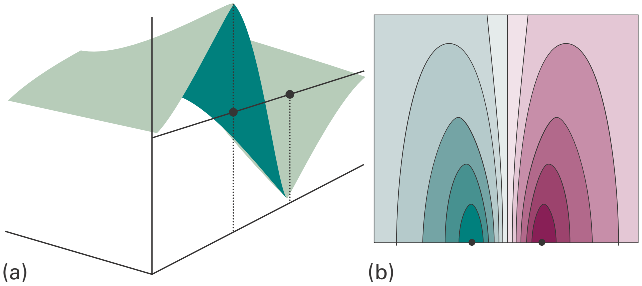

Figure 23.9 (a) The amplitude of the antibonding molecular orbital in a hydrogen molecule-ion in a plane containing the two nuclei and (b) a contour representation of the amplitude. Note the internuclear node.

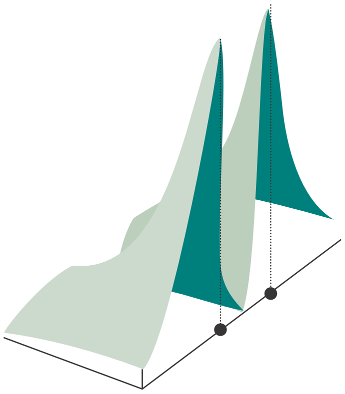

Figure 23.10 The electron density calculated by forming the square of the wavefunction used to construct Fig. 23.9. Note the reduction of electron density in the internuclear region.

The energy $E_{2\sigma}$ of the 2σ antibonding orbital is given by (see Problem 23.3)

$$E_{2\sigma} = E_{\mathrm{H1s}} + \frac{j_0}{R} - \frac{j-k}{1-S} \qquad (23.7)$$

where the integrals S, j, and k are the same as before (eqn 23.5). The variation of $E_{2\sigma}$ with R is shown in Fig. 23.6, where we see the destabilizing effect of an antibonding electron. The effect is partly due to the fact that an antibonding electron is excluded from the internuclear region and hence is distributed largely outside the bonding region. In effect, whereas a bonding electron pulls two nuclei together, an antibonding electron pulls the nuclei apart (Fig. 23.11). Figure 23.6 also shows another feature that we draw on later: $|E_- - E_{\mathrm{H1s}}| > |E_+ - E_{\mathrm{H1s}}|$, which indicates that *the antibonding orbital is more antibonding than the bonding orbital is bonding*. This important conclusion stems in part from the presence of the nucleus–nucleus repulsion (j_0/R): this contribution raises the energy of both molecular orbitals. Antibonding orbitals are often labelled with an asterisk (*), so the 2σ orbital could also be denoted 2σ* (and read '2 sigma star').

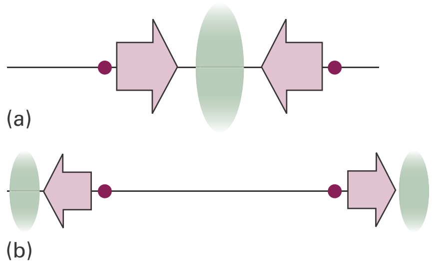

Figure 23.11 A partial explanation of the origin of bonding and antibonding effects. (a) In a bonding orbital, the nuclei are attracted to the accumulation of electron density in the internuclear region. (b) In an antibonding orbital, the nuclei are attracted to an accumulation of electron density outside the internuclear region.

Brief illustration 23.3 Antibonding energies

At the minimum of the bonding orbital energy we have seen that $R=2.45a_0$, and from *Brief illustration* 23.2 we know that $S=0.47$, $j=11$ eV, and $k=8.2$ eV. It follows that at that separation, the energy of the antibonding orbital relative to that of a hydrogen atom 1s orbital is

$$(E_{2\sigma}-E_{\mathrm{H1s}})/\mathrm{eV}=\frac{27.2}{2.45}-\frac{11-8.2}{1-0.47}=5.8$$

That is, the antibonding orbital lies above the bonding orbital at this internuclear separation.

Self-test 23.4 What is the separation of the antibonding and bonding orbital energies at twice that internuclear distance?

Answer: 1.4 eV

23.2 Orbital notation

For homonuclear diatomic molecules and ions such as H_2^+ and analogous many-electron species it proves helpful (for example, in electronic spectroscopy, Topic 45) to label a molecular orbital according to its **inversion symmetry**, the behaviour of the wavefunction when it is inverted through the centre (more formally, the centre of inversion) of the molecule. Thus, if we consider any point on the bonding σ orbital, and then project it through the centre of the molecule and out an equal distance on the other side, we arrive at an identical value of the wavefunction (Fig. 23.12). This so-called **gerade symmetry** (from the German word for 'even') is denoted by a subscript g, as in σ_g. The same procedure applied to the antibonding 2σ orbital results in the same amplitude but opposite sign of the wavefunction. This **ungerade symmetry** ('odd symmetry') is denoted by a subscript u, as in σ_u.

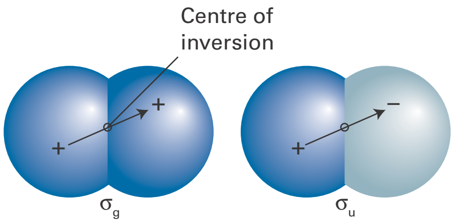

Figure 23.12 The parity of an orbital is even (g) if its wavefunction is unchanged under inversion through the centre of symmetry of the molecule, but odd (u) if the wavefunction changes sign. Heteronuclear diatomic molecules do not have a centre of inversion, so for them the g,u classification is irrelevant.

Brief illustration 23.4 Inversion symmetry

Consider the 1σ orbital given in eqn 23.2 by $N(A+B)$ where the atomic orbitals A and B are specified in *Brief illustration* 23.1. At the location of nucleus A, $r_{A1}=0$ and $r_{B1}=R$. The wavefunction at that point has the value $N(\chi_{\mathrm{H1s_A}}(0)+\chi_{\mathrm{H1s_B}}(R))=N(1/\pi a_0^3)^{1/2}(1+e^{-R/a})$. Upon inversion through the centre of the molecule, which takes that point to $r_{A1}=R$ and $r_{B1}=0$, the wavefunction has the value corresponding to a point on nucleus B, namely, $N(1/\pi a_0^3)^{1/2}(e^{-R/a_0}+1)$. The wavefunction has the same value and the σ orbital is gerade.

Self-test 23.5 Consider the antibonding 2σ orbital and show in a similar way that it has ungerade symmetry.

Answer: $1-e^{-R/a_0}\rightarrow e^{-R/a_0}-1$

When using the g,u notation, each set of orbitals of the same inversion symmetry are labelled separately so, whereas 1σ becomes $1\sigma_g$, its antibonding partner, which so far we have called 2σ, is the first orbital of a different symmetry, and is denoted $1\sigma_u$. The general rule is that *each set of orbitals of the same symmetry designation is labelled separately*. This point is developed in Topic 24. The inversion symmetry classification is not applicable to the discussion of heteronuclear diatomic molecules in Topic 25 because these molecules do not have a centre of inversion.

Checklist of concepts

☐ 1. A **molecular orbital** is constructed as a linear combination of atomic orbitals.

☐ 2. A **bonding orbital** arises from the constructive overlap of neighbouring atomic orbitals.

☐ 3. An **antibonding orbital** arises from the destructive overlap of neighbouring atomic orbitals.

☐ 4. σ **Orbitals** have cylindrical symmetry and zero orbital angular momentum around the internuclear axis.

☐ 5. A molecular orbital in a homonuclear diatomic molecule is labelled 'gerade' or 'ungerade' according to its behaviour under **inversion symmetry**.

Checklist of equations

Property	Equation	Comment	Equation number
Linear combination of atomic orbitals	$\psi_{\pm} = N(A \pm B)$	Homonuclear diatomic molecule	23.2
Energies of σ orbitals	$E_{1\sigma} = E_{\mathrm{H1s}} + j_0/R - (j+k)/(1+S)$	$S = \int AB\,\mathrm{d}\tau$,	23.4
	$E_{2\sigma} = E_{\mathrm{H1s}} + j_0/R - (j-k)/(1-S)$	$j = j_0 \int (A^2/r_{\mathrm{B}})\,\mathrm{d}\tau$ $k = j_0 \int (AB/r_{\mathrm{B}})\,\mathrm{d}\tau$	23.7

TOPIC 24

Homonuclear diatomic molecules

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➤ Why do you need to know this material?

Although the hydrogen molecule-ion establishes the basic approach to the construction of molecular orbitals, almost all chemically significant molecules have more than one electron, and we need to see how to construct their electron configurations. Homonuclear diatomic molecules are a good starting point, not only because they are simple to describe but because they include such important species as H_2, N_2, O_2, and the dihalogens.

➤ What is the key idea?

Each molecular orbital can accommodate up to two electrons.

➤ What do you need to know already?

You need to be familiar with the discussion of the bonding and antibonding linear combinations of atomic orbitals in Topic 23 and the building-up principle for atoms (Topic 19).

In Topic 19 the hydrogenic atomic orbitals and the building-up principle are used as a basis for the discussion and prediction of the ground electronic configurations of many-electron atoms. We now do the same for many-electron diatomic molecules by using the H_2^+ molecular orbitals as a basis for their discussion.

24.1 Electron configurations

The starting point of the building-up principle for diatomic molecules is the construction of molecular orbitals by combining the available atomic orbitals. Once they are available, we adopt the following procedure, which is essentially the same as the building-up principle for atoms (Topic 19):

- The electrons supplied by the atoms are accommodated in the orbitals so as to achieve the lowest overall energy subject to the constraint of the Pauli exclusion principle, that no more than two electrons may occupy a single orbital (and then must be paired).
- If several degenerate molecular orbitals are available, electrons are added singly to each individual orbital before doubly occupying any one orbital (because that minimizes electron–electron repulsions).
- According to Hund's maximum multiplicity rule (Topics 20 and 21), if two electrons do occupy different degenerate orbitals, then a lower energy is obtained if they do so with parallel spins.

Building-up principle for molecules

(a) σ Orbitals and π orbitals

Consider H_2, the simplest many-electron diatomic molecule. Each H atom contributes a 1s orbital (as in H_2^+), so we can form the $1\sigma_g$ and $1\sigma_u$ orbitals from them, as explained in Topic 23. At the experimental internuclear separation these orbitals will have the energies shown in Fig. 24.1, which is called a **molecular orbital energy level diagram**. Note that from two atomic

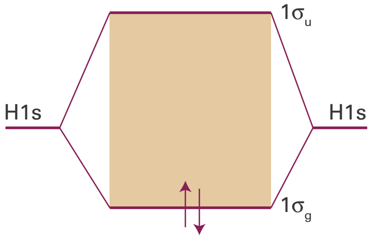

Figure 24.1 A molecular orbital energy level diagram for orbitals constructed from the overlap of H1s orbitals; the separation of the levels corresponds to that found at the equilibrium bond length. The ground electronic configuration of H_2 is obtained by accommodating the two electrons in the lowest available orbital (the bonding orbital).

orbitals we can build two molecular orbitals. In general, from *N* atomic orbitals we can build *N* molecular orbitals.

There are two electrons to accommodate, and both can enter $1\sigma_g$ by pairing their spins, as required by the Pauli principle (just as for atoms, Topic 19). The ground-state configuration is therefore $1\sigma_g^2$ and the atoms are joined by a bond consisting of an electron pair in a bonding σ orbital. This approach shows that an electron pair, which was the focus of Lewis's account of chemical bonding, represents the maximum number of electrons that can enter a bonding molecular orbital.

The same argument explains why He does not form diatomic molecules. Each He atom contributes a 1s orbital, so $1\sigma_g$ and $1\sigma_u$ molecular orbitals can be constructed. Although these orbitals differ in detail from those in H_2, their general shapes are the same and we can use the same qualitative energy level diagram in the discussion. There are four electrons to accommodate. Two can enter the $1\sigma_g$ orbital, but then it is full, and the next two must enter the $1\sigma_u$ orbital (Fig. 24.2). The ground electronic configuration of He_2 is therefore $1\sigma_g^2 1\sigma_u^2$. We see that there is one bond and one antibond. Because $1\sigma_u$ is raised in energy relative to the separate atoms more than $1\sigma_g$ is lowered, an He_2 molecule has a higher energy than the separated atoms, so it is unstable relative to them.

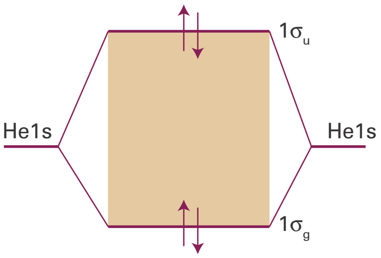

Figure 24.2 The ground electronic configuration of the hypothetical four-electron molecule He_2 has two bonding electrons and two antibonding electrons. It has a higher energy than the separated atoms, and so is unstable.

We shall now see how the concepts we have introduced apply to homonuclear diatomic molecules in general. In elementary treatments, only the orbitals of the valence shell are used to form molecular orbitals so, for molecules formed with atoms from Period 2 elements, only the 2s and 2p atomic orbitals are considered. We shall make that approximation here too.

A general principle of molecular orbital theory is that *all orbitals of the appropriate symmetry* contribute to a molecular orbital. Thus, to build σ orbitals, we form linear combinations of all atomic orbitals that have cylindrical symmetry about the internuclear axis. These orbitals include the 2s orbitals on each atom and the $2p_z$ orbitals on the two atoms (Fig. 24.3). The general form of the σ orbitals that may be formed is therefore

$$\psi = c_{A2s}\chi_{A2s} + c_{B2s}\chi_{B2s} + c_{A2p_z}\chi_{A2p_z} + c_{B2p_z}\chi_{B2p_z} \qquad (24.1)$$

From these four atomic orbitals we can form four molecular orbitals of σ symmetry by an appropriate choice of the coefficients *c*.

The procedure for calculating the coefficients is described in Topic 25. Here we adopt a simpler route, and suppose that, because the 2s and $2p_z$ orbitals have distinctly different energies, they may be treated separately. That is, the four σ orbitals fall approximately into two sets, one consisting of two molecular orbitals of the form

$$\psi = c_{A2s}\chi_{A2s} + c_{B2s}\chi_{B2s} \qquad (24.2a)$$

and another consisting of two orbitals of the form

$$\psi = c_{A2p_z}\chi_{A2p_z} + c_{B2p_z}\chi_{B2p_z} \qquad (24.2b)$$

Because atoms A and B are identical, the energies of their 2s orbitals are the same, so the coefficients are equal (apart from a possible difference in sign); the same is true of the $2p_z$ orbitals. Therefore, the two sets of orbitals have the form $\chi_{A2s} \pm \chi_{B2s}$ and $\chi_{A2p_z} \pm \chi_{B2p_z}$.

The 2s orbitals on the two atoms overlap to give a bonding and an antibonding σ orbital ($1\sigma_g$ and $1\sigma_u$, respectively) in exactly the same way as we have already seen for 1s orbitals. The two $2p_z$ orbitals directed along the internuclear axis overlap strongly. They may interfere either constructively or destructively, and give a bonding or antibonding σ orbital (Fig. 24.4).

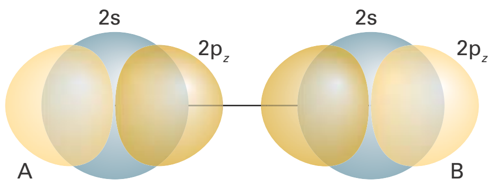

Figure 24.3 According to molecular orbital theory, σ orbitals are built from all orbitals that have the appropriate symmetry. In homonuclear diatomic molecules of Period 2, that means that two 2s and two $2p_z$ orbitals should be used. From these four orbitals, four molecular orbitals can be built.

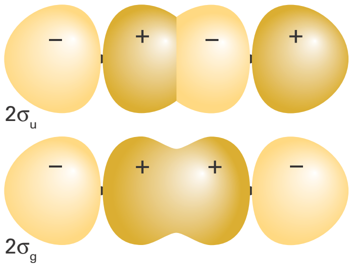

Figure 24.4 A representation of the composition of bonding and antibonding σ orbitals built from the overlap of p orbitals. These illustrations are schematic.

These two σ orbitals are labelled $2\sigma_g$ and $2\sigma_u$, respectively. In general, note how the numbering follows the order of increasing energy. We number only the molecular orbitals formed from atomic orbitals in the valence shell.

Brief illustration 24.1 Ground-state configurations

The valence configuration of a sodium atom is [Ne]$3s^1$, so 3s and 3p orbitals are used to construct molecular orbitals. At this level of approximation, we consider (3s,3s) and (3p,3p) overlap separately. In fact, because there are only two electrons to accommodate (one from each 3s orbital), we need consider only the former. That overlap results in $1\sigma_g$ and $1\sigma_u$ molecular orbitals. The only two valence electrons occupy the former, so the ground-state configuration of Na_2 is $1\sigma_g^2$.

Self-test 24.1 Identify the ground-state configuration of Be_2.

Answer: $1\sigma_g^2 1\sigma_u^2$ built from Be2s orbitals

Now consider the $2p_x$ and $2p_y$ orbitals of each atom. These orbitals are perpendicular to the internuclear axis and may overlap broadside-on. This overlap may be constructive or destructive and results in a bonding or an antibonding **π orbital** (Fig. 24.5). The notation π is the analogue of p in atoms, for when viewed along the axis of the molecule, a π orbital looks like a p orbital and has one unit of orbital angular momentum around the internuclear axis. More formally, the orbital has a single nodal plane that includes the internuclear axis. The two neighbouring $2p_x$ orbitals overlap to give a bonding and an antibonding π_x orbital, and the two $2p_y$ orbitals overlap to give two π_y orbitals. The π_x and π_y bonding orbitals are degenerate; so too are their antibonding partners. We also see from Fig. 24.5 that a bonding π orbital has odd parity and is denoted π_u and an antibonding π orbital has even parity, denoted π_g.

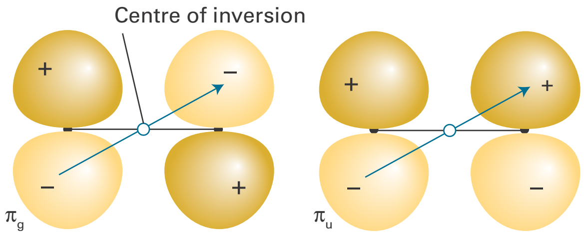

Figure 24.5 A schematic representation of the structure of π bonding and antibonding molecular orbitals. The figure also shows that the bonding π orbital has odd parity, whereas the antibonding π orbital has even parity.

(b) The overlap integral

The extent to which two atomic orbitals on different atoms overlap is measured by the **overlap integral**, *S*:

$$S=\int \chi_A^* \chi_B \, d\tau \qquad \textit{Definition} \quad \text{Overlap integral} \qquad (24.3)$$

This integral also appears in Example 23.1 of Topic 23 and eqn 23.5a. If the atomic orbital χ_A on A is small wherever the orbital χ_B on B is large, or vice versa, then the product of their amplitudes is everywhere small and the integral—the sum of these products—is small (Fig. 24.6). If χ_A and χ_B are both large in some region of space, then *S* may be large. If the two normalized atomic orbitals are identical (for instance, 1s orbitals on the same nucleus), then $S=1$. In some cases, simple formulas can be given for overlap integrals. For instance, the variation of *S* with internuclear separation for hydrogenic 1s orbitals on atoms of atomic number *Z* is given by

$$S(1s,1s)=\left\{1+\frac{ZR}{a_0}+\frac{1}{3}\left(\frac{ZR}{a_0}\right)^2\right\}e^{-ZR/a_0} \qquad \text{(1s,1s)-overlap integral} \qquad (24.4)$$

and is plotted in Fig. 24.7 (eqn 24.4 is a generalization of eqn 23.5a, which is for H1s orbitals).

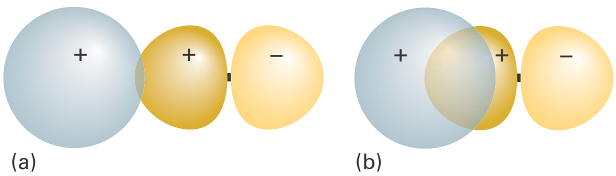

Figure 24.6 (a) When two orbitals are on atoms that are far apart, the wavefunctions are small where they overlap, so *S* is small. (b) When the atoms are closer, both orbitals have significant amplitudes where they overlap, and *S* may approach 1. Note that *S* will decrease again as the two atoms approach more closely than shown here, because the region of negative amplitude of the p orbital starts to overlap the positive amplitude of the s orbital. When the centres of the atoms coincide, $S=0$.

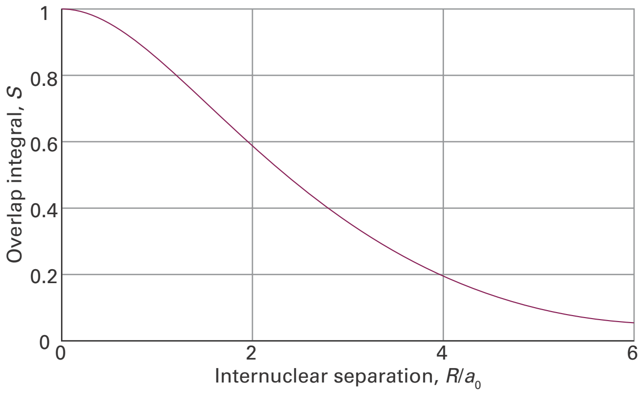

Figure 24.7 The overlap integral, S, between two H1s orbitals as a function of their separation R.

Brief illustration 24.2 Overlap integrals

Familiarity with the magnitudes of overlap integrals is useful when considering bonding abilities of atoms, and hydrogenic orbitals give an indication of their values. The overlap integral between two hydrogenic 2s orbitals (see Problem 24.5) is

$$S(2\text{s},2\text{s})=\left\{1+\frac{ZR}{2a_0}+\frac{1}{12}\left(\frac{ZR}{a_0}\right)^2+\frac{1}{240}\left(\frac{ZR}{a_0}\right)^4\right\}\mathrm{e}^{-ZR/2a_0}$$

This expression is plotted in Fig. 24.8. For an internuclear distance of $8a_0/Z$, $S(2\text{s},2\text{s})=0.50$.

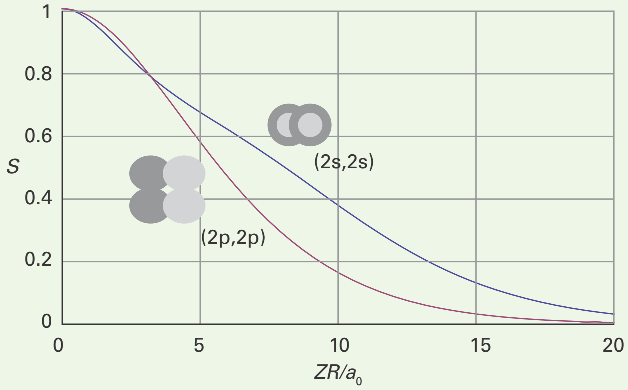

Figure 24.8 The overlap integral, S, between two hydrogenic 2s orbitals and between two side-by-side 2p orbitals as a function of their separation R.

Self-test 24.2 The side-by-side overlap of two 2p orbitals of atoms of atomic number Z is

$$S(2\text{p},2\text{p})=\left\{1+\frac{ZR}{2a_0}+\frac{1}{10}\left(\frac{ZR}{a_0}\right)^2+\frac{1}{120}\left(\frac{ZR}{a_0}\right)^3\right\}\mathrm{e}^{-ZR/2a_0}$$

Evaluate this overlap integral for $R=8a_0/Z$.

Answer: See Fig. 24.8; 0.29

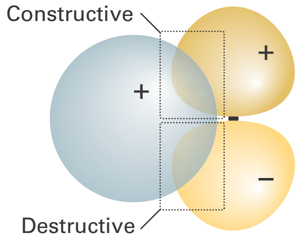

Figure 24.9 A p orbital in the orientation shown here has zero net overlap ($S=0$) with the s orbital at all internuclear separations.

Now consider the arrangement in which an s orbital is superimposed on a p_x orbital of a different atom (Fig. 24.9). The integral over the region where the product of orbitals is positive exactly cancels the integral over the region where the product of orbitals is negative, so overall $S=0$ exactly. Therefore, there is no net overlap between the s and p orbitals in this arrangement.

(c) Period 2 diatomic molecules

To construct the molecular orbital energy level diagram for Period 2 homonuclear diatomic molecules, we form eight molecular orbitals from the eight valence shell orbitals (four from each atom). In some cases, π orbitals are less strongly bonding than σ orbitals because their maximum overlap occurs off-axis. This relative weakness suggests that the molecular orbital energy level diagram ought to be as shown in Fig. 24.10. However, we must remember that we have assumed that 2s and 2p_z orbitals contribute to different sets of molecular orbitals whereas in fact all four atomic orbitals have the same symmetry around the internuclear axis and contribute jointly to the four σ orbitals. Hence, there is no guarantee that this order of energies should prevail, and it is found experimentally (by

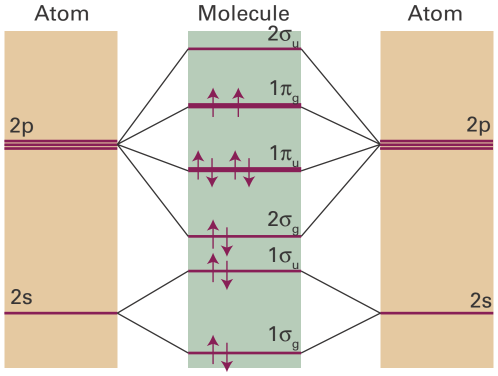

Figure 24.10 The molecular orbital energy level diagram for homonuclear diatomic molecules. The lines in the middle are an indication of the energies of the molecular orbitals that can be formed by overlap of atomic orbitals. As remarked in the text, this diagram should be used for O_2 (the configuration shown) and F_2.

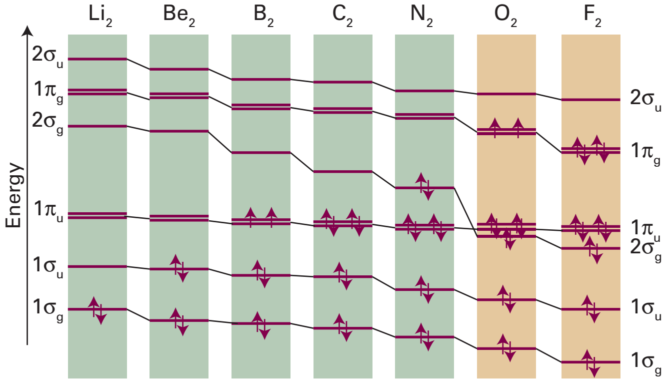

Figure 24.11 The variation of the orbital energies of Period 2 homonuclear diatomics.

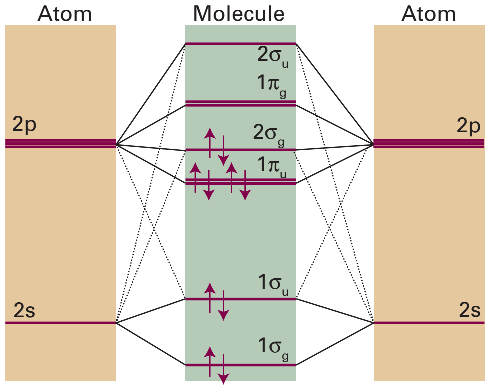

Figure 24.12 An alternative molecular orbital energy level diagram for homonuclear diatomic molecules. As remarked in the text, this diagram should be used for diatomics up to and including N_2 (the configuration shown).

spectroscopy) and by detailed calculation that the order varies along Period 2 (Fig. 24.11). The order shown in Fig. 24.12 is appropriate as far as N_2, and Fig. 24.10 is appropriate for O_2 and F_2. The relative order is controlled by the separation of the 2s and 2p orbitals in the atoms, which increases across the group: as the atomic number increases, the 2s electrons are pulled closer to the nucleus and thus increasingly shield the 2p electrons. The consequent switch in order occurs at about N_2.

With the molecular orbital energy level diagram established, we can deduce the probable ground-state configurations of the molecules by adding the appropriate number of electrons to the orbitals and following the building-up rules. Anionic species (such as the peroxide ion, O_2^{2-}) need more electrons than the parent neutral molecules; cationic species (such as O_2^+) need fewer.

Consider N_2, which has 10 valence electrons. Two electrons pair, occupy, and fill the $1\sigma_g$ orbital; the next two occupy and fill the $1\sigma_u$ orbital. Six electrons remain. There are two $1\pi_u$ orbitals, so four electrons can be accommodated in them. The last two enter the $2\sigma_g$ orbital. Therefore, the ground-state configuration of N_2 is $1\sigma_g^2 1\sigma_u^2 1\pi_u^4 2\sigma_g^2$. It is sometimes helpful to include an asterisk to denote an antibonding orbital, in which case this configuration would be denoted $1\sigma_g^2 1\sigma_u^{*2} 1\pi_u^4 2\sigma_g^2$.

A measure of the net bonding in a diatomic molecule is its **bond order**, b:

$$b=\tfrac{1}{2}(N-N^*) \tag{24.5}$$

Definition Bond order

where N is the number of electrons in bonding orbitals and N^* is the number of electrons in antibonding orbitals.

Brief illustration 24.3 Bond order

Each electron pair in a bonding orbital increases the bond order by 1 and each pair in an antibonding orbital decreases b by 1. For H_2, $b=1$, corresponding to a single bond, H–H, between the two atoms. In He_2, $b=0$, and there is no bond. In N_2, $b=\tfrac{1}{2}(8-2)=3$. This bond order accords with the Lewis structure of the molecule (:N≡N:).

Self-test 24.3 Evaluate the bond orders of O_2, O_2^+, and O_2^-.

Answer: 2, $\tfrac{5}{2}$, $\tfrac{3}{2}$

The ground-state electron configuration of O_2, with 12 valence electrons, is based on Fig. 24.10, and is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^2$ (or $1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 1\pi_u^4 1\pi_g^{*2}$). Its bond order is 2. According to the building-up principle, however, the two $1\pi_g$ electrons occupy different orbitals: one will enter $1\pi_{g,x}$ and the other will enter $1\pi_{g,y}$. Because the electrons are in different orbitals, they will have parallel spins. Therefore, we can predict that an O_2 molecule will have a net spin angular momentum $S=1$ and, in the language introduced in Topic 21, be in a triplet state. As electron spin is the source of a magnetic moment, we can go on to predict that oxygen should be paramagnetic, a substance that tends to move into a magnetic field (see Topic 39). This prediction, which VB theory does not make, is confirmed by experiment.

An F_2 molecule has two more electrons than an O_2 molecule. Its configuration is therefore $1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 1\pi_u^4 1\pi_g^{*4}$ and $b=1$. We conclude that F_2 is a singly bonded molecule, in agreement with its Lewis structure. The hypothetical molecule dineon, Ne_2, has two additional electrons: its configuration is $1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 1\pi_u^4 1\pi_g^{*4} 2\sigma_u^{*2}$ and $b=0$. The zero bond order is consistent with the monatomic nature of Ne.

The bond order is a useful parameter for discussing the characteristics of bonds, because it correlates with bond length and bond strength. For bonds between atoms of a given pair of elements:

- The greater the bond order, the shorter the bond.
- The greater the bond order, the greater the bond strength.

Table 24.1 lists some typical bond lengths in diatomic and polyatomic molecules. The strength of a bond is measured by its bond dissociation energy, $hc\tilde{D}_0$, the energy required to

Table 24.1* Bond lengths

Bond	Order	R_e/pm
HH	1	74.14
NN	3	109.76
HCl	1	127.45
CH	1	*114*
CC	1	*154*
CC	2	*134*
CC	3	*120*

*More values are given in the *Resource section*. Numbers in italics are mean values for polyatomic molecules.

Table 24.2* Bond dissociation energies

Bond	Order	$hc\tilde{D}_0/(\text{kJ mol}^{-1})$
HH	1	432.1
NN	3	941.7
HCl	1	427.7
CH	1	*435*
CC	1	*368*
CC	2	*720*
CC	3	*962*

*More values are given in the *Resource section*. Numbers in italics are mean values for polyatomic molecules.

separate the atoms to infinity or by the well depth, $hc\tilde{D}_e$, with $hc\tilde{D}_0 = hc\tilde{D}_e - \frac{1}{2}\hbar\omega$. Table 24.2 lists some experimental values of $hc\tilde{D}_0$.

Example 24.1 Judging the relative bond strengths of molecules and ions

Predict whether N_2^+ is likely to have a larger or smaller bond dissociation energy than N_2.

Method Because the molecule with the higher bond order is likely to have the higher dissociation energy, compare their electronic configurations and assess their bond orders.

Answer From Fig. 24.12, the electron configurations and bond orders are

$$N_2 \quad 1\sigma_g^2 1\sigma_u^{*2} 1\pi_u^4 2\sigma_g^2 \quad b=3$$
$$N_2^+ \quad 1\sigma_g^2 1\sigma_u^{*2} 1\pi_u^4 2\sigma_g^1 \quad b=2\tfrac{1}{2}$$

Because the cation has the smaller bond order, we expect it to have the smaller bond dissociation energy. The experimental dissociation energies are 942 kJ mol^{-1} for N_2 and 842 kJ mol^{-1} for N_2^+.

Self-test 24.4 Which can be expected to have the higher dissociation energy, F_2 or F_2^+?

Answer: F_2^+

24.2 Photoelectron spectroscopy

So far we have treated molecular orbitals as purely theoretical constructs, but is there experimental evidence for their existence? **Photoelectron spectroscopy** (PES) measures the ionization energies of molecules when electrons are ejected from different orbitals by absorption of a photon of known energy, and uses the information to infer the energies of molecular orbitals. The technique is also used to study solids, and in Topic 95 we see the important information that it gives about species at or on surfaces.

Because energy is conserved when a photon ionizes a sample, the sum of the ionization energy, I, of the sample and the kinetic energy of the **photoelectron**, the ejected electron, must be equal to the energy of the incident photon $h\nu$ (Fig. 24.13):

$$h\nu = \tfrac{1}{2}m_e v^2 + I \tag{24.6}$$

This equation (which is like the one used for the photoelectric effect, eqn 4.5 written as $h\nu = \frac{1}{2}m_e v^2 + \Phi$) can be refined in two ways. First, photoelectrons may originate from one of a number of different orbitals, and each one has a different ionization energy. Hence, a series of different kinetic energies of the photoelectrons will be obtained, each one satisfying $h\nu = \frac{1}{2}m_e v^2 + I_i$, where I_i is the ionization energy for ejection of an electron from an orbital i. Therefore, by measuring the kinetic energies of the photoelectrons, and knowing ν, these ionization energies can be determined. Photoelectron spectra are interpreted in terms of an approximation called **Koopmans' theorem**, which states that the ionization energy I_i is equal to the orbital energy of the ejected electron (formally, $I_i = -\varepsilon_i$). That is, we can identify the ionization energy with the energy of the orbital from which it is ejected. The theorem is only an approximation because it ignores the fact that the remaining electrons adjust their distributions when ionization occurs.

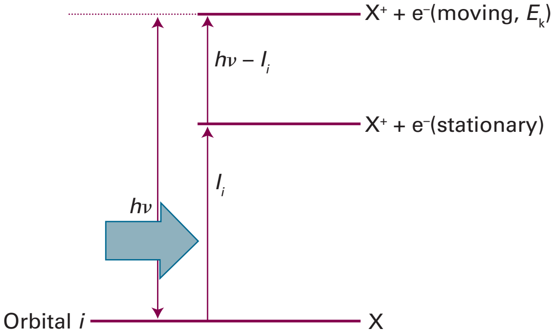

Figure 24.13 An incoming photon carries an energy $h\nu$; an energy I_i is needed to remove an electron from an orbital i, and the difference appears as the kinetic energy of the electron.

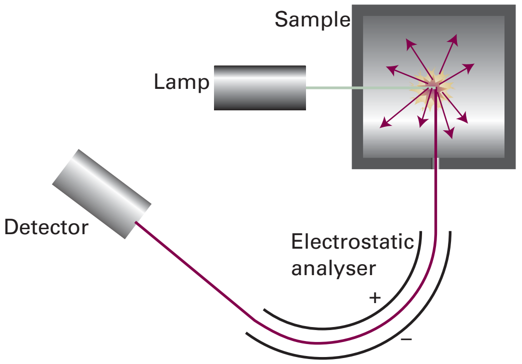

Figure 24.14 A photoelectron spectrometer consists of a source of ionizing radiation (such as a helium discharge lamp for UPS and an X-ray source for XPS), an electrostatic analyser, and an electron detector. The deflection of the electron path caused by the analyser depends on the speed of the electrons.

The ionization energies of molecules are several electronvolts even for valence electrons, so it is essential to work in at least the ultraviolet region of the spectrum and with wavelengths of less than about 200 nm. Much work has been done with radiation generated by a discharge through helium: the He(I) line ($1s^12p^1 \rightarrow 1s^2$) lies at 58.43 nm, corresponding to a photon energy of 21.22 eV. Its use gives rise to the technique of **ultraviolet photoelectron spectroscopy** (UPS). When core electrons are being studied, photons of even higher energy are needed to expel them: X-rays are used, and the technique is denoted XPS.

The kinetic energies of the photoelectrons are measured using an electrostatic deflector that produces different deflections in the paths of the photoelectrons as they pass between charged plates (Fig. 24.14). As the field strength is increased, electrons of different speeds, and therefore kinetic energies, reach the detector. The electron flux can be recorded and plotted against kinetic energy to obtain the photoelectron spectrum.

Brief illustration 24.4 A photoelectron spectrum

Photoelectrons ejected from N_2 with He(I) radiation have kinetic energies of 5.63 eV (1 eV = 8065.5 cm^{-1}, Fig. 24.15). Helium(I) radiation of wavelength 58.43 nm has wavenumber 1.711×10^5 cm^{-1} and therefore corresponds to an energy of 21.22 eV. Then, from eqn 24.6, 21.22 eV = 5.63 eV + I_i, so I_i = 15.59 eV. This ionization energy is the energy needed to remove an electron from the occupied molecular orbital with the highest energy of the N_2 molecule, the $2\sigma_g$ bonding orbital.

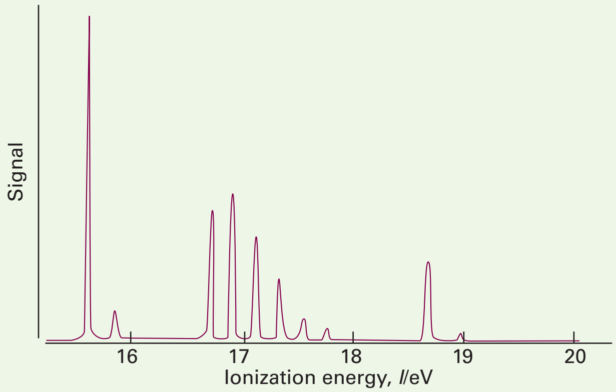

Figure 24.15 The photoelectron spectrum of N_2.

Self-test 24.5 Under the same circumstances, photoelectrons are also detected at 4.53 eV. To what ionization energy does that correspond? Suggest an origin.

Answer: 16.7 eV, $1\pi_u$

It is often observed that photoejection results in cations that are excited vibrationally. Because different energies are needed to excite different vibrational states of the ion, the photoelectrons appear with different kinetic energies. The result is **vibrational fine structure**, a progression of lines with a frequency spacing that corresponds to the vibrational frequency of the molecule. Figure 24.16 shows an example of vibrational fine structure in the photoelectron spectrum of HBr.

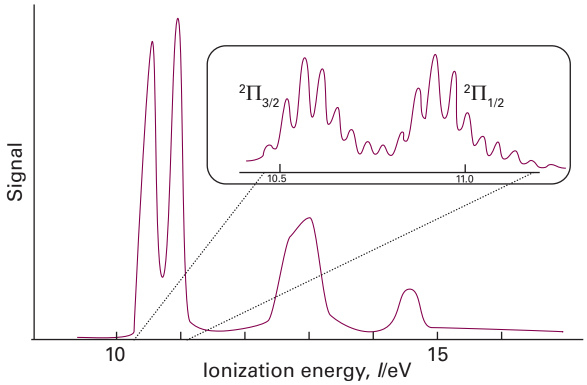

Figure 24.16 The photoelectron spectrum of HBr.

Checklist of concepts

☐ 1. Electrons are added to available molecular orbitals in a manner that achieves the lowest overall energy.

☐ 2. As a first approximation, σ orbitals are constructed separately from valence s and p orbitals.

☐ 3. σ **Orbitals** have cylindrical symmetry and zero orbital angular momentum around the internuclear axis.

☐ 4. π **Orbitals** are constructed from the side-by-side overlap of orbitals of the appropriate symmetry; they have a nodal plane that includes the internuclear axis.

☐ 5. An **overlap integral** is a measure of the extent of orbital overlap.

☐ 6. **Photoelectron spectroscopy** is a technique for determining the energies of electrons in molecular orbitals.

☐ 7. The greater the **bond order** of a molecule, the shorter and stronger the bond.

Checklist of equations

Property	Equation	Comment	Equation number
Overlap integral	$S=\int \chi_A^* \chi_B \,d\tau$		24.3
Bond order	$b=\frac{1}{2}(N-N^*)$		24.5
Photoelectron spectroscopy	$h\nu=\frac{1}{2}m_e v^2+I_i$	I_i is the ionization energy from orbital i	24.6

TOPIC 25

Heteronuclear diatomic molecules

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➤ Why do you need to know this material?

Most molecules are heteronuclear, so you need to appreciate the differences in their electronic structure from homonuclear species, and how to treat those differences quantitatively.

➤ What is the key idea?

The bonding molecular orbital of a heteronuclear diatomic molecule is composed mostly of the atomic orbital of the more electronegative atom; the opposite is true of the antibonding orbital.

➤ What do you need to know already?

You need to know about the molecular orbitals of homonuclear diatomic molecules (Topic 24) and the concepts of normalization and orthogonality (Topics 5 and 7). This Topic makes use of determinants (*Mathematical background* 5) and rules about differentiation (*Mathematical background* 1).

The electron distribution in a covalent bond in a heteronuclear diatomic molecule is not shared equally by the atoms because it is energetically favourable for the electron pair to be found closer to one atom than the other. This imbalance results in a **polar bond**, a covalent bond in which the electron pair is shared unequally by the two atoms. The bond in HF, for instance, is polar, with the electron pair closer to the F atom. The accumulation of the electron pair near the F atom results in that atom having a net negative charge, which is called a **partial negative charge** and denoted $\delta-$. There is a matching **partial positive charge**, $\delta+$, on the H atom (Fig. 25.1).

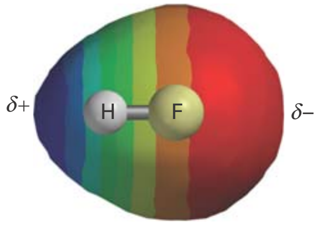

Figure 25.1 The electron density of the molecule HF, computed with one of the methods described in Topic 29. Different colours show the distribution of electrostatic potential and hence net charge, with blue representing the region with largest partial positive charge, and red the region with largest partial negative charge.

25.1 Polar bonds

The description of polar bonds in terms of molecular orbital theory is a straightforward extension of that for homonuclear diatomic molecules, the central difference being that the atomic orbitals on the two atoms have different energies and spatial extensions.

(a) The molecular orbital formulation

A polar bond consists of two electrons in a bonding molecular orbital of the form

$$\psi = c_A A + c_B B \qquad \text{Wavefunction of a polar bond} \qquad (25.1)$$

with unequal coefficients. The proportion of the atomic orbital A in the bond is $|c_A|^2$ and that of B is $|c_B|^2$. A nonpolar bond has $|c_A|^2 = |c_B|^2$ and a pure ionic bond has one coefficient zero (so the species A^+B^- would have $c_A = 0$ and $c_B = 1$). The atomic orbital with the lower energy makes the larger contribution to the bonding molecular orbital. The opposite is true of the antibonding orbital, for which the dominant component comes from the atomic orbital with higher energy.

Deciding what values to use for the energies of the atomic orbitals in eqn 25.1 presents a dilemma because they are known only after a complicated calculation of the kind described in Topic 29 has been performed. An alternative, one that gives some insight into the origin of the energies, is to estimate them from ionization energies and electron affinities. Thus, the extreme cases of an atom X in a molecule are X^+ if it has lost control of the electron it supplied, X if it is sharing the electron pair equally with its bonded partner, and X^- if it has gained control of both electrons in the bond. If X^+ is taken as defining the energy 0, then X lies at $-I(X)$ and X^- lies at $-\{I(X)+E_{ea}(X)\}$, where I is the ionization energy and E_{ea} the electron affinity (Fig. 25.2). The actual energy of the orbital lies at an intermediate value, and in the absence of further information, we shall estimate it as halfway down to the lowest of these values, namely $-\frac{1}{2}\{I(X)+E_{ea}(X)\}$. Then, to establish the MO composition and energies, we form linear combinations of atomic orbitals with these values of the energy and anticipate that the atom with the more negative value of $-\frac{1}{2}\{I(X)+E_{ea}(X)\}$ contributes the greater amount to the bonding orbital. As we shall see shortly, the quantity $\frac{1}{2}\{I(X)+E_{ea}(X)\}$ also has a further significance.

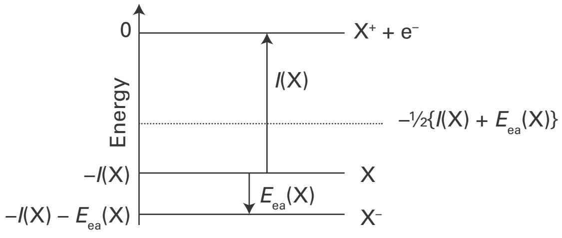

Figure 25.2 The procedure for estimating the energy of an atomic orbital in a molecule.

Brief illustration 25.1 Heteronuclear diatomic molecules 1

These points can be illustrated by considering HF. The general form of the molecular orbital is $\psi = c_H\chi_H + c_F\chi_F$, where χ_H is an H1s orbital and χ_F is an F2p$_z$ orbital (with z along the internuclear axis, the convention for linear molecules). The relevant data are as follows:

	I/eV	E_{ea}/eV	$\frac{1}{2}\{I+E_{ea}\}$/eV
H	13.6	0.75	7.2
F	17.4	3.34	10.4

We see that the electron distribution in HF is likely to be predominantly on the F atom. We take the calculation further below (in *Brief illustrations* 25.3 and 25.4).

Self-test 25.1 Which atomic orbital, H1s or N2p$_z$ makes the dominant contribution to the bonding σ orbital in the HN molecular radical? For data, see Tables 20.2 and 20.3.

Answer: N2p$_z$

(b) Electronegativity

The charge distribution in bonds is commonly discussed in terms of the **electronegativity**, χ (chi), of the elements involved (there should be little danger of confusing this use of χ with its use to denote an atomic orbital, which is another common convention). The electronegativity is a parameter introduced by Linus Pauling as a measure of the power of an atom to attract electrons to itself when it is part of a compound. Pauling used valence-bond arguments to suggest that an appropriate numerical scale of electronegativities could be defined in terms of bond dissociation energies, D_0, and proposed that the difference in electronegativities could be expressed as

$$|\chi_A - \chi_B| = \{D_0(AB) - \tfrac{1}{2}[D_0(AA)+D_0(BB)]\}^{1/2} \qquad \text{Definition} \quad \text{Pauling electronegativity} \qquad (25.2)$$

where $D_0(AA)$ and $D_0(BB)$ are the dissociation energies of A–A and B–B bonds and $D_0(AB)$ is the dissociation energy of an A–B bond, all in electronvolts. (In later work Pauling used the geometrical mean of dissociation energies in place of the arithmetic mean.) This expression gives differences of electronegativities; to establish an absolute scale Pauling chose individual values that gave the best match to the values obtained from eqn 25.2. Electronegativities based on this definition are called

Table 25.1* Pauling electronegativities

Element	χ_{Pauling}
H	2.2
C	2.6
N	3.0
O	3.4
F	4.0
Cl	3.2
Cs	0.79

* More values are given in the *Resource section*.

Pauling electronegativities (Table 25.1). The most electronegative elements are those close to F (excluding the noble gases); the least are those close to Cs. It is found that the greater the difference in electronegativities, the greater the polar character of the bond. The difference for HF, for instance, is 1.78; a C–H bond, which is commonly regarded as almost nonpolar, has an electronegativity difference of 0.35.

Brief illustration 25.2 Electronegativity

The bond dissociation energies of hydrogen, chlorine, and hydrogen chloride are 4.52 eV, 2.51 eV, and 4.47 eV, respectively. From eqn 25.2 we find

$$|\chi_{\text{Pauling}}(\text{H})-\chi_{\text{Pauling}}(\text{Cl})|=\{4.47-\tfrac{1}{2}(4.52+2.51)\}^{1/2}=0.98\approx 1.0$$

Self-test 25.2 Repeat the analysis for HBr. Use data from Table 24.2.

Answer: $|\chi_{\text{Pauling}}(\text{H})-\chi_{\text{Pauling}}(\text{Br})|=0.73$

The spectroscopist Robert Mulliken proposed an alternative definition of electronegativity. He argued that an element is likely to be highly electronegative if it has a high ionization energy (so it will not release electrons readily) and a high electron affinity (so it is energetically favourable to acquire electrons). The **Mulliken electronegativity scale** is therefore based on the definition

$$\chi=\tfrac{1}{2}(I+E_{\text{ea}}) \qquad \textit{Definition} \quad \text{Mulliken electronegativity} \qquad (25.3)$$

where I is the ionization energy of the element and E_{ea} is its electron affinity (both in electronvolts). It will be recognized that this combination of energies is precisely the one we have used to estimate the energy of an atomic orbital in a molecule, and we can therefore see that the greater the value of the Mulliken electronegativity the greater is the contribution of that atom to the electron distribution in the bond. There is one word of caution: the values of I and E_{ea} in eqn 25.3 are strictly those for a special 'valence state' of the atom, not a true spectroscopic state. We ignore that complication here. The Mulliken and Pauling scales are approximately in line with each other. A reasonably reliable conversion relation between the two is

$$\chi_{\text{Pauling}}=1.35\chi_{\text{Mulliken}}^{1/2}-1.37 \qquad (25.4)$$

25.2 The variation principle

A more systematic way of discussing bond polarity and finding the coefficients in the linear combinations used to build molecular orbitals is provided by the **variation principle**, which is proved in the following *Justification*:

> If an arbitrary wavefunction is used to calculate the energy, the value calculated is never less than the true energy. Variation principle

This principle, which is also described briefly in Topic 22, is the basis of all modern molecular structure calculations (Topics 27–30). The arbitrary wavefunction is called the **trial wavefunction**. The principle implies that, if we vary the coefficients in the trial wavefunction until the lowest energy is achieved (by evaluating the expectation value of the hamiltonian for each wavefunction), then those coefficients will be the best. We might get a lower energy if we use a more complicated wavefunction (for example, by taking a linear combination of several atomic orbitals on each atom), but we shall have the optimum (minimum energy) molecular orbital that can be built from the chosen **basis set**, the given set of atomic orbitals.

Justification 25.1 The variation principle

To justify the variation principle, consider a trial (normalized) wavefunction written as a linear combination $\psi_{\text{trial}}=\sum_n c_n\psi_n$ of the true (but unknown), normalized, and orthogonal eigenfunctions of the hamiltonian $\hat{H}$. The energy associated with this trial function is the expectation value

$$E=\int\psi_{\text{trial}}^{*}\hat{H}\psi_{\text{trial}}\,\mathrm{d}\tau$$

The true lowest energy of the system is E_0, the eigenvalue corresponding to ψ_0. Consider the following difference:

$$\begin{aligned}E-E_0&=\int\psi_{\text{trial}}^{*}\hat{H}\psi_{\text{trial}}\,\mathrm{d}\tau-E_0\overbrace{\int\psi_{\text{trial}}^{*}\psi_{\text{trial}}\,\mathrm{d}\tau}^{(1)}\\&=\int\psi_{\text{trial}}^{*}\hat{H}\psi_{\text{trial}}\,\mathrm{d}\tau-\int\psi_{\text{trial}}^{*}E_0\psi_{\text{trial}}\,\mathrm{d}\tau\\&=\int\psi_{\text{trial}}^{*}(\hat{H}-E_0)\psi_{\text{trial}}\,\mathrm{d}\tau\\&=\int\left(\sum_n c_n^{*}\psi_n^{*}\right)(\hat{H}-E_0)\left(\sum_{n'} c_{n'}\psi_{n'}\right)\mathrm{d}\tau\\&=\sum_{n,n'}c_n^{*}c_{n'}\int\psi_n^{*}(\hat{H}-E_0)\psi_{n'}\,\mathrm{d}\tau\end{aligned}$$

Because $\int \psi_n^* \hat{H} \psi_{n'} \mathrm{d}\tau = E_{n'} \int \psi_n^* \psi_{n'} \mathrm{d}\tau$ and $\int \psi_n^* E_0 \psi_{n'} \mathrm{d}\tau = E_0 \int \psi_n^* \psi_{n'} \mathrm{d}\tau$, we write

$$\int \psi_n^* (\hat{H} - E_0) \psi_{n'} \mathrm{d}\tau = (E_{n'} - E_0) \int \psi_n^* \psi_{n'} \mathrm{d}\tau$$

and

$$E - E_0 = \sum_{n,n'} c_n^* c_{n'} (E_{n'} - E_0) \overbrace{\int \psi_n^* \psi_{n'} \mathrm{d}\tau}^{0 \text{ unless } n' = n}$$

The eigenfunctions are orthogonal, so only $n' = n$ contributes to this sum, and as each eigenfunction is normalized, each integral is 1. Consequently

$$E - E_0 = \sum_n \overbrace{c_n^* c_n}^{\geq 0} \overbrace{(E_n - E_0)}^{\geq 0} \geq 0$$

That is, $E \geq E_0$, as we set out to prove.

(a) The procedure

The method can be illustrated by the trial wavefunction in eqn 25.1. We show in the following *Justification* that the coefficients are given by the solutions of the two **secular equations**[1]

$$(\alpha_A - E)c_A + (\beta - ES)c_B = 0 \tag{25.5a}$$

$$(\beta - ES)c_A + (\alpha_B - E)c_B = 0 \tag{25.5b}$$

where

$$\alpha_A = \int A\hat{H}A\,\mathrm{d}\tau \quad \alpha_B = \int B\hat{H}B\,\mathrm{d}\tau \qquad \text{Coulomb integrals} \tag{25.5c}$$

$$\beta = \int A\hat{H}B\,\mathrm{d}\tau = \int B\hat{H}A\,\mathrm{d}\tau \qquad \text{Resonance integral} \tag{25.5d}$$

The parameter α is called a **Coulomb integral**. It is negative and can be interpreted as the energy of the electron when it occupies A (for α_A) or B (for α_B). In a homonuclear diatomic molecule, $\alpha_A = \alpha_B$. The parameter β is called a **resonance integral** (for classical reasons). It vanishes when the orbitals do not overlap, and at equilibrium bond lengths it is normally negative.

Justification 25.2 The variation principle applied to a heteronuclear diatomic molecule

The trial wavefunction in eqn 25.1 is real but not normalized because at this stage the coefficients can take arbitrary values. Therefore, we can write $\psi^* = \psi$ but we do not assume that $\int \psi^2 \mathrm{d}\tau = 1$. When a wavefunction is not normalized, we write the expression for the energy (Topic 7) as

$$E = \frac{\int \psi^* \hat{H} \psi \,\mathrm{d}\tau}{\int \psi^* \psi \,\mathrm{d}\tau} \xrightarrow{\psi \text{ real}} \frac{\int \psi \hat{H} \psi \,\mathrm{d}\tau}{\int \psi^2 \,\mathrm{d}\tau} \qquad \text{Energy} \tag{25.6}$$

We now search for values of the coefficients in the trial function that minimize the value of E. This is a standard problem in calculus, and is solved by finding the coefficients for which

$$\frac{\partial E}{\partial c_A} = 0 \qquad \frac{\partial E}{\partial c_B} = 0$$

The first step is to express the two integrals in eqn 25.6 in terms of the coefficients. The denominator is

$$\int \psi^2 \,\mathrm{d}\tau = \int (c_A A + c_B B)^2 \,\mathrm{d}\tau$$

$$= c_A^2 \overbrace{\int A^2 \mathrm{d}\tau}^{1} + c_B^2 \overbrace{\int B^2 \mathrm{d}\tau}^{1} + 2c_A c_B \overbrace{\int AB \,\mathrm{d}\tau}^{S} = c_A^2 + c_B^2 + 2c_A c_B S$$

because the individual atomic orbitals are normalized and the third integral is the overlap integral S (eqn 24.3). The numerator is

$$\int \psi \hat{H} \psi \,\mathrm{d}\tau = \int (c_A A + c_B B) \hat{H} (c_A A + c_B B) \mathrm{d}\tau$$

$$= c_A^2 \overbrace{\int A\hat{H}A \,\mathrm{d}\tau}^{\alpha_A} + c_B^2 \overbrace{\int B\hat{H}B \,\mathrm{d}\tau}^{\alpha_B} + c_A c_B \overbrace{\int A\hat{H}B \,\mathrm{d}\tau}^{\beta} + c_A c_B \overbrace{\int B\hat{H}A \,\mathrm{d}\tau}^{\beta}$$

With the integrals written as shown (the two β integrals are equal by hermiticity, Topic 6), the numerator is

$$\int \psi \hat{H} \psi \,\mathrm{d}\tau = c_A^2 \alpha_A + c_B^2 \alpha_B + 2c_A c_B \beta$$

At this point we can write the complete expression for E as

$$E = \frac{c_A^2 \alpha_A + c_B^2 \alpha_B + 2c_A c_B \beta}{c_A^2 + c_B^2 + 2c_A c_B S}$$

Its minimum is found by differentiation with respect to the two coefficients and setting the results equal to 0. After some straightforward work we obtain

$$\frac{\partial E}{\partial c_A} = \frac{2\{(\alpha_A - E)c_A + (\beta - SE)c_B\}}{c_A^2 + c_B^2 + 2c_A c_B S}$$

$$\frac{\partial E}{\partial c_B} = \frac{2\{(\alpha_B - E)c_B + (\beta - SE)c_A\}}{c_A^2 + c_B^2 + 2c_A c_B S}$$

---

[1] The name 'secular' is derived from the Latin word for age or generation. The term comes from astronomy, where the same equations appear in connection with slowly accumulating modifications of planetary orbits.

For the derivatives to be equal to 0, the numerators of these expressions must vanish. That is, we must find values of c_A and c_B that satisfy the conditions

$$(\alpha_A - E)c_A + (\beta - SE)c_B = 0$$
$$(\alpha_B - E)c_B + (\beta - SE)c_A = 0$$

which are the secular equations (eqn 25.5).

To solve the secular equations for the coefficients we need to know the energy E of the orbital. As for any set of simultaneous equations (*Mathematical background* 5), the secular equations have a solution if the **secular determinant**, the determinant of the coefficients, is zero; that is, if

$$\begin{vmatrix} \alpha_A - E & \beta - SE \\ \beta - SE & \alpha_B - E \end{vmatrix} = (\alpha_A - E)(\alpha_B - E) - (\beta - SE)^2$$
$$= (1-S^2)E^2 + \{2\beta S - (\alpha_A + \alpha_B)\}E + (\alpha_A\alpha_B - \beta^2) = 0 \qquad (25.7)$$

This quadratic equation has two roots that give the energies of the bonding and antibonding molecular orbitals formed from the atomic orbitals:

$$E_\pm = \frac{\alpha_A + \alpha_B - 2\beta S \pm \{(\alpha_A + \alpha_B - 2\beta S)^2 - 4(1-S^2)(\alpha_A\alpha_B - \beta^2)\}^{1/2}}{2(1-S^2)} \qquad (25.8a)$$

This expression becomes more transparent in two cases. For a *homonuclear diatomic molecule* we can set $\alpha_A = \alpha_B = \alpha$ and obtain

$$E_\pm = \frac{2\alpha - 2\beta S \pm \left\{\overbrace{(2\alpha - 2\beta S)^2 - 4(1-S^2)(\alpha^2 - \beta^2)}^{(2\beta - 2\alpha S)^2}\right\}^{1/2}}{\underbrace{2(1-S^2)}_{(1+S)(1-S)}}$$
$$= \frac{\alpha - \beta S \pm (\beta - \alpha S)}{(1+S)(1-S)} = \frac{(\alpha \pm \beta)(1 \mp S)}{(1+S)(1-S)}$$

and therefore

$$E_+ = \frac{\alpha + \beta}{1+S} \qquad E_- = \frac{\alpha - \beta}{1-S} \qquad (25.8b)$$

Homonuclear diatomic molecules

For $\beta < 0$, E_+ is the lower-energy solution. For *heteronuclear diatomic molecules* we can make the approximation that $S = 0$ (simply to get a more transparent expression), and find

$$E_\pm = \tfrac{1}{2}(\alpha_A + \alpha_B) \pm \tfrac{1}{2}(\alpha_A - \alpha_B)\left\{1 + \left(\frac{2\beta}{\alpha_A - \alpha_B}\right)^2\right\}^{1/2} \qquad (25.8c)$$

Zero overlap approximation

Brief illustration 25.3 Heteronuclear diatomic molecules 2

In *Brief illustration* 25.1 we estimated the H1s and F2p orbital energies in HF as −7.2 eV and −10.4 eV, respectively. Therefore we set $\alpha_H = -7.2$ eV and $\alpha_F = -10.4$ eV. We take $\beta = -1.0$ eV as a typical value and $S = 0$. Substituting these values into eqn 25.8c gives

$$E_\pm/\text{eV} = \tfrac{1}{2}(-7.2 - 10.4) \pm \tfrac{1}{2}(-7.2 + 10.4)\left\{1 + \left(\frac{-2.0}{-7.2 + 10.4}\right)^2\right\}^{1/2}$$
$$= -8.8 \pm 1.9 = -10.7 \text{ and } -6.9$$

These values, representing a bonding orbital at −10.7 eV and an antibonding orbital at −6.9 eV, are shown in Fig. 25.3.

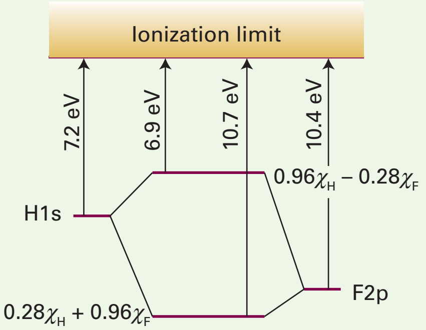

Figure 25.3 The estimated energies of the atomic orbitals in HF and the molecular orbitals they form.

Self-test 25.3 Use $S = 0.20$ (a typical value), to find the two energies.

Answer: $E_+ = -10.8$ eV, $E_- = -7.1$ eV

(b) The features of the solutions

An important feature of eqn 25.8c is that as the energy difference $|\alpha_A - \alpha_B|$ between the interacting atomic orbitals increases, the bonding and antibonding effects decrease (Fig. 25.4). Thus, when $|\alpha_A - \alpha_B| \gg 2|\beta|$ we can make the approximation $(1+x)^{1/2} \approx 1 + \tfrac{1}{2}x$ and obtain from eqn 25.8c

$$E_+ \approx \alpha_A + \frac{\beta^2}{\alpha_A - \alpha_B} \qquad E_- \approx \alpha_B - \frac{\beta^2}{\alpha_A - \alpha_B} \qquad (25.9)$$

As these expressions show, and as can be seen from the graph, when the energy difference is very large, the energies of the resulting molecular orbitals differ only slightly from those of the atomic orbitals, which implies in turn that the bonding and antibonding effects are small. That is:

> The strongest bonding and antibonding effects are obtained when the two contributing orbitals have closely similar energies.

Orbital contribution criterion

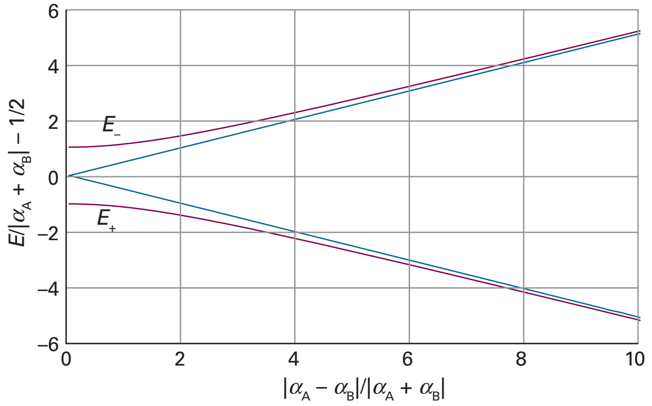

Figure 25.4 The variation of the energies of the molecular orbitals as the energy difference of the contributing atomic orbitals is changed. The plots are for $\beta=-1$; the blue lines are for the energies in the absence of mixing (that is, $\beta=0$).

The difference in energy between core and valence orbitals is the justification for neglecting the contribution of core orbitals to bonding. The core orbitals of one atom have a similar energy to the core orbitals of the other atom; but core–core interaction is largely negligible because the overlap between them (and hence the value of β) is so small.

The values of the coefficients in the linear combination in eqn 25.5 are obtained by solving the secular equations using the two energies obtained from the secular determinant. The lower energy, E_+, gives the coefficients for the bonding molecular orbital, and the upper energy, E_-, the coefficients for the antibonding molecular orbital. The secular equations give expressions for the ratio of the coefficients. Thus, the first of the two secular equations in eqn 25.5a, $(\alpha_A-E)c_A+(\beta-ES)c_B=0$, gives

$$c_B=-\left(\frac{\alpha_A-E}{\beta-ES}\right)c_A \tag{25.10}$$

The wavefunction should also be normalized. This condition means that the term $c_A^2+c_B^2+2c_Ac_BS$ established in *Justification* 25.2 must satisfy

$$c_A^2+c_B^2+2c_Ac_BS=1 \tag{25.11}$$

When the preceding relation is substituted into this expression, we find

$$c_A=\frac{1}{\left\{1+\left(\frac{\alpha_A-E}{\beta-ES}\right)^2-2S\left(\frac{\alpha_A-E}{\beta-ES}\right)\right\}^{1/2}} \tag{25.12}$$

which, together with eqn 25.10, gives explicit expressions for the coefficients once we substitute the appropriate values of $E=E_\pm$ given in eqn 25.8a. As before, this expression becomes more transparent in two cases. First, for a homonuclear diatomic molecule, with $\alpha_A=\alpha_B=\alpha$ and $E_\pm$ given in eqn 25.8b we find

$$E_+=\frac{\alpha+\beta}{1+S}\quad c_A=\frac{1}{\{2(1+S)\}^{1/2}}\quad c_B=c_A \tag{25.13a}$$

Homonuclear diatomic molecules

$$E_-=\frac{\alpha-\beta}{1-S}\quad c_A=\frac{1}{\{2(1-S)\}^{1/2}}\quad c_B=-c_A \tag{25.13b}$$

For a heteronuclear diatomic molecule with $S=0$, the coefficients for the orbital with energy E_+ are given by

$$c_A=\frac{1}{\left\{1+\left(\frac{\alpha_A-E_+}{\beta}\right)^2\right\}^{1/2}}\quad c_B=\frac{1}{\left\{1+\left(\frac{\beta}{\alpha_A-E_+}\right)^2\right\}^{1/2}} \tag{25.14a}$$

Zero overlap approximation

and those for the energy E_- are

$$c_A=\frac{1}{\left\{1+\left(\frac{\alpha_A-E_-}{\beta}\right)^2\right\}^{1/2}}\quad c_B=\frac{-1}{\left\{1+\left(\frac{\beta}{\alpha_A-E_-}\right)^2\right\}^{1/2}} \tag{25.14b}$$

Zero overlap approximation

with the values of $E_\pm$ taken from eqn 25.8c.

Brief illustration 25.4 Heteronuclear diatomic molecules 3

Here we continue *Brief illustration* 25.3 using HF. With $\alpha_H=-7.2$ eV, $\alpha_F=-10.4$ eV, $\beta=-1.0$ eV, and $S=0$ the two orbital energies were found to be $E_+=-10.7$ eV and $E_-=-6.9$ eV. When these values are substituted into eqn 25.14 we find the following coefficients:

$E_+=-10.7$ eV	$\psi_+=0.28\chi_H+0.96\chi_F$
$E_-=-6.9$ eV	$\psi_-=0.96\chi_H-0.28\chi_F$

Notice that the lower-energy orbital (the one with energy −10.7 eV) has a composition that is more F2p orbital than H1s, and that the opposite is true of the higher-energy, antibonding orbital.

Self-test 25.4 Find the energies and forms of the σ orbitals in the HCl molecule using $\beta=-1.0$ eV and $S=0$. Use data from Tables 20.2 and 20.3.

Answer: $E_+=-8.9$ eV, $E_-=-6.6$ eV; $\psi_-=0.86\chi_H-0.51\chi_{Cl}$; $\psi_+=0.51\chi_H+0.86\chi_{Cl}$

Checklist of concepts

☐ 1. A **polar bond** can be regarded as arising from a molecular orbital that is concentrated more on one atom than on its partner.

☐ 2. The **electronegativity** of an element is a measure of the power of an atom to attract electrons to itself when it is part of a compound.

☐ 3. The **variation principle** provides a criterion of acceptability of an approximate wavefunction.

☐ 4. A **basis set** refers to the given set of atomic orbitals from which the molecular orbitals are constructed.

☐ 5. The bonding and antibonding effects are strongest when contributing atomic orbitals have similar energies.

Checklist of equations

Property	Equation	Comment	Equation number
Molecular orbital	$\psi = c_A A + c_B B$		25.1
Pauling electronegativity	$\lvert\chi_A - \chi_B\rvert = \{D_0(AB) - \frac{1}{2}[D_0(AA) + D_0(BB)]\}^{1/2}$		25.2
Mulliken electronegativity	$\chi = \frac{1}{2}(I + E_{ea})$		25.3
Coulomb integral	$\alpha_A = \int A\hat{H}A\,d\tau$		25.5c
Resonance integral	$\beta = \int A\hat{H}B\,d\tau = \int B\hat{H}A\,d\tau$		25.5d
Energy	$E = \int \psi\hat{H}\psi\,d\tau \Big/ \int \psi^2\,d\tau$	Unnormalized real wavefunction	25.6

TOPIC 26

Polyatomic molecules

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➤ Why do you need to know this material?

Most molecules of interest in chemistry are polyatomic, so it is important to be able to discuss their electronic structure. Although sophisticated computational procedures are now widely available, to understand them it is helpful to see how they emerged from the more primitive approach described here.

➤ What is the key idea?

Molecular orbitals can be expressed as linear combinations of all the atomic orbitals of the appropriate symmetry.

➤ What do you need to know already?

This Topic extends the approach used for heteronuclear diatomic molecules in Topic 25, particularly the concepts of secular determinants and secular equations. The principal mathematical technique used is matrix algebra (*Mathematical background* 5); you should be, or become, familiar with the use of mathematical software to manipulate matrices numerically.

The molecular orbitals of polyatomic molecules are built in the same way as in diatomic molecules (Topics 24 and 25), the only difference being that more atomic orbitals are used to construct them. As for diatomic molecules, polyatomic molecular orbitals spread over the entire molecule. A molecular orbital has the general form

$$\psi = \sum_o c_o \chi_o \qquad \text{General form of LCAO} \qquad (26.1)$$

where χ_o is an atomic orbital and the sum extends over all the valence orbitals of all the atoms in the molecule. To find the coefficients, we set up the secular equations and the secular determinant, just as for diatomic molecules, solve the latter for the energies, and then use these energies in the secular equations to find the coefficients of the atomic orbitals for each molecular orbital.

The principal difference between diatomic and polyatomic molecules lies in the greater range of shapes that are possible: a diatomic molecule is necessarily linear, but a triatomic molecule, for instance, may be either linear or angular (bent) with a characteristic bond angle. The shape of a polyatomic molecule—the specification of its bond lengths and its bond angles—can be predicted by calculating the total energy of the molecule for a variety of nuclear positions, and then identifying the conformation that corresponds to the lowest energy. Such calculations are best done using the latest software, but a more primitive approach gives useful insight for conjugated polyenes, in which there is an alternation of single and double bonds along a chain of carbon atoms and on which we focus here, and sets the scene for more sophisticated approaches.

The planarity of conjugated polyenes is an aspect of their symmetry, and considerations of molecular symmetry play a vital role in setting up molecular orbitals. In the present case, planarity provides a distinction between the σ and π orbitals of the molecule, and in elementary approaches such molecules are commonly discussed in terms of the characteristics of their π orbitals, with the σ bonds providing an unchanging underlying scaffolding, which forms a rigid framework that determines the general shape of the molecule.

26.1 The Hückel approximation

The π molecular orbital energy level diagrams of conjugated molecules can be constructed using a set of approximations suggested by Erich Hückel in 1931. All the C atoms are treated identically, so all the Coulomb integrals α (eqn 25.5c, $\alpha_A = \int A\hat{H}A\,d\tau$) for the atomic orbitals that contribute to the π orbitals are set equal. For example, in ethene, which we use to introduce the method, we take the σ bonds as fixed, and concentrate on finding the energies of the single π bond and its companion antibond.

(a) An introduction to the method

We express the π orbitals as LCAOs of the C2p orbitals that lie perpendicular to the molecular plane. In ethene, for instance, we would write

$$\psi = c_A A + c_B B \tag{26.2}$$

where the A is a C2p orbital on atom A, and so on. Next, the optimum coefficients and energies are found by the variation principle as explained in Topic 25. That is, we solve the secular determinant, which in the case of ethene is eqn 25.7 with $\alpha_A = \alpha_B = \alpha$:

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0 \tag{26.3}$$

and where β is the resonance integral (eqn 25.5d, $\beta = \int A\hat{H}B\,d\tau$) and S is the overlap integral (eqn 24.3, $S = \int AB\,d\tau$). In a modern computation all the resonance integrals and overlap integrals would be included, but an indication of the molecular orbital energy level diagram can be obtained very readily if we make the following additional **Hückel approximations**:

- All overlap integrals are set equal to zero.
- All resonance integrals between non-neighbours are set equal to zero.
- All remaining resonance integrals are set equal (to β).

Hückel approximation

These approximations are obviously very severe, but they let us calculate at least a general picture of the molecular orbital energy levels with very little work. The assumptions result in the following structure of the secular determinant:

- All diagonal elements: $\alpha - E$.
- Off-diagonal elements between neighbouring atoms: β.
- All other elements: 0.

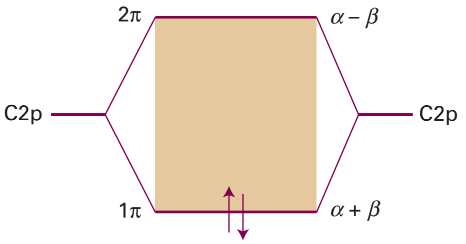


Figure 26.1 The Hückel molecular orbital energy levels of ethene. Two electrons occupy the lower π orbital.

These approximations convert eqn 26.3 to

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = (\alpha - E)^2 - \beta^2 = (\alpha - E + \beta)(\alpha - E - \beta) = 0 \tag{26.4}$$

The roots of the equation are $E_\pm = \alpha \pm \beta$. The + sign corresponds to the bonding combination (β is negative) and the − sign corresponds to the antibonding combination (Fig. 26.1).

The building-up principle leads to the configuration $1\pi^2$, because each carbon atom supplies one electron to the π system. The **highest occupied molecular orbital** in ethene, its HOMO, is the 1π orbital; the **lowest unoccupied molecular orbital**, its LUMO, is the 2π orbital (or, as it is sometimes denoted, the 2π* orbital). These two orbitals jointly form the **frontier orbitals** of the molecule. The frontier orbitals are important because they are largely responsible for many of the chemical and spectroscopic properties of the molecule.

Brief illustration 26.1 Ethene

We can estimate that the $\pi^* \leftarrow \pi$ excitation energy of ethene is $2|\beta|$, the energy required to excite an electron from the 1π to the 2π orbital. This transition occurs at close to 40 000 cm^{-1}, corresponding to 4.8 eV. It follows that a plausible value of β is about −2.4 eV (−230 kJ mol^{-1}).

Self-test 26.1 The ionization energy of ethane is 10.5 eV. Estimate α.

Answer: −8.1 eV

(b) The matrix formulation of the method

In preparation for making Hückel theory more sophisticated and readily applicable to bigger molecules, we need to reformulate it in terms of matrices and vectors (see *Mathematical background* 5). Our starting point is the pair of secular equations developed for a heteronuclear diatomic molecule in Topic 25:

$$(\alpha_A - E)c_A + (\beta - ES)c_B = 0$$
$$(\beta - ES)c_A + (\alpha_B - E)c_B = 0$$

To prepare to generalize this expression we write $\alpha_J = H_{JJ}$ (with J = A or B), $\beta = H_{AB}$, and label the overlap integrals with their respective atoms, so S becomes S_{AB}. We can introduce more symmetry into the equations by replacing the E in $\alpha_J - E$ by ES_{JJ}, with $S_{JJ} = 1$. There is one further notational change. The coefficients c_J in the secular equations depend on the value of E, so we need to distinguish the two sets corresponding to the two energies, which we denote E_1 and E_2. We therefore write them as $c_{i,J}$, with $i = 1$ (for energy E_1) or 2 (for energy E_2). With these notational changes, the two equations become

$$(H_{AA} - E_i S_{AA})c_{i,A} + (H_{AB} - E_i S_{AB})c_{i,B} = 0 \tag{26.5a}$$

$$(H_{BA} - E_i S_{BA})c_{i,A} + (H_{BB} - E_i S_{BB})c_{i,B} = 0 \tag{26.5b}$$

with $i = 1$ and 2, giving four equations in all. Each pair of equations can be written in matrix form as

$$\begin{pmatrix} H_{AA} - E_i S_{AA} & H_{AB} - E_i S_{AB} \\ H_{BA} - E_i S_{BA} & H_{BB} - E_i S_{BB} \end{pmatrix} \begin{pmatrix} c_{i,A} \\ c_{i,B} \end{pmatrix} = 0$$

because multiplying out the matrices gives eqn 26.5. If we introduce the following matrices and column vectors

$$\boldsymbol{H} = \begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} \quad \boldsymbol{S} = \begin{pmatrix} S_{AA} & S_{AB} \\ S_{BA} & S_{BB} \end{pmatrix} \quad \boldsymbol{c}_i = \begin{pmatrix} c_{i,A} \\ c_{i,B} \end{pmatrix} \tag{26.6}$$

so that

$$\boldsymbol{H} - E_i \boldsymbol{S} = \begin{pmatrix} H_{AA} - E_i S_{AA} & H_{AB} - E_i S_{AB} \\ H_{BA} - E_i S_{BA} & H_{BB} - E_i S_{BB} \end{pmatrix}$$

then each pair of equations may be written more succinctly as

$$(\boldsymbol{H} - E_i \boldsymbol{S})c_i = 0 \quad \text{or} \quad \boldsymbol{H}\boldsymbol{c}_i = \boldsymbol{S}\boldsymbol{c}_i E_i \tag{26.7}$$

As shown in the following *Justification*, the two sets of equations like these (with $i = 1$ and 2) can be combined into a single matrix equation by introducing the matrices

$$\boldsymbol{c} = (\boldsymbol{c}_1 \quad \boldsymbol{c}_2) = \begin{pmatrix} c_{1,A} & c_{2,A} \\ c_{1,B} & c_{2,B} \end{pmatrix} \quad \boldsymbol{E} = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \tag{26.8}$$

for then all four equations in eqn 26.7 are summarized by the single expression

$$\boldsymbol{H}\boldsymbol{c} = \boldsymbol{S}\boldsymbol{c}\boldsymbol{E} \tag{26.9}$$

Justification 26.1 The matrix formulation

Substitution of the matrices into eqn 26.9 gives

$$\begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} \begin{pmatrix} c_{1,A} & c_{2,A} \\ c_{1,B} & c_{2,B} \end{pmatrix} = \begin{pmatrix} S_{AA} & S_{AB} \\ S_{BA} & S_{BB} \end{pmatrix} \begin{pmatrix} c_{1,A} & c_{2,A} \\ c_{1,B} & c_{2,B} \end{pmatrix} \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}$$

The product on the left is

$$\begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} \begin{pmatrix} c_{1,A} & c_{2,A} \\ c_{1,B} & c_{2,B} \end{pmatrix} = \begin{pmatrix} H_{AA}c_{1,A} + H_{AB}c_{1,B} & H_{AA}c_{2,A} + H_{AB}c_{2,B} \\ H_{BA}c_{1,A} + H_{BB}c_{1,B} & H_{BA}c_{2,A} + H_{BB}c_{2,B} \end{pmatrix}$$

The product on the right is

$$\begin{pmatrix} S_{AA} & S_{AB} \\ S_{BA} & S_{BB} \end{pmatrix} \begin{pmatrix} c_{1,A} & c_{2,A} \\ c_{1,B} & c_{2,B} \end{pmatrix} \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} = \begin{pmatrix} S_{AA} & S_{AB} \\ S_{BA} & S_{BB} \end{pmatrix} \begin{pmatrix} c_{1,A}E_1 & c_{2,A}E_2 \\ c_{1,B}E_1 & c_{2,B}E_2 \end{pmatrix}$$
$$= \begin{pmatrix} E_1 S_{AA}c_{1,A} + E_1 S_{AB}c_{1,B} & E_2 S_{AA}c_{2,A} + E_2 S_{AB}c_{2,B} \\ E_1 S_{BA}c_{1,A} + E_1 S_{BB}c_{1,B} & E_2 S_{BA}c_{2,A} + E_2 S_{BB}c_{2,B} \end{pmatrix}$$

Comparison of matching terms (such as those in blue) recreates the four secular equations (two for each value of i).

In the Hückel approximation, $H_{AA} = H_{BB} = \alpha$, $H_{AB} = H_{BA} = \beta$, and we neglect overlap, setting $\boldsymbol{S} = \boldsymbol{1}$, the unit matrix (with 1 on the diagonal and 0 elsewhere). Then

$$\boldsymbol{H}\boldsymbol{c} = \boldsymbol{c}\boldsymbol{E}$$

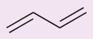
At this point, we multiply from the left by the inverse matrix $\boldsymbol{c}^{-1}$, use $\boldsymbol{c}^{-1}\boldsymbol{c} = 1$, and find

$$\boldsymbol{c}^{-1}\boldsymbol{H}\boldsymbol{c} = \boldsymbol{E} \tag{26.10}$$

In other words, to find the eigenvalues E_i, we have to find a transformation of $\boldsymbol{H}$ that makes it diagonal. This procedure is called **matrix diagonalization**. The diagonal elements then correspond to the eigenvalues E_i and the columns of the matrix $\boldsymbol{c}$ that brings about this diagonalization are the coefficients of the members of the **basis set**, the set of atomic orbitals used in the calculation, and hence give us the composition of the molecular orbitals.

Example 26.1 Finding molecular orbitals by matrix diagonalization

Set up and solve the matrix equations within the Hückel approximation for the π orbitals of butadiene (**1**).



1 Butadiene

Method The matrices will be four-dimensional for this four-atom system. Ignore overlap, and construct the matrix $\boldsymbol{H}$ by using the Hückel approximation and the parameters α and β. Find the matrix $\boldsymbol{c}$ that diagonalizes $\boldsymbol{H}$: for this step, use mathematical software. Full details are given in *Mathematical background* 5.

Answer

$$\boldsymbol{H}=\begin{pmatrix} H_{11} & H_{12} & H_{13} & H_{14} \\ H_{21} & H_{22} & H_{23} & H_{24} \\ H_{31} & H_{32} & H_{33} & H_{34} \\ H_{41} & H_{42} & H_{43} & H_{44} \end{pmatrix} \xrightarrow{\text{Hückel approximation}} \begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix}$$

We write this matrix as

$$\boldsymbol{H}=\alpha\boldsymbol{1}+\beta\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

because most mathematical software can deal only with numerical matrices. The diagonalized form of the second matrix is

$$\begin{pmatrix} +1.62 & 0 & 0 & 0 \\ 0 & +0.62 & 0 & 0 \\ 0 & 0 & -0.62 & 0 \\ 0 & 0 & 0 & -1.62 \end{pmatrix}$$

so we can infer that the diagonalized hamiltonian matrix is

$$\boldsymbol{E}=\begin{pmatrix} \alpha+1.62\beta & 0 & 0 & 0 \\ 0 & \alpha+0.62\beta & 0 & 0 \\ 0 & 0 & \alpha-0.62\beta & 0 \\ 0 & 0 & 0 & \alpha-1.62\beta \end{pmatrix}$$

The matrix that achieves the diagonalization is

$$\boldsymbol{c}=\begin{pmatrix} 0.372 & 0.602 & 0.602 & -0.372 \\ 0.602 & 0.372 & -0.372 & 0.602 \\ 0.602 & -0.372 & -0.372 & -0.602 \\ 0.372 & -0.602 & 0.602 & 0.372 \end{pmatrix}$$

with each column giving the coefficients of the atomic orbitals for the corresponding molecular orbital. We can conclude that the energies and molecular orbitals are

$$\begin{aligned} E_1&=\alpha+1.62\beta & \psi_1&=0.372\chi_A+0.602\chi_B+0.602\chi_C+0.372\chi_D \\ E_2&=\alpha+0.62\beta & \psi_2&=0.602\chi_A+0.372\chi_B-0.372\chi_C-0.602\chi_D \\ E_3&=\alpha-0.62\beta & \psi_3&=0.602\chi_A-0.372\chi_B-0.372\chi_C+0.602\chi_D \\ E_4&=\alpha-1.62\beta & \psi_4&=-0.372\chi_A+0.602\chi_B-0.602\chi_C+0.372\chi_D \end{aligned}$$

where the C2p atomic orbitals are denoted by $\chi_A, \ldots, \chi_D$. Note that the molecular orbitals are mutually orthogonal and, with overlap neglected, normalized.

Self-test 26.2 Repeat the exercise for the allyl radical, $\cdot CH_2{-}CH{=}CH_2$.

Answer: $E=\alpha+1.41\beta$, α, $\alpha-1.41\beta$; $\psi_1 = 0.500\chi_A+0.707\chi_B + 0.500\chi_C$, $\psi_2 = 0.707\chi_A - 0.707\chi_C$, $\psi_3 = 0.500\chi_A-0.707\chi_B + 0.500\chi_C$

26.2 Applications

Although the Hückel method is very primitive, it can be used to account for some of the properties of conjugated polyenes.

(a) Butadiene and π-electron binding energy

As we saw in Example 26.1, the energies of the four LCAO-MOs for butadiene are

$$E=\alpha\pm1.62\beta,\ \alpha\pm0.62\beta \qquad (26.11)$$

These orbitals and their energies are drawn in Fig. 26.2. Note that the greater the number of internuclear nodes, the higher the energy of the orbital. There are four electrons to accommodate, so the ground-state configuration is $1\pi^2 2\pi^2$. The frontier orbitals of butadiene are the 2π orbital (the HOMO, which is largely bonding) and the 3π orbital (the LUMO, which is largely antibonding). 'Largely' bonding means that an orbital has both bonding and antibonding interactions between various neighbours, but the bonding effects dominate. 'Largely antibonding' indicates that the antibonding effects dominate.

An important point emerges when we calculate the total **π-electron binding energy**, E_π, the sum of the energies of each π electron, and compare it with what we find in ethene. In ethene the total energy is

$$E_\pi=2(\alpha+\beta)=2\alpha+2\beta$$

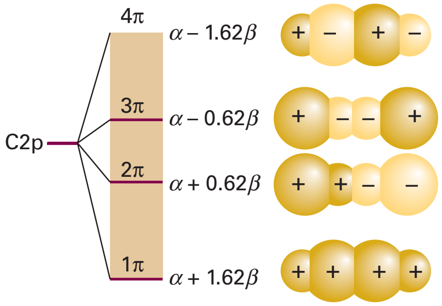


Figure 26.2 The Hückel molecular orbital energy levels of butadiene and the top view of the corresponding π orbitals. The four p electrons (one supplied by each C) occupy the two lower π orbitals. Note that the orbitals are delocalized.

In butadiene it is

$$E_\pi = 2(\alpha+1.62\beta)+2(\alpha+0.62\beta)=4\alpha+4.48\beta$$

Therefore, the energy of the butadiene molecule lies lower by 0.48β (about 110 kJ mol^{-1}) than the sum of two individual π bonds. This extra stabilization of a conjugated system compared with a set of localized π bonds is called the **delocalization energy** of the molecule.

A closely related quantity is the **π-bond formation energy**, E_{bf}, the energy released when a π bond is formed. Because the contribution of α is the same in the molecule as in the atoms, we can find the π-bond formation energy from the π-electron binding energy by writing

$$E_{\mathrm{bf}} = E_\pi - N_{\mathrm{C}}\alpha \qquad \textit{Definition} \qquad \text{π-bond formation energy} \tag{26.12}$$

where N_{C} is the number of carbon atoms in the molecule. The π-bond formation energy in butadiene, for instance, is 4.48β.

Example 26.2 Estimating the delocalization energy

Use the Hückel approximation to find the energies of the π orbitals of cyclobutadiene (**2**), and estimate the delocalization energy.

2 Cyclobutadiene

Method Set up the secular determinant using the same basis as for butadiene, but note that atoms A and D are also now neighbours. Then solve for the roots of the secular equation and assess the total π-bond energy. For the delocalization energy, subtract from the total π-bond energy the energy of two π bonds.

Answer The hamiltonian matrix is

$$\boldsymbol{H}=\begin{pmatrix}\alpha&\beta&0&\beta\\ \beta&\alpha&\beta&0\\ 0&\beta&\alpha&\beta\\ \beta&0&\beta&\alpha\end{pmatrix}=\alpha\mathbf{1}+\beta\begin{pmatrix}0&1&0&1\\ 1&0&1&0\\ 0&1&0&1\\ 1&0&1&0\end{pmatrix}\xrightarrow{\text{Diagonalize}}\begin{pmatrix}2&0&0&0\\ 0&0&0&0\\ 0&0&0&0\\ 0&0&0&-2\end{pmatrix}$$

Diagonalization gives the energies of the orbitals as

$$E=\alpha+2\beta, \alpha, \alpha, \alpha-2\beta$$

Four electrons must be accommodated. Two occupy the lowest orbital (of energy $\alpha+2\beta$), and two occupy the doubly degenerate orbitals (of energy α). The total energy is therefore $4\alpha+4\beta$. Two isolated π bonds would have an energy $4\alpha+4\beta$; therefore, in this case, the delocalization energy is zero and there is no extra stability arising from delocalization.

Self-test 26.3 Repeat the calculation for benzene (use software!).

Answer: See next subsection

(b) Benzene and aromatic stability

The most notable example of delocalization conferring extra stability is benzene and the aromatic molecules based on its structure. In elementary accounts, benzene and other aromatic compounds are often described in a mixture of valence-bond and molecular orbital terms, with typically valence-bond language used for its σ framework and molecular orbital language used to describe its π electrons.

First, consider the valence-bond component. The six C atoms are regarded as sp^2 hybridized, with a single unhybridized perpendicular 2p orbital. One H atom is bonded by (Csp^2,H1s) overlap to each C carbon, and the remaining hybrids overlap to give a regular hexagon of atoms (Fig. 26.3). The internal angle of a regular hexagon is 120°, so sp^2 hybridization is ideally suited for forming σ bonds. We see that the hexagonal shape of benzene permits strain-free σ bonding.

Now consider the molecular orbital component of the description. The six C2p orbitals overlap to give six π orbitals that spread all round the ring. Their energies are calculated within the Hückel approximation by diagonalizing the hamiltonian matrix

$$\boldsymbol{H}=\begin{pmatrix}\alpha&\beta&0&0&0&\beta\\ \beta&\alpha&\beta&0&0&0\\ 0&\beta&\alpha&\beta&0&0\\ 0&0&\beta&\alpha&\beta&0\\ 0&0&0&\beta&\alpha&\beta\\ \beta&0&0&0&\beta&\alpha\end{pmatrix}$$

$$=\alpha\mathbf{1}+\beta\begin{pmatrix}0&1&0&0&0&1\\ 1&0&1&0&0&0\\ 0&1&0&1&0&0\\ 0&0&1&0&1&0\\ 0&0&0&1&0&1\\ 1&0&0&0&1&0\end{pmatrix}\xrightarrow{\text{Diagonalize}}\begin{pmatrix}2&0&0&0&0&0\\ 0&1&0&0&0&0\\ 0&0&1&0&0&0\\ 0&0&0&-1&0&0\\ 0&0&0&0&-1&0\\ 0&0&0&0&0&-2\end{pmatrix}$$

The MO energies, the eigenvalues of this matrix, are simply

$$E=\alpha\pm2\beta, \alpha\pm\beta, \alpha\pm\beta \tag{26.13}$$

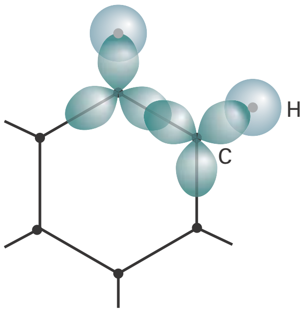


Figure 26.3 The σ framework of benzene is formed by the overlap of Csp² hybrids, which fit without strain into a hexagonal arrangement.

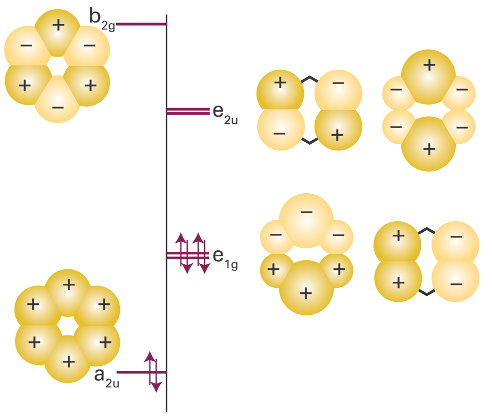


Figure 26.4 The Hückel orbitals of benzene and the corresponding energy levels. The symmetry labels are explained in Topic 32. The bonding and antibonding character of the delocalized orbitals reflects the numbers of nodes between the atoms. In the ground state, only the net bonding orbitals are occupied.

as shown in Fig. 26.4. The orbitals there have been given symmetry labels that are explained in Topic 32. Note that the lowest energy orbital is bonding between all neighbouring atoms, the highest energy orbital is antibonding between each pair of neighbours, and the intermediate orbitals are a mixture of bonding, nonbonding, and antibonding character between adjacent atoms.

The simple form of the eigenvalues in eqn 26.13 suggests that there is a more direct way of determining them than by using mathematical software. That is in fact the case, for symmetry arguments of the kind described in Topic 32 show that the 6×6 matrix can be factorized into two 1×1 matrices and two 2×2 matrices, which are very easy to deal with.

We now apply the building-up principle to the π system. There are six electrons to accommodate (one from each C atom), so the three lowest orbitals (a_{2u} and the doubly degenerate pair e_{1g}) are fully occupied, giving the ground-state configuration $a_{2u}^2e_{1g}^4$. A significant point is that the only molecular orbitals occupied are those with net bonding character.

The π-electron energy of benzene is

$$E=2(\alpha+2\beta)+4(\alpha+\beta)=6\alpha+8\beta$$

If we ignored delocalization and thought of the molecule as having three isolated π bonds, it would be ascribed a π-electron energy of only $3(2\alpha+2\beta)=6\alpha+6\beta$. The delocalization energy, the difference between the π-electron energy and the energy of the same molecule with localized π bonds, is therefore $2\beta\approx-460\,\text{kJ mol}^{-1}$, which is considerably more than for butadiene. The π-bond formation energy in benzene is 8β.

This discussion suggests that aromatic stability can be traced to two main contributions. First, the shape of the regular hexagon is ideal for the formation of strong σ bonds: the σ framework is relaxed and without strain. Second, the π orbitals are such as to be able to accommodate all the electrons in bonding orbitals, and the delocalization energy is large.

Example 26.3 Judging the aromatic character of a molecule

Decide whether the molecules C_4H_4 and the molecular ion $C_4H_4^{2+}$ are aromatic when planar.

Method Follow the procedure for benzene. Set up and solve the secular equations within the Hückel approximation, assuming a planar σ framework, and then decide whether the ion has nonzero delocalization energy. Use mathematical software to diagonalize the hamiltonian (in Topic 32 it is shown how to use symmetry to arrive at the eigenvalues more simply.)

Answer It follows from Example 26.2 that the energy levels of the two species are $E=\alpha\pm2\beta$, α, α. Because there are four π electrons to accommodate in C_4H_4, its total π-bonding energy is $2(\alpha+2\beta)+2\alpha=4(\alpha+\beta)$. The energy of two localized π bonds is also $4(\alpha+\beta)$. Therefore, the delocalization energy is zero and the molecule is not aromatic. There are only two π electrons to accommodate in $C_4H_4^{2+}$, so the total π-bonding energy is $2(\alpha+2\beta)=2\alpha+4\beta$. The energy of a single localized π bond is $2(\alpha+\beta)$, so the delocalization energy is 2β and the molecular ion is aromatic.

Self-test 26.4 What is the total π-bonding energy of $C_3H_3^-$?

Answer: $[4\alpha+2\beta]$

Checklist of concepts

☐ 1. The **Hückel method** neglects overlap and interactions between atoms that are not neighbours.

☐ 2. The Hückel method may be expressed in a compact manner by introducing matrices.

☐ 3. The **π-bond formation energy** is the energy released when a π bond is formed.

☐ 4. The **π-electron binding energy** is the sum of the energies of each π electron.

☐ 5. The **delocalization energy** is the difference between the π-electron energy and the energy of the same molecule with localized π bonds.

☐ 6. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) form the **frontier orbitals** of a molecule.

☐ 7. The stability of benzene arises from the geometry of the ring and the high delocalization energy.

Checklist of equations

Property	Equation	Comment	Equation number
Linear combination of atomic orbitals (LCAO)	$\psi=\sum_{o} c_o\chi_o$	χ_o are atomic orbitals	26.1
Hückel equations	$\boldsymbol{Hc}=\boldsymbol{ScE}$	Hückel approximation: $\boldsymbol{S}=\boldsymbol{1}$	26.9
Diagonalization	$\boldsymbol{c}^{-1}\boldsymbol{Hc}=\boldsymbol{E}$	Hückel approximation: $\boldsymbol{S}=\boldsymbol{1}$	26.10
π-Bond formation energy	$E_{\mathrm{bf}}=E_{\pi}-N_{\mathrm{C}}\alpha$	Hückel approximation: $\boldsymbol{S}=\boldsymbol{1}$	26.12

TOPIC 27

Self-consistent fields

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➤ Why do you need to know this material?

Modern computational procedures for predicting molecular structure and reactivity are now widely available and used throughout chemistry. Like any tool, it is important to know its foundations.

➤ What is the key idea?

Numerical procedures in computational chemistry typically proceed by solving equations until they converge, that is, do not change on successive iterations.

➤ What do you need to know already?

This Topic develops the approach introduced in Topic 26 and makes extensive use of matrix manipulations (*Mathematical background* 5). It is based on the variation principle (Topic 25).

The field of **computational chemistry**, the use of computers to predict molecular structure and reactivity, has grown in the past few decades due to the tremendous advances in computer hardware and to the development of efficient software packages. The latter are now applied routinely to compute molecular properties in a wide variety of chemical applications, including pharmaceuticals and drug design, atmospheric and environmental chemistry, nanotechnology, and materials science. Many software packages have sophisticated graphical interfaces that permit the visualization of results. The maturation of the field of computational chemistry was recognized by the awarding of the 1998 Nobel Prize in Chemistry to J.A. Pople and W. Kohn for their contributions to the development of computational techniques for the elucidation of molecular structure and reactivity.

27.1 The central challenge

The goal of electronic structure calculations in computational chemistry is the solution of the electronic Schrödinger equation, $\hat{H}\Psi = E\Psi$, where E is the electronic energy and Ψ is the many-electron wavefunction, a function of the coordinates of all the electrons and the nuclei. To make progress, we invoke at the outset the Born–Oppenheimer approximation and the separation of electronic and nuclear motion (Topic 22). The electronic hamiltonian is

$$\hat{H} = \overbrace{-\frac{\hbar^2}{2m_e}\sum_{i=1}^{N_e}\nabla_i^2}^{\text{Kinetic energy of electrons}} \overbrace{-\sum_{i=1}^{N_e}\sum_{I=1}^{N_n}\frac{Z_I e^2}{4\pi\varepsilon_0 r_{Ii}}}^{\text{Their attraction to all the nuclei}} + \overbrace{\frac{1}{2}\sum_{i\neq j}^{N_e}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}}^{\text{Their mutual repulsion}} \qquad \text{The hamiltonian} \qquad (27.1)$$

where r_{Ii} is the distance from electron i to nucleus I of charge Ze and r_{ij} is the electron–electron separation. The factor of $\frac{1}{2}$ in the final sum ensures that each repulsion is counted only once. The combination $e^2/4\pi\varepsilon_0$ occurs throughout computational chemistry, and we shall denote it j_0. Then the hamiltonian becomes

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{N_e}\nabla_i^2 - j_0\sum_{i=1}^{N_e}\sum_{I=1}^{N_n}\frac{Z_I}{r_{Ii}} + \frac{1}{2}j_0\sum_{i\neq j}^{N_e}\frac{1}{r_{ij}}$$

We shall use the following labels:

Species	Label	Number used
Electrons	i and $j=1, 2, \ldots$	N_e
Nuclei	$I=\mathrm{A}, \mathrm{B}, \ldots$	N_n
Molecular orbitals, ψ	$m=a, b, \ldots$	N_m*
Atomic orbitals used to construct the molecular orbitals (the 'basis'), χ	$o=1, 2, \ldots$	N_b

* The number occupied in the ground state

Another general point is that the theme we develop in the sequence of *Brief illustrations* and Examples in this and related Topics is aimed at showing explicitly how to use the equations that are presented and thereby give them a sense of reality. To do so, we shall take the simplest possible many-electron molecule, dihydrogen (H_2). Some of the techniques we introduce do not need to be applied to this simple molecule, but they serve to illustrate them in a simple manner and introduce problems that successive sections show how to solve. One consequence of choosing to develop a story in relation to H_2, we have to confess, is that not all the illustrations are actually as brief as we would wish; but we decided that it was more important to show the details of each little calculation than to adhere strictly to our normal use of the term 'brief'. It is worthwhile to note however that, although we restrict our examples to H_2, calculations on larger molecules using computational software based on methods described here and in related Topics may take only a few seconds.

Brief illustration 27.1 The hamiltonian

The notation we use for the description of H_2 is shown in Fig. 27.1. For this two-electron ($N_e=2$), two-nucleus ($N_n=2$) molecule the hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2+\nabla_2^2) - j_0\left(\frac{1}{r_{A1}}+\frac{1}{r_{A2}}+\frac{1}{r_{B1}}+\frac{1}{r_{B2}}\right)+\frac{j_0}{r_{12}}$$

To keep the notation simple, we introduce the one-electron operator

$$\hat{h}_i = -\frac{\hbar^2}{2m_e}\nabla_i^2 - j_0\left(\frac{1}{r_{Ai}}+\frac{1}{r_{Bi}}\right)$$

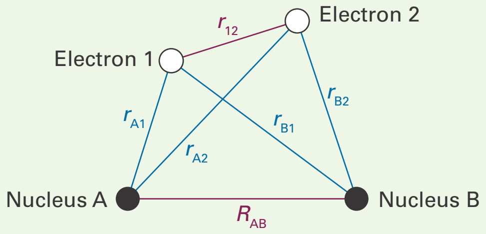

Figure 27.1 The notation used for the description of molecular hydrogen, introduced in *Brief illustration* 27.1 and used throughout the text.

which should be recognized as the hamiltonian for electron i in an H_2^+ molecule-ion. Then

$$\hat{H} = \hat{h}_1 + \hat{h}_2 + \frac{j_0}{r_{12}}$$

We see that the hamiltonian for H_2 is essentially that of each electron in an H_2^+-like molecule-ion but with the addition of the electron–electron repulsion term.

Self-test 27.1 What additional terms are needed for the description of H_3^-?

Answer: $\hat{h}_3 + j_0/r_{13} + j_0/r_{23}$

It is hopeless to expect to find analytical solutions with a hamiltonian of the complexity of that shown in eqn 27.1, even for H_2 with only a single electron–electron repulsion term, and the whole thrust of computational chemistry is to formulate and implement numerical procedures that give ever more reliable results.

27.2 The Hartree–Fock formalism

The electronic wavefunction of a many-electron molecule is a function of the positions of all the electrons, $\Psi(r_1,r_2,\ldots)$. To formulate one very widely used approximation, we build on the material in Topic 24, where in the MO description of H_2 it is supposed that each electron occupies an orbital and that the overall wavefunction can be written $\psi(r_1)\psi(r_2)\ldots$. Note that this **orbital approximation** is quite severe and loses many of the details of the dependence of the wavefunction on the relative locations of the electrons. We do the same here, with two small changes of notation. To simplify the appearance of the expressions we write $\psi(r_1)\psi(r_2)\ldots$ as $\psi(1)\psi(2)\ldots$. Next, we suppose that electron 1 occupies a molecular orbital ψ_a with spin α, electron 2 occupies the same orbital with spin β, and so on, and hence write the many-electron wavefunction Ψ as the product $\Psi=\psi_a^{\alpha}(1)\psi_a^{\beta}(2)\ldots$. The combination of a molecular orbital and a spin function, such as $\psi_a^\alpha(1)$, is called a **spinorbital**. For example, the spinorbital ψ_a^α should be interpreted as the product of the spatial wavefunction ψ_a and the spin state α, so

$$\overbrace{\psi_a^\alpha(1)}^{\text{spinorbital}}=\overbrace{\psi_a(1)}^{\substack{\text{spatial}\\ \text{factor}}}\overbrace{\alpha(1)}^{\substack{\text{spin}\\ \text{factor}}}$$

and likewise for the other spinorbitals. We shall consider only closed-shell molecules but the techniques we describe can be extended to open-shell molecules.

A simple product wavefunction does not satisfy the Pauli principle and change sign under the interchange of any pair of electrons (Topic 19). To ensure that the wavefunction does satisfy the principle, we modify it to a sum of all possible permutations, using plus and minus signs appropriately:

$$\Psi=\psi_a^\alpha(1)\psi_a^\beta(2)\cdots\psi_z^\beta(N_e)-\psi_a^\alpha(2)\psi_a^\beta(1)\cdots\psi_z^\beta(N_e)+\cdots$$

There are $N_e!$ terms in this sum, and the entire sum can be represented by a determinant called a **Slater determinant**, for its expansion (see *Mathematical background* 5) generates the same alternating sum of terms:

$$\Psi=\frac{1}{(N_e!)^{1/2}}\begin{vmatrix}\psi_a^\alpha(1) & \psi_a^\beta(1) & \cdots & \psi_z^\beta(1)\\ \psi_a^\alpha(2) & \psi_a^\beta(2) & \cdots & \psi_z^\beta(2)\\ \vdots & \vdots & \vdots & \vdots\\ \psi_a^\alpha(N_e) & \psi_a^\beta(N_e) & \cdots & \psi_z^\beta(N_e)\end{vmatrix}\qquad \text{Slater determinant}\tag{27.2a}$$

The factor $1/(N_e!)^{1/2}$ ensures that the wavefunction is normalized if the component molecular orbitals ψ_m are normalized. To save the tedium of writing out large determinants, the wavefunction is normally written by using only its principal diagonal:

$$\Psi=(1/N_e!)^{1/2}\left|\psi_a^\alpha(1)\psi_a^\beta(2)\cdots\psi_z^\beta(N_e)\right|\tag{27.2b}$$

Brief illustration 27.2 A many-electron wavefunction

The Slater determinant for the ground state of H_2 ($N_e=2$) is

$$\Psi=\frac{1}{2^{1/2}}\begin{vmatrix}\psi_a^\alpha(1) & \psi_a^\beta(1)\\ \psi_a^\alpha(2) & \psi_a^\beta(2)\end{vmatrix}$$

where both electrons occupy the molecular wavefunction ψ_a. Expansion of the determinant gives

$$\begin{aligned}\Psi&=\frac{1}{2^{1/2}}\left\{\psi_a^\alpha(1)\psi_a^\beta(2)-\psi_a^\alpha(2)\psi_a^\beta(1)\right\}\\ &=\frac{1}{2^{1/2}}\psi_a(1)\psi_a(2)\left\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\right\}\end{aligned}$$

We should recognize the spin factor as that corresponding to a singlet state (eqn 19.2b, $\sigma_-=(1/2^{1/2})\{\alpha\beta-\beta\alpha\}$), so Ψ corresponds to two spin-paired electrons in ψ_a. Note that interchange of the electrons labelled 1 and 2 changes the sign of Ψ as required by the Pauli principle.

Self-test 27.2 Confirm that if any two rows of a Slater determinant are interchanged, then the determinant changes sign.

Answer: Review properties of determinants, *Mathematical background* 5

According to the variation principle (Topic 25) the best form of Ψ is the one that corresponds to the lowest achievable energy as the ψ are varied; that is, we need the wavefunctions ψ that will minimize the expectation value $\int\Psi^*\hat{H}\Psi\,d\tau$. Because the electrons interact with one another, a variation in the form of ψ_a, for instance, will affect what will be the best form of all the other ψs, so finding the best form of the ψs is a far from trivial problem. However, D.R. Hartree and V. Fock showed that the optimum ψs each satisfy what is at first sight a very simple set of equations:

$$\hat{f}_1\psi_a(1)=\varepsilon_a\psi_a(1)\qquad \text{Hartree–Fock equations}\tag{27.3}$$

where $\hat{f}_1$ is called the **Fock operator**. This is the equation to solve to find ψ_a; there are analogous equations for all the other orbitals. This Schrödinger-like equation has the form we should expect (but its formal derivation is quite involved). Thus, $\hat{f}_1$ has the following structure:

$$\begin{aligned}\hat{f}_1=\;&\text{core hamiltonian for electron 1 }(\hat{h}_1)\\ &+\text{average Coulomb repulsion from}\\ &\text{electrons 2,3,... }(V_{\text{Coulomb}})+\text{average}\\ &\text{correction due to spin correlation }(V_{\text{exchange}})\\ =\;&\hat{h}_1+V_{\text{Coulomb}}+V_{\text{exchange}}\end{aligned}\qquad \text{Physical interpretation}$$

By the **core hamiltonian** we mean the one-electron hamiltonian $\hat{h}_1$ defined in *Brief illustration* 27.1 and representing the energy of electron 1 in the field of the nuclei. The Coulomb repulsion from all the other electrons contributes a term that acts as follows (Fig. 27.2):

$$\hat{J}_m(1)\psi_a(1)=j_0\int\psi_a(1)\frac{1}{r_{12}}\psi_m^*(2)\psi_m(2)\,d\tau_2\qquad \text{Coulomb operator}\tag{27.4}$$

This integral represents the repulsion experienced by electron 1 in orbital ψ_a from electron 2 in orbital ψ_m, where it is distributed with probability density $\psi_m{}^*\psi_m$. There are two electrons in each orbital, so we can expect a total contribution of the form

$$V_{\text{Coulomb}}\psi_a(1)=2\sum_{m,\,\text{occ}}\hat{J}_m(1)\psi_a(1)\tag{27.5}$$

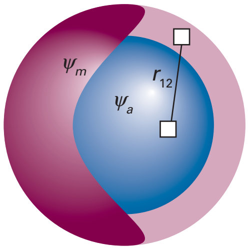

Figure 27.2 A schematic interpretation of the Coulomb repulsion term, eqn 27.4. An electron in orbital ψ_a experiences repulsion from an electron in orbital ψ_m where it has probability density $|\psi_m|^2$.

where the sum is over all the occupied orbitals, including orbital *a*. You should be alert to the fact that counting 2 for the orbital with $m=a$ is incorrect, because electron 1 interacts only with the second electron in the orbital, not with itself. This error will be corrected in a moment. The spin correlation term takes into account the fact that electrons of the same spin tend to avoid each other (Topic 20) which reduces the net Coulomb interaction between them. This contribution has the following form:

$$\hat{K}_m(1)\psi_a(1) = j_0 \int \psi_m(1)\frac{1}{r_{12}}\psi_m^*(2)\psi_a(2)\,\mathrm{d}\tau_2 \qquad \text{Exchange operator} \tag{27.6}$$

For a given electron 1 there is only one electron of the same spin in all the occupied orbitals of the closed-shell species we are considering, so we can expect a total contribution of the form

$$V_{\text{exchange}}\psi_a(1) = -\sum_{m,\text{occ}} \hat{K}_m(1)\psi_a(1) \tag{27.7}$$

The negative sign reminds us that spin correlation keeps electrons apart, and so reduces their classical, Coulombic repulsion. By collecting terms, we arrive at a specific expression for the effect of the Fock operator:

$$\hat{f}_1\psi_a(1) = \hat{h}_1\psi_a(1) + \sum_{m,\text{occ}} \{2\hat{J}_m(1) - \hat{K}_m(1)\}\psi_a(1) \tag{27.8}$$

This expression applies to all the molecular orbitals, but the sum extends over only the N_m occupied orbitals. Note that $\hat{K}_a(1)\psi_a(1) = \hat{J}_a(1)\psi_a(1)$, so the term in the sum with $m=a$ loses one of its $2\hat{J}_a$, which is the correction that avoids the electron repelling itself, which we referred to above.

Equation 27.8 reveals a second principal approximation of the Hartree–Fock formalism (the first being its dependence on the orbital approximation). Instead of electron 1 (or any other electron) responding to the instantaneous positions of the other electrons in the molecule through terms of the form $1/r_{1j}$, it responds to an *averaged* location of the other electrons through integrals of the kind that appear in eqn 27.8. We say that the Hartree–Fock method ignores **electron correlation**, the instantaneous tendency of electrons to avoid one another to minimize repulsions. This failure to take into account electron correlation is a principal reason for inaccuracies in the calculations and leads to calculated energies that are higher than the 'true' (that is, experimental) values.

Although eqn 27.8 is the equation we have to solve to find ψ_a, it implies that it is necessary to know all the other occupied wavefunctions in order to set up the operators $\hat{J}$ and $\hat{K}$ and hence to find ψ_a. To make progress with this difficulty, we can guess the initial form of all the one-electron wavefunctions, use them in the definition of the Coulomb and exchange operators, and solve the Hartree–Fock equations. That process is then continued using the newly found wavefunctions until each cycle of calculation leaves the energies ε_m and wavefunctions ψ_m unchanged to within a chosen criterion. This is the origin of the term **self-consistent field** (SCF) for this type of procedure in general and of **Hartree–Fock self-consistent field** (HF-SCF) for the approach based on the orbital approximation. (A brief description of the HF-SCF method as applied to many-electron atoms is provided in Topic 19.)

Brief illustration 27.3 The Hartree–Fock equations

We continue with the H_2 example. According to eqn 27.8, the Hartree–Fock equation for ψ_a is $\hat{f}_1\psi_a(1) = \varepsilon_a\psi_a(1)$ with

$$\hat{f}_1\psi_a(1) = \hat{h}_1\psi_a(1) + 2\hat{J}_a(1)\psi_a(1) - \hat{K}_a(1)\psi_a(1)$$

where

$$\hat{J}_a(1)\psi_a(1) = \hat{K}_a(1)\psi_a(1) = j_0 \int \psi_a(1)\frac{1}{r_{12}}\psi_a^*(2)\psi_a(2)\,\mathrm{d}\tau_2$$

Note that there is only one occupied orbital in this case so the summation in eqn 27.8 is a single term. The equation to solve is therefore

$$-\frac{\hbar^2}{2m_\text{e}}\nabla_1^2\psi_a(1) - j_0\left(\frac{1}{r_{\text{A}1}} + \frac{1}{r_{\text{B}1}}\right)\psi_a(1) + j_0\int \psi_a(1)\frac{1}{r_{12}}\psi_a^*(2)\psi_a(2)\,\mathrm{d}\tau_2 = \varepsilon_a\psi_a(1)$$

This equation for ψ_a must be solved self-consistently (and numerically) because the integral that governs the form of ψ_a requires us to know ψ_a already. In the following examples we shall illustrate some of the procedures that have been adopted.

Self-test 27.3 Identify the additional terms that would arise in a closed-shell four-electron homonuclear diatomic molecule in which two electrons also occupy a molecular orbital *b*.

Answer: $+2\hat{J}_b(1)\psi_a(1) - \hat{K}_b(1)\psi_a(1)$

Once the Hartree–Fock equations have been solved for the spatial wavefunctions ψ, the ground-state wavefunction Ψ (eqn 27.2) can be constructed and the SCF energy computed from the expectation value $\int \Psi^* \hat{H} \Psi \mathrm{d}\tau$. The final, complicated, expression is a sum over all the electrons in the molecule, of integrals involving the wavefunctions ψ.[1]

27.3 The Roothaan equations

The difficulty with the HF-SCF procedure lies in the numerical solution of the Hartree–Fock equations, an onerous task even for powerful computers. As a result, a modification of the technique was needed before the procedure could be of use to chemists. Topic 23 explains how molecular orbitals are constructed as linear combinations of atomic orbitals. This simple approach was adopted in 1951 by C.C.J. Roothaan and G.G. Hall independently, who found a way to convert the Hartree–Fock equations for the molecular orbitals into equations for the coefficients that appear in the LCAO used to simulate the molecular orbital. Thus, they wrote

$$\psi_m = \sum_{o=1}^{N_\mathrm{b}} c_{om} \chi_\mathrm{o}$$

A general LCAO (27.9)

where c_{om} are unknown coefficients and the χ_o are the (known) atomic orbitals (which we take to be real). This LCAO approximation is in addition to the approximations underlying the Hartree–Fock equations because the basis is finite and so cannot reproduce the molecular orbital exactly. The size of the basis set (N_b) is not necessarily the same as the number of atomic nuclei in the molecule (N_n), because we might use several atomic orbitals on each nucleus (such as the four 2s and 2p orbitals of a carbon atom). From N_b basis functions, we obtain N_b linearly independent molecular orbitals ψ_m, some (N_m) of which will be occupied. The remaining, unoccupied linear combinations are called **virtual orbitals**.

We show in the following *Justification* that the use of a linear combination like eqn 27.9 leads to a set of simultaneous equations for the coefficients called the **Roothaan equations**. These equations are best summarized in matrix form by writing

$$\boldsymbol{Fc} = \boldsymbol{Sc\varepsilon}$$

Roothaan equations (27.10)

where $\boldsymbol{F}$ is the $N_\mathrm{b} \times N_\mathrm{b}$ matrix with elements

$$F_{o'o} = \int \chi_{\mathrm{o}'}(1) \hat{f}_1 \chi_\mathrm{o}(1) \mathrm{d}\tau_1$$

Fock matrix elements (27.11a)

$\boldsymbol{S}$ is the $N_\mathrm{b} \times N_\mathrm{b}$ matrix of overlap integrals:

$$S_{o'o} = \int \chi_{\mathrm{o}'}(1) \chi_\mathrm{o}(1) \mathrm{d}\tau_1$$

Overlap matrix elements (27.11b)

$\boldsymbol{c}$ is an $N_\mathrm{b} \times N_\mathrm{b}$ matrix of all the coefficients we have to find:

$$\boldsymbol{c} = \begin{pmatrix} c_{1a} & c_{1b} & \cdots & c_{1N_\mathrm{b}} \\ c_{2a} & c_{2b} & \cdots & c_{2N_\mathrm{b}} \\ \vdots & \vdots & \cdots & \vdots \\ c_{N_\mathrm{b}a} & c_{N_\mathrm{b}b} & \cdots & c_{N_\mathrm{b}N_\mathrm{b}} \end{pmatrix}$$

Matrix of coefficients (27.11c)

and $\boldsymbol{\varepsilon}$ is an $N_\mathrm{b} \times N_\mathrm{b}$ diagonal matrix with the values $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_{N_\mathrm{b}}$ along the diagonal; of these eigenvalues, the first N_m refer to the occupied orbitals.

Justification 27.1 The Roothaan equations

To construct the Roothaan equations we substitute the linear combination of eqn 27.9 with $m = a$ into both sides of eqn 27.3, which gives

$$\hat{f}_1 \psi_a(1) = \hat{f}_1 \sum_{o=1}^{N_\mathrm{b}} c_{oa} \chi_\mathrm{o}(1) = \varepsilon_a \sum_{o=1}^{N_\mathrm{b}} c_{oa} \chi_\mathrm{o}(1)$$

Now multiply from the left by $\chi_{\mathrm{o}'}(1)$ and integrate over the coordinates of electron 1:

$$\sum_{o=1}^{N_\mathrm{b}} c_{oa} \overbrace{\int \chi_{\mathrm{o}'}(1) \hat{f}_1 \chi_\mathrm{o}(1) \mathrm{d}\tau_1}^{F_{o'o}} = \varepsilon_a \sum_{o=1}^{N_\mathrm{b}} c_{oa} \overbrace{\int \chi_{\mathrm{o}'}(1) \chi_\mathrm{o}(1) \mathrm{d}\tau_1}^{S_{o'o}}$$

That is,

$$\overbrace{\sum_{o=1}^{N_\mathrm{b}} F_{o'o} c_{oa}}^{(\boldsymbol{Fc})_{o'a}} = \varepsilon_a \overbrace{\sum_{o=1}^{N_\mathrm{b}} S_{o'o} c_{oa}}^{(\boldsymbol{Sc})_{o'a}}$$

This expression has the form of the matrix equation in eqn 27.10.

Example 27.1 Setting up the Roothaan equations

Set up the Roothaan equations for H_2.

Method Adopt a basis set of real, normalized functions χ_A and χ_B, centred on nuclei A and B, respectively. We can think of these functions as H1s orbitals on each nucleus, but they could be more general than that, and in a later Example we shall make a computationally more friendly choice. Then establish the $\boldsymbol{c}$, $\boldsymbol{S}$, and $\boldsymbol{F}$ matrices.

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[1] For details, see our *Molecular quantum mechanics*, Oxford University Press (2011).

Answer The two possible linear combinations corresponding to eqn 27.9 are $\psi_m = c_{\mathrm{A}m}\chi_{\mathrm{A}} + c_{\mathrm{B}m}\chi_{\mathrm{B}}$, with $m = a$ (occupied) and b (virtual), so the matrix $\boldsymbol{c}$ is

$$\boldsymbol{c} = \begin{pmatrix} c_{\mathrm{A}a} & c_{\mathrm{A}b} \\ c_{\mathrm{B}a} & c_{\mathrm{B}b} \end{pmatrix}$$

and the overlap matrix $\boldsymbol{S}$ of the individually normalized atomic orbitals is

$$\boldsymbol{S} = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix} \qquad S = \int \chi_{\mathrm{A}}\chi_{\mathrm{B}}\,\mathrm{d}\tau$$

The Fock matrix is

$$\boldsymbol{F} = \begin{pmatrix} F_{\mathrm{AA}} & F_{\mathrm{AB}} \\ F_{\mathrm{BA}} & F_{\mathrm{BB}} \end{pmatrix} \qquad F_{\mathrm{XY}} = \int \chi_{\mathrm{X}} \hat{f}_1 \chi_{\mathrm{Y}}\,\mathrm{d}\tau$$

We explore the explicit form of the elements of $\boldsymbol{F}$ in a later Example; for now, just regard them as variable quantities. The Roothaan equations are therefore

$$\begin{pmatrix} F_{\mathrm{AA}} & F_{\mathrm{AB}} \\ F_{\mathrm{BA}} & F_{\mathrm{BB}} \end{pmatrix}\begin{pmatrix} c_{\mathrm{A}a} & c_{\mathrm{A}b} \\ c_{\mathrm{B}a} & c_{\mathrm{B}b} \end{pmatrix} = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix}\begin{pmatrix} c_{\mathrm{A}a} & c_{\mathrm{A}b} \\ c_{\mathrm{B}a} & c_{\mathrm{B}b} \end{pmatrix}\begin{pmatrix} \varepsilon_a & 0 \\ 0 & \varepsilon_b \end{pmatrix}$$

After multiplying out these matrices and matching the elements corresponding to the occupied orbital a, we obtain

$$F_{\mathrm{AA}}c_{\mathrm{A}a} + F_{\mathrm{AB}}c_{\mathrm{B}a} = \varepsilon_a c_{\mathrm{A}a} + \varepsilon_a S c_{\mathrm{B}a}$$
$$F_{\mathrm{BA}}c_{\mathrm{A}a} + F_{\mathrm{BB}}c_{\mathrm{B}a} = \varepsilon_a c_{\mathrm{B}a} + \varepsilon_a S c_{\mathrm{A}a}$$

Thus, to find the coefficients for the molecular orbital ψ_a we need to solve this pair of simultaneous equations.

Self-test 27.4 Write the additional two equations for the virtual orbital b constructed from the same basis.

Answer: $F_{\mathrm{AA}}c_{\mathrm{A}b} + F_{\mathrm{AB}}c_{\mathrm{B}b} = \varepsilon_b c_{\mathrm{A}b} + \varepsilon_b S c_{\mathrm{B}b}$, $F_{\mathrm{BA}}c_{\mathrm{A}b} + F_{\mathrm{BB}}c_{\mathrm{B}b} = \varepsilon_b c_{\mathrm{B}b} + \varepsilon_b S c_{\mathrm{A}b}$

The Roothaan equations, eqn 27.10, are simply a collection of N_{b} simultaneous equations for the N_{b} coefficients c_{om}. We can use the properties of matrices and determinants as shown in the following *Justification* to show that the energies are the solutions of the secular equation

$$|\boldsymbol{F} - \varepsilon\boldsymbol{S}| = 0 \qquad (27.12)$$

Justification 27.2 The secular determinant

To determine the form of the secular determinant arising from the Roothaan equations, we begin by multiplying both sides of eqn 27.10 by $\boldsymbol{S}^{-1}$, the matrix inverse of $\boldsymbol{S}$, and, in the resulting expression $\boldsymbol{S}^{-1}\boldsymbol{F}\boldsymbol{c} = \boldsymbol{c}\boldsymbol{\varepsilon}$, denote the matrix product $\boldsymbol{S}^{-1}\boldsymbol{F}$ by $\boldsymbol{M}$. The equation then becomes $\boldsymbol{M}\boldsymbol{c} = \boldsymbol{c}\boldsymbol{\varepsilon}$. The matrix $\boldsymbol{c}$ of coefficients is given by eqn 27.11c and can be written in the form

$$\boldsymbol{c} = (\boldsymbol{c}^{(a)}, \boldsymbol{c}^{(b)}, \ldots \boldsymbol{c}^{(N_{\mathrm{b}})})$$

where $\boldsymbol{c}^{(m)}$ is the column vector composed of the coefficients c_{om} for the molecular orbital ψ_m of energy ε_m:

$$\boldsymbol{c}^{(m)} = \begin{pmatrix} c_{1m} \\ c_{2m} \\ \vdots \\ c_{N_{\mathrm{b}}m} \end{pmatrix}$$

In terms of these column vectors, the equation $\boldsymbol{M}\boldsymbol{c} = \boldsymbol{c}\boldsymbol{\varepsilon}$ consists of the set of equations of the form $\boldsymbol{M}\boldsymbol{c}^{(m)} = \varepsilon_m \boldsymbol{c}^{(m)}$, or $(\boldsymbol{M} - \varepsilon_m \mathbf{1})\boldsymbol{c}^{(m)} = 0$. As explained in *Mathematical background* 5, this set of equations has nontrivial solutions ($\boldsymbol{c}^{(m)} \neq \mathbf{0}$) only if

$$|\boldsymbol{M} - \varepsilon_m \mathbf{1}| = 0, \text{ or } |\boldsymbol{S}^{-1}\boldsymbol{F} - \varepsilon_m \mathbf{1}| = 0$$

The roots of this secular equation are the energies ε_m, $m = 1, 2, \ldots N_{\mathrm{b}}$ (the elements of the diagonal matrix $\boldsymbol{\varepsilon}$). Multiplication of both sides by the determinant $|\boldsymbol{S}|$ and using the property of determinants that $|\boldsymbol{AB}| = |\boldsymbol{A}| \times |\boldsymbol{B}|$ results in

$$|\boldsymbol{F} - \varepsilon_m \boldsymbol{S}| = 0$$

The set of equations $\boldsymbol{M}\boldsymbol{c}^{(m)} = \varepsilon_m \boldsymbol{c}^{(m)}$ holds for all $m = 1, 2, \ldots, N_{\mathrm{b}}$ and solution of the secular equation results in all (N_{b}) energies ε, so we can drop the subscript m and thereby obtain eqn 27.12.

In principle, we can find the orbital energies ε by looking for the roots of this equation and then using those energies to find the coefficients that make up the matrix $\boldsymbol{c}$ by solving the Roothaan equations. There is a catch, though: the elements of $\boldsymbol{F}$ depend on the coefficients (through the presence of $\hat{J}$ and $\hat{K}$ in the expression for $\hat{f}_1$). Therefore, we have to proceed iteratively: we guess an initial set of values for $\boldsymbol{c}$, solve the secular equation for the orbital energies, use them to solve the Roothaan equations for $\boldsymbol{c}$, and compare the resulting values with the ones we started with. In general they will be different, so we use those new values in another cycle of calculation, and continue until convergence has been achieved (Fig. 27.3). For small, closed-shell molecules, the convergence is often achieved within a few cycles.

Example 27.2 Finding the energy levels

Solve the secular equations for the H_2 molecule established in Example 27.1.

Method Set up the secular determinant for the orbitals using the notation in Example 27.1, expand it, and find the roots of the resulting quadratic equation.

Answer The secular determinant for the H_2 molecule is

$$\begin{vmatrix} F_{AA}-\varepsilon & F_{AB}-\varepsilon S \\ F_{BA}-\varepsilon S & F_{BB}-\varepsilon \end{vmatrix}=0$$

The determinant expands to give the following equation:

$$(F_{AA}-\varepsilon)(F_{BB}-\varepsilon)-(F_{AB}-S\varepsilon)(F_{BA}-S\varepsilon)=0$$

On collecting terms, we arrive at

$$(1-S^2)\varepsilon^2-(F_{AA}+F_{BB}-SF_{AB}-SF_{BA})\varepsilon+(F_{AA}F_{BB}-F_{AB}F_{BA})=0$$

This is a quadratic equation for the orbital energies ε_a and ε_b, and may be solved by using the quadratic formula. Thus, if we summarize the equation as $a\varepsilon^2+b\varepsilon+c=0$, then

$$\varepsilon=\frac{-b\pm(b^2-4ac)^{1/2}}{2a} \qquad \begin{aligned} a&=1-S^2 \\ b&=-(F_{AA}+F_{BB}-SF_{AB}-SF_{BA}) \\ c&=F_{AA}F_{BB}-F_{AB}F_{BA} \end{aligned}$$

With these energies established, and the lower value accepted for ε_a, we can construct the coefficients by substituting into

$$c_{Aa}=-\frac{F_{AB}-S\varepsilon_a}{F_{AA}-\varepsilon_a}c_{Ba}$$

in conjunction with the normalization condition $c_{Aa}^2+c_{Ba}^2+2c_{Aa}c_{Ba}S=1$. (For this homonuclear diatomic molecule, there is, of course, a much simpler method of arriving at $c_{Aa}=c_{Ba}$ for the lower of the two energies.)

Self-test 27.5 Use the orbital energy ε_b to write the expressions relating c_{Ab} and c_{Bb}.

Answer: $c_{Ab}=-\dfrac{F_{BB}-\varepsilon_b}{F_{BA}-S\varepsilon_b}c_{Bb}$, $c_{Ab}^2+c_{Bb}^2+2c_{Ab}c_{Bb}S=1$

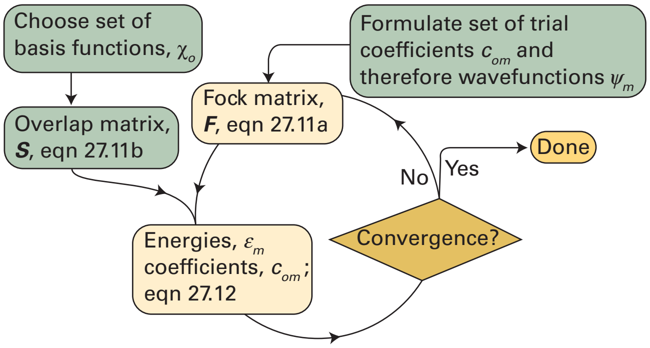

Figure 27.3 The iteration procedure for a Hartree–Fock self-consistent field calculation.

The principal outstanding problem is the form of the elements of the Fock matrix $\boldsymbol{F}$ and its dependence on the LCAO coefficients. The explicit form of $F_{oo'}$ is

$$\begin{aligned} F_{oo'} &= \int \chi_o \hat{h}_1 \chi_{o'}\,\mathrm{d}\tau \\ &\quad +2j_0 \sum_{m,\mathrm{occ}} \int \chi_o(1)\chi_{o'}(1)\frac{1}{r_{12}}\psi_m(2)\psi_m(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2 \\ &\quad -j_0 \sum_{m,\mathrm{occ}} \int \chi_o(1)\psi_m(1)\frac{1}{r_{12}}\psi_m(2)\chi_{o'}(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2 \end{aligned} \tag{27.13}$$

where the sums are over the occupied molecular orbitals. The dependence of $\boldsymbol{F}$ on the coefficients can now be seen to arise from the presence of the ψ_m in the two integrals, for these molecular orbitals depend on the coefficients in their LCAOs.

Example 27.3 Establishing the integrals

Expand the matrix element F_{AA} developed in Example 27.2 in terms of molecular integrals.

Method Implement eqn 27.13.

Answer Only one molecular orbital is occupied, so eqn 27.13 becomes

$$\begin{aligned} F_{AA} &= \int \chi_A \hat{h}_1 \chi_A\,\mathrm{d}\tau + 2j_0\int \chi_A(1)\chi_A(1)\frac{1}{r_{12}}\psi_a(2)\psi_a(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2 \\ &\quad - j_0\int \chi_A(1)\psi_a(1)\frac{1}{r_{12}}\psi_a(2)\chi_A(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2 \end{aligned}$$

With $\psi_a=c_{Aa}\chi_A+c_{Ba}\chi_B$, the second integral on the right is

$$\begin{aligned} &\int \chi_A(1)\chi_A(1)\frac{1}{r_{12}}\psi_a(2)\psi_a(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2 \\ &= \int \chi_A(1)\chi_A(1)\frac{1}{r_{12}}\{c_{Aa}\chi_A(2)+c_{Ba}\chi_B(2)\} \\ &\qquad \times\{c_{Aa}\chi_A(2)+c_{Ba}\chi_B(2)\}\,\mathrm{d}\tau_1\mathrm{d}\tau_2 \\ &= c_{Aa}c_{Aa}\int \chi_A(1)\chi_A(1)\frac{1}{r_{12}}\chi_A(2)\chi_A(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2+\cdots \end{aligned}$$

with four such terms. At this point we can see explicitly that the matrix elements of F depend on the coefficients that we are trying to find.

Self-test 27.6 Write the integral that is a factor of the term $c_{Aa}c_{Ba}$.

Answer: $\displaystyle\int \chi_A(1)\chi_A(1)\frac{1}{r_{12}}\chi_A(2)\chi_B(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2$

The integrals that appear in expressions like those developed in this Example are becoming seriously cumbersome to write. From now on we shall use the notation

$$(\mathrm{AB}|\mathrm{CD})=j_0\int \chi_A(1)\chi_B(1)\frac{1}{r_{12}}\chi_C(2)\chi_D(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2 \tag{27.14}$$

Integrals like this are fixed throughout the calculation (for a particular nuclear geometry) because they depend only on the choice of basis, so they can be tabulated once and for all and then used whenever required. How they are estimated or calculated is explained in Topics 28–30. For the time being, we can treat them as constants.

Brief illustration 27.4 The integral notation

In the notation of eqn 27.14, the integral written explicitly in Example 27.3 becomes

$$j_0\int \chi_A(1)\chi_A(1)\frac{1}{r_{12}}\psi_a(2)\psi_a(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$
$$= c_{Aa}^2(AA|AA) + 2c_{Aa}c_{Ba}(AA|BA) + c_{Ba}^2(AA|BB)$$

(We have used (AA|BA) = (AA|AB).) There is a similar term for the third integral in the expression for F_{AA} developed there, and overall

$$F_{AA} = E_A + c_{Aa}^2(AA|AA) + 2c_{Aa}c_{Ba}(AA|BA)$$
$$+ c_{Ba}^2\{2(AA|BB) - (AB|BA)\}$$

where

$$E_A = \int \chi_A \hat{h}_1 \chi_A \mathrm{d}\tau$$

is the energy of an electron in orbital χ_A based on nucleus A, taking into account its interaction with both nuclei. Similar expressions may be derived for the other three matrix elements of $\boldsymbol{F}$. The crucial point, though, is that we now see how $\boldsymbol{F}$ depends on the coefficients that we are trying to find.

Self-test 27.7 Construct the element F_{AB} using the same basis.

Answer: $F_{AB} = \int \chi_A \hat{h}_1 \chi_B \mathrm{d}\tau + c_{Aa}^2(BA|AA)$
$+ c_{Aa}c_{Ba}\{3(BA|AB) - (AA|BB)\}$
$+ c_{Ba}^2(BA|BB)$

27.4 Basis sets

One of the problems with molecular structure calculations now becomes apparent. The basis functions appearing in eqn 27.14 may in general be centred on different atomic nuclei so (AB|CD) is in general a so-called 'four-centre, two-electron integral'. If there are several dozen basis functions used to build the one-electron wavefunctions, there will be tens of thousands of integrals of this form to evaluate (the number of integrals increases as N_b^4). The efficient calculation of such integrals poses the greatest challenge in an HF-SCF calculation but can be alleviated by a clever choice of basis functions.

The simplest approach is to use a **minimal basis set**, in which one basis function is used to represent each of the orbitals in an elementary valence theory treatment of the molecule. Minimal basis set calculations, however, frequently yield results that are far from agreement with experiment and the development of basis sets that go beyond the minimal basis is an active area of research within computational chemistry.

Brief illustration 27.5 Minimal basis sets

The following choices for constituent atoms correspond to minimal basis sets:

H, He	Li to Ne	Na to Ar
1 (1s)	5 (1s, 2s, 2p)	9 (1s, 2s, 2p, 3s, 3p)

Thus, a minimal basis set for CH_4 consists of nine functions: four basis functions to represent the four H1s orbitals, and one basis function each for the 1s, 2s, $2p_x$, $2p_y$, and $2p_z$ orbitals of carbon.

Self-test 27.8 How many orbitals would constitute a minimal basis set for PF_5 (discounting d orbitals)?

Answer: 34

One of the earliest choices for basis-set functions was that of **Slater-type orbitals** (STO) centred on each of the atomic nuclei in the molecule and of the form

$$\chi = Nr^a e^{-br} Y_{lm_l}(\theta,\phi) \qquad \text{Slater-type orbitals} \tag{27.15}$$

N is a normalization constant, a and b are (non-negative) parameters, Y_{lm_l} is a spherical harmonic (Table 14.1), and (r, θ, ϕ) are the spherical polar coordinates describing the location of the electron relative to the atomic nucleus. Several such basis functions are typically centred on each atom, with each basis function characterized by a unique set of values of a, b, l, and m_l. The values of a and b generally vary with the element and there are several rules for assigning reasonable values. For molecules containing hydrogen, there is an STO centred on each proton with $a = 0$ and $b = 1/a_0$, which simulates the correct behaviour of the 1s orbital at the nucleus. However, using the STO basis set in HF-SCF calculations on molecules with three or more atoms requires the evaluation of so many two-electron integrals (AB|CD) that the procedure becomes computationally impractical.

The introduction of **Gaussian-type orbitals** (GTO) by S.F. Boys largely overcame the problem. Cartesian Gaussian functions centred on atomic nuclei have the form

$$\chi = Nx^i y^j z^k e^{-\alpha r^2} \qquad \text{Gaussian-type orbitals} \tag{27.16}$$

where (x, y, z) are the Cartesian coordinates of the electron at a distance r from the nucleus, (i, j, k) are a set of non-negative

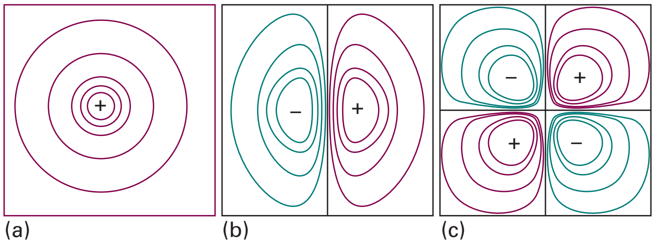

Figure 27.4 Contour plots for Gaussian-type orbitals: (a) s-type Gaussian, e^{-r^2}; (b) p-type Gaussian, xe^{-r^2}; (c) d-type Gaussian, xye^{-r^2}.

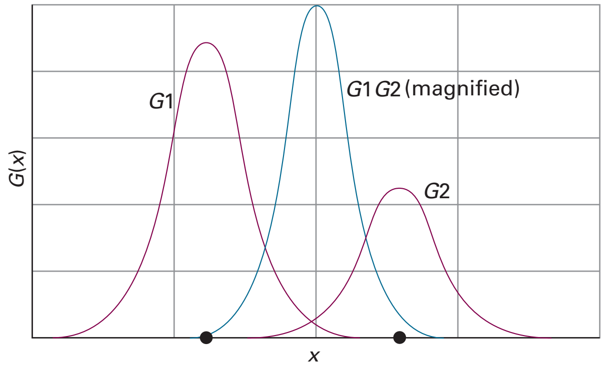

Figure 27.5 The product of two Gaussian functions on different centres is itself a Gaussian function located at a point between the two contributing Gaussians. The scale of the product has been increased relative to that of its two components.

integers, and α is a positive constant. An **s-type** Gaussian has $i=j=k=0$; a **p-type** Gaussian has $i+j+k=1$; a **d-type** Gaussian has $i+j+k=2$, and so on. Figure 27.4 shows contour plots for various Gaussian-type orbitals. The advantage of GTOs is that, as we show in the following *Justification*, the product of two Gaussian functions on different centres is equivalent to a single Gaussian function located at a point between the two centres (Fig. 27.5). Therefore, two-electron integrals on three and four different atomic centres can be reduced to integrals over two different centres, which are much easier to evaluate numerically. This advantage generally outweighs the disadvantage of using Gaussian functions, namely that, on account of the $e^{-\alpha r^2}$ term, GTOs do not simulate the correct behaviour of the 1s orbital at the nucleus, and as a result more Gaussian functions are needed than for a calculation using STOs.

Justification 27.3 Gaussian-type orbitals

There are no four-centre integrals in H_2, but we can illustrate the principle by considering one of the two-centre integrals that appear in the Fock matrix, and, to be definite, we consider

$$(\mathrm{AB}|\mathrm{AB})=j_0\int \chi_{\mathrm{A}}(1)\chi_{\mathrm{B}}(1)\frac{1}{r_{12}}\chi_{\mathrm{A}}(2)\chi_{\mathrm{B}}(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2$$

We choose an s-type Gaussian basis and write

$$\chi_{\mathrm{A}}(1)=N\mathrm{e}^{-\alpha|\boldsymbol{r}_1-\boldsymbol{R}_{\mathrm{A}}|^2}\qquad \chi_{\mathrm{B}}(1)=N\mathrm{e}^{-\alpha|\boldsymbol{r}_1-\boldsymbol{R}_{\mathrm{B}}|^2}$$

where $\boldsymbol{r}_1$ is the location of electron 1 and $\boldsymbol{R}_I$ is that of nucleus I. The product of these two Gaussians is

$$\chi_{\mathrm{A}}(1)\chi_{\mathrm{B}}(1)=N^2\mathrm{e}^{-\alpha|\boldsymbol{r}_1-\boldsymbol{R}_{\mathrm{A}}|^2-\alpha|\boldsymbol{r}_1-\boldsymbol{R}_{\mathrm{B}}|^2}$$

By using the relation

$$|\boldsymbol{r}-\boldsymbol{R}|^2=(\boldsymbol{r}-\boldsymbol{R})\cdot(\boldsymbol{r}-\boldsymbol{R})=|\boldsymbol{r}|^2+|\boldsymbol{R}|^2-2\boldsymbol{r}\cdot\boldsymbol{R}$$

we can confirm that

$$|\boldsymbol{r}_1-\boldsymbol{R}_{\mathrm{A}}|^2+|\boldsymbol{r}_1-\boldsymbol{R}_{\mathrm{B}}|^2=\tfrac{1}{2}R^2+2|\boldsymbol{r}_1-\boldsymbol{R}_{\mathrm{C}}|^2$$

where $\boldsymbol{R}_{\mathrm{C}}=\tfrac{1}{2}(\boldsymbol{R}_{\mathrm{A}}+\boldsymbol{R}_{\mathrm{B}})$ is the midpoint of the molecule and $R=|R_{\mathrm{A}}-R_{\mathrm{B}}|$ is the bond length. Hence

$$\chi_{\mathrm{A}}(1)\chi_{\mathrm{B}}(1)=\mathrm{e}^{-\alpha R^2/2}\,\overbrace{N^2\mathrm{e}^{-2\alpha|\boldsymbol{r}_1-\boldsymbol{R}_{\mathrm{C}}|^2}}^{\chi_{\mathrm{C}}(1)}$$

The product $\chi_{\mathrm{A}}(2)\chi_{\mathrm{B}}(2)$ is the same, except for the index 2 in place of 1 on r. Therefore, the two-centre, two-electron integral (AB|AB) reduces to

$$(\mathrm{AB}|\mathrm{AB})=j_0\mathrm{e}^{-\alpha R^2}\int \chi_{\mathrm{C}}(1)\frac{1}{r_{12}}\chi_{\mathrm{C}}(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2$$

This is a single-centre, two-electron integral, with both exponential functions spherically symmetrical Gaussians centred on the midpoint of the bond, and much faster to evaluate than the original two-centre integral.

Checklist of concepts

☐ 1. A **spinorbital** is the product of a molecular orbital and a spin function.

☐ 2. A **Slater determinant** expresses the fact that the interchange of any pair of electrons changes the sign of the wavefunction.

☐ 3. The **Hartree–Fock** (HF) method uses a single Slater determinant, built from molecular orbitals that satisfy the HF equations, to represent the ground-state electronic wavefunction.

☐ 4. In the **self-consistent field** (SCF) method, equations are solved iteratively until each cycle of calculation leaves the energies and wavefunctions unchanged to within a chosen criterion.

☐ 5. The Hartree–Fock equations involve the **Fock operator**, which consists of the core hamiltonian and terms representing the average Coulomb repulsion (J) and average correction due to spin correlation (K).

☐ 6. The Hartree–Fock method neglects **electron correlation**, the tendency of electrons to avoid one another to minimize repulsion.

☐ 7. The **Roothaan equations** are a set of simultaneous equations, written in matrix form, that result from using a basis set of functions to expand the molecular orbitals.

☐ 8. In a **minimal basis set**, one basis set function represents each of the valence orbitals of the molecule.

☐ 9. **Slater-type orbitals** (STO) and **Gaussian-type orbitals** (GTO) centred on each of the atomic nuclei are commonly used as basis set functions.

☐ 10. The product of two Gaussian-type orbitals on different centres is a single Gaussian function located between the centres.

Checklist of equations

Property	Equation	Comment	Equation number
Many-electron wavefunction	$\Psi=(1/N_e!)^{1/2}\left\|\psi_a^{\alpha}(1)\psi_a^{\beta}(2)\cdots\psi_z^{\beta}(N_e)\right\|$	Closed-shell species	27.2
Hartee–Fock equations	$\hat{f}_1\psi_m(1)=\varepsilon_m\psi_m(1)$	m labels an occupied molecular orbital	27.3
Coulomb operator	$\hat{J}_m(1)\psi_a(1)=j_0\int\psi_a(1)(1/r_{12})\psi_m^*(2)\psi_m(2)\mathrm{d}\tau_2$	$j_0=e^2/4\pi\varepsilon_0$	27.4
Exchange operator	$\hat{K}_m(1)\psi_a(1)=j_0\int\psi_m(1)(1/r_{12})\psi_m^*(2)\psi_a(2)\mathrm{d}\tau_2$		27.6
Effect of Fock operator	$\hat{f}_1\psi_a(1)=\hat{h}_1\psi_a(1)+\sum_m\{2\hat{J}_m(1)-\hat{K}_m(1)\}\psi_a(1)$	Sum over occupied orbitals	27.8
Roothaan equations	$\boldsymbol{Fc}=\boldsymbol{Sc\varepsilon}$		27.10
Fock matrix elements	$F_{o'o}=\int\chi_{o'}(1)\hat{f}_1\chi_o(1)\mathrm{d}\tau_1$	χ_o are atomic basis functions	27.11
Four-centre integral	$(\mathrm{AB}\|\mathrm{CD})=j_0\int\chi_A(1)\chi_B(1)(1/r_{12})\chi_C(2)\chi_D(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$	Notation	27.14
Slater-type orbital	$\chi=Nr^a\mathrm{e}^{-br}Y_{lm_l}(\theta,\phi)$	STO	27.15
Gaussian-type orbital	$\chi=Nx^iy^jz^k\mathrm{e}^{-\alpha r^2}$	GTO	27.16

TOPIC 28

Semi-empirical methods

Contents

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➤ Why do you need to know this material?

Modern computational procedures include semi-empirical methods, and it is important to know their approximations. These methods are useful because they can be applied with computational efficiency to complex systems.

➤ What is the key idea?

Semi-empirical procedures typically identify integrals that may either be neglected or replaced by empirical parameters.

➤ What do you need to know already?

You should review the Hartree–Fock and Roothaan procedures introduced in Topic 27 and should be familiar with the Hückel approximation (Topic 26).

In **semi-empirical methods**, many of the integrals that occur in an electronic structure calculation are estimated by appealing to spectroscopic data or physical properties such as ionization energies, or by using a series of rules to set certain integrals equal to zero. These methods are applied routinely to molecules containing large numbers of atoms because of their computational speed but there is often a sacrifice in the accuracy of the results.

28.1 The Hückel approximation revisited

Semi-empirical methods were first developed for conjugated π systems, the most famous version being Hückel molecular orbital theory (HMO theory, Topic 26).

The initial assumption of HMO theory is the separate treatment of π and σ electrons, which is justified by the different energies and symmetries of the orbitals. As explained in Topic 26, the π-orbital energies and wavefunctions are obtained by solution of eqn 26.9 of that Topic ($\boldsymbol{Hc}=\boldsymbol{ScE}$); the latter equation is composed of sets of matrix equations of the form of eqn 26.7, $(\boldsymbol{H}-E_i\boldsymbol{S})\boldsymbol{c}_i=0$, where E_i is an element of the diagonal matrix $\boldsymbol{E}$. This equation implies (see *Mathematical background* 5) that we need to find solutions of the secular determinant $|\boldsymbol{H}-E_i\boldsymbol{S}|=0$ with, in HMO theory, the overlap integrals set to 0 or 1, the diagonal hamiltonian matrix elements set to a parameter α, and off-diagonal elements set either to 0 or to the parameter β. If instead we start from eqn 27.12 of Topic 27 ($|\boldsymbol{F}-\varepsilon\boldsymbol{S}|=0$), then we can generate HMO theory by making similar choices for the integrals. The HMO approach is useful for qualitative, rather than quantitative, discussions of conjugated π systems because it treats repulsions between electrons very poorly.

Brief illustration 28.1 The Hückel method

Here we return to Example 27.2 of Topic 27 and set $S=0$. The diagonal Fock matrix elements are set equal to α (that is, we set $F_{AA}=F_{BB}=\alpha$), and the off-diagonal elements are set equal to β (that is, we set $F_{AB}=F_{BA}=\beta$). Note that the dependence of these integrals on the coefficients is swept aside, so we do not have to work towards self-consistency. The quadratic equation for the energies

$$(1-S^2)\varepsilon^2-(F_{AA}+F_{BB}-SF_{AB}-SF_{BA})\varepsilon+(F_{AA}F_{BB}-F_{AB}F_{BA})=0$$

becomes simply

$$\varepsilon^2 - 2\alpha\varepsilon + \alpha^2 - \beta^2 = 0$$

and the roots are $\varepsilon = \alpha \pm \beta$, exactly as we found in Topic 25.

Self-test 28.1 What would the energies be if overlap were not neglected?

Answer: $(\alpha+\beta)/(1+S)$ and $(\alpha-\beta)/(1-S)$

28.2 Differential overlap

In the second most primitive and severe approach, called **complete neglect of differential overlap** (CNDO), all two-electron integrals of the form (AB|CD) introduced in Topic 27,

$$(\mathrm{AB}|\mathrm{CD}) = j_0 \int \chi_\mathrm{A}(1)\chi_\mathrm{B}(1)\frac{1}{r_{12}}\chi_\mathrm{C}(2)\chi_\mathrm{D}(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \qquad (28.1)$$

are set to zero unless χ_A and χ_B are the same, and likewise for χ_C and χ_D. That is, only integrals of the form

$$(\mathrm{AA}|\mathrm{CC}) = j_0 \int \chi_\mathrm{A}(1)^2 \frac{1}{r_{12}}\chi_\mathrm{C}(2)^2 \mathrm{d}\tau_1\mathrm{d}\tau_2 \qquad (28.2)$$

survive and they are often taken to be parameters with values adjusted until the calculated energies are in agreement with experiment. The origin of the term 'differential overlap' is that what we normally take to be a measure of 'overlap' is the integral $\int \chi_\mathrm{A}\chi_\mathrm{B}\mathrm{d}\tau$. The differential of an integral of a function is the function itself, so in this sense the 'differential' overlap is the product $\chi_\mathrm{A}\chi_\mathrm{B}$. The implication is that we then simply compare orbitals: if they are the same, the integral is retained; if different, it is discarded.

Brief illustration 28.2 Neglect of differential overlap

The expression for F_AA derived in *Brief illustration* 27.4 of Topic 27 is

$$F_\mathrm{AA} = E_\mathrm{A} + c_{\mathrm{A}a}^2(\mathrm{AA}|\mathrm{AA}) + 2c_{\mathrm{A}a}c_{\mathrm{B}a}(\mathrm{AA}|\mathrm{BA}) \\ + c_{\mathrm{B}a}^2\{2(\mathrm{AA}|\mathrm{BB}) - (\mathrm{AB}|\mathrm{BA})\}$$

The final (blue) integral has the form

$$(\mathrm{AB}|\mathrm{BA}) = j_0 \int \chi_\mathrm{A}(1)\chi_\mathrm{B}(1)\frac{1}{r_{12}}\chi_\mathrm{B}(2)\chi_\mathrm{A}(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$

The 'differential overlap' term $\chi_\mathrm{A}(1)\chi_\mathrm{B}(1)$ is set equal to zero, so in the CNDO approximation the integral is set equal to zero. The same is true of the integral (AA|BA). It follows that we write

$$F_\mathrm{AA} = E_\mathrm{A} + c_{\mathrm{A}a}^2(\mathrm{AA}|\mathrm{AA}) + 2c_{\mathrm{B}a}^2(\mathrm{AA}|\mathrm{BB})$$

and identify the surviving two two-electron integrals as empirical parameters.

Self-test 28.2 Apply the CNDO approximation to F_AB for the same system.

Answer: $F_\mathrm{AB} = \int \chi_\mathrm{A}\hat{h}_1\chi_\mathrm{B}\mathrm{d}\tau - c_{\mathrm{A}a}c_{\mathrm{B}a}(\mathrm{AA}|\mathrm{BB})$

More recent semi-empirical methods make less draconian decisions about which integrals are to be ignored, but they are all descendants of the early CNDO technique. Whereas CNDO sets integrals of the form (AB|AB) to zero for all different χ_A and χ_B, **intermediate neglect of differential overlap (INDO)** does not neglect the (AB|AB) for which different basis functions χ_A and χ_B are centred on the same nucleus. Because these integrals are important for explaining energy differences between terms corresponding to the same electronic configuration, INDO is much preferred over CNDO for spectroscopic investigations. A still less severe approximation is **neglect of diatomic differential overlap (NDDO)** in which (AB|CD) is neglected only when χ_A and χ_B are centred on different nuclei or when χ_C and χ_D are centred on different nuclei.

There are other semi-empirical methods, with names such as **modified intermediate neglect of differential overlap** (MINDO), **modified neglect of differential overlap** (MNDO), Austin model 1 (AM1), PM3, and **pairwise distance directed Gaussian** (PDDG). In each case, the values of integrals are either set to zero or set to parameters with values that have been determined by attempting to optimize agreement with experiment, such as measured values of enthalpies of formation, dipole moments, and ionization energies. MINDO is useful for the study of hydrocarbons; it tends to give more accurate computed results than MNDO but it gives poor results for systems with hydrogen bonds. AM1, PM3, and PDDG are improved versions of MNDO.

Checklist of concepts

- ☐ **1.** In **semi-empirical methods**, the two-electron integrals are set to zero or to empirical parameters with values that optimize agreement with a variety of experimental quantities.
- ☐ **2.** The **Hückel method** is a simple semi-empirical method for conjugated π systems.
- ☐ **3.** In the **complete neglect of differential overlap** (CNDO) approximation, two-electron integrals are set to zero unless the two basis set functions for electron 1 are the same and the two basis functions for electron 2 are the same.

Checklist of equations

Property	Equation	Comment	Equation number
Molecular integrals	$(AB\|CD)=j_0\int\chi_A(1)\chi_B(1)(1/r_{12})\chi_C(2)\chi_D(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$	Parameterized in a variety of ways	28.1

TOPIC 29

Ab initio methods

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➤ Why do you need to know this material?

Modern computational procedures focus on the formulation of reliable *ab initio* methods. To use commercially available software sensibly and to understand the underlying problems it is important to know how they are being overcome.

➤ What is the key idea?

Ab initio procedures typically seek to compute molecular structures and properties from first principles without introducing empirical constants.

➤ What do you need to know already?

You should review the Hartree–Fock and Roothaan procedures introduced in Topic 27 and be familiar with Slater determinants (Topic 27) and time-independent perturbation theory (Topic 15).

In *ab initio* methods, the two-electron integrals (AB|CD) introduced in Topic 27 are evaluated numerically. However, even for small molecules, Hartree–Fock calculations with large basis sets and efficient and accurate calculation of two-electron integrals can give very poor results because they are rooted in the orbital approximation and the average effect of the other electrons on the electron of interest. Thus, the true wavefunction for H_2 is a function of the form $\Psi(r_1,r_2)$, with a complicated behaviour as r_1 and r_2 vary and perhaps approach one another. This complexity is lost when the wavefunction is written as $\psi(r_1)\psi(r_2)$ and each electron is treated as moving in the average field of the other electrons. That is, the approximations of the Hartree–Fock method imply that no attempt is made to take into account electron correlation, the tendency of electrons to stay apart in order to minimize their mutual repulsion.

Most modern work in electronic structure, such as the approaches discussed here as well as more sophisticated approaches that are beyond the scope of this text, tries to take electron correlation into account. Here we give an introduction to just two of the procedures. Topic 30 (density functional theory) presents another way to take electron correlation into account.

29.1 Configuration interaction

A basis set of N_b orbitals can be used to generate N_b molecular orbitals. However, if there are N_e electrons to accommodate, in the ground state only $N_m = \frac{1}{2}N_e$ of these N_b orbitals are occupied, leaving $N_b - \frac{1}{2}N_e$ so-called **virtual orbitals** unoccupied. For example, in the H_2 model calculation used in Topics 27 and 28 the two atomic orbitals give rise to a bonding and an antibonding molecular orbital, but only the former is occupied; the latter is present but 'virtual'.

The ground state of an N_e-electron closed-shell species is

$$\Psi_0 = (1/N_e!)^{1/2}\left|\psi_a^{\alpha}(1)\psi_a^{\beta}(2)\psi_b^{\alpha}(3)\psi_b^{\beta}(4)\cdots\psi_u^{\beta}(N_e)\right|$$

where ψ_u is the highest occupied molecular orbital (the HOMO). We can envisage transferring an electron from an occupied orbital to a virtual orbital ψ_v, and forming the corresponding **singly excited determinant**, such as

$$\Psi_1 = (1/N_e!)^{1/2}\left|\psi_a^{\alpha}(1)\psi_a^{\beta}(2)\psi_b^{\alpha}(3)\psi_v^{\beta}(4)\cdots\psi_u^{\beta}(N_e)\right|$$

Here a β electron, 'electron 4', has been promoted from ψ_b into ψ_v, but there are many other possible choices. We can also envisage doubly excited determinants, and so on. Each of the Slater determinants constructed in this way is called a **configuration state function** (CSF).

In 1959, P.-O. Löwdin proved that the *exact* wavefunction (within the Born–Oppenheimer approximation) can be expressed as a linear combination of CSFs found from the exact solution of the Hartree–Fock equations:

$$\Psi = C_0\Psi_0(\text{≣}) + C_1\Psi_1(\text{≣}) + C_2\Psi_2(\text{≣}) + \cdots \qquad (29.1)$$

Configuration interaction

The inclusion of CSFs to improve the wavefunction in this way is called **configuration interaction** (CI). Configuration interaction can, at least in principle, yield the exact ground-state wavefunction and energy and thus accounts for the electron correlation neglected in Hartree–Fock methods. However, the wavefunction and energy are exact only if an infinite number of CSFs (composed using an infinite number of basis-set orbitals) are used in the expansion in eqn 29.1; in practice, we have to be resigned to using a finite number of CSFs (composed from a finite basis set). One simplification, however, is that there might be symmetry arguments that eliminate the need to include certain contributions.

Brief illustration 29.1 Configuration interaction

We can begin to appreciate why CI improves the wavefunction of a molecule by considering H_2. The ground state (after expanding the Slater determinant) is $\Psi_0 = \psi_a(1)\psi_a(2)\sigma\_(1,2)$ where $\sigma\_(1,2)$ is the singlet spin state wavefunction. We also know that if we use a minimal basis set and ignore overlap, we can write $\psi_a = 1/2^{1/2}\{\chi_A + \chi_B\}$. Therefore

$$\begin{aligned}\Psi_0 &= \tfrac{1}{2}\{\chi_A(1)+\chi_B(1)\}\{\chi_A(2)+\chi_B(2)\}\sigma\_(1,2)\\ &= \tfrac{1}{2}\{\chi_A(1)\chi_A(2)+\chi_A(1)\chi_B(2)+\chi_B(1)\chi_A(2)\\ &\quad +\chi_B(1)\chi_B(2)\}\sigma\_(1,2)\end{aligned}$$

We can see a deficiency in this wavefunction: there are equal probabilities of finding both electrons on A or on B (the blue terms) as there are for finding one electron on A and the other on B (the remaining two terms). That is, electron correlation has not been taken into account and we can expect the calculated energy to be too high.

Self-test 29.1 Show that the superposition of a doubly excited determinant Ψ_2 based on the virtual orbital $\psi_b = 1/2^{1/2}\{\chi_A - \chi_B\}$ reduces the probability that both electrons will be found on the same atom.

Answer: $\Psi = C_0\Psi_0 + C_2\Psi_2 = \tfrac{1}{2}\{A\chi_A(1)\chi_A(2) + B\chi_A(1)\chi_B(2) + B\chi_B(1)\chi_A(2) + A\chi_B(1)\chi_B(2)\} \times\sigma\_(1,2), A = C_0 + C_2 < B = C_0 - C_2$

Brief illustration 29.1 shows that even a limited amount of CI can introduce some electron correlation; **full CI**—using orbitals built from a finite basis and allowing for all possible excitations—will take electron correlation into account more fully. The optimum procedure, using orbitals that form an infinite basis and allowing all excitations, is computationally impractical.

The optimum expansion coefficients in eqn 29.1 are found by using the variation principle. As in *Justification* 27.1 for the Hartree–Fock method, application of the variation principle for CI results in a set of simultaneous equations for the expansion coefficients.

Example 29.1 Finding the energy lowering due to CI

Set up the equations that must be solved in order to find the optimum values of the expansion coefficients for a CI treatment of H_2.

Method Use the $\Psi = C_0\Psi_0 + C_2\Psi_2$ superposition from *Brief illustration* 29.1. We do not need to consider the singly excited determinant because it is of opposite symmetry to the ground state (which is g, Topic 23) of dihydrogen. Set up the secular equation $|\boldsymbol{H} - E\boldsymbol{S}| = 0$ and express the integrals in terms of the (AB|CD) notation introduced in Topic 27 (eqn 27.14):

$$(\text{AB}|\text{CD}) = j_0\int \chi_A(1)\chi_B(1)\frac{1}{r_{12}}\chi_C(2)\chi_D(2)\,d\tau$$

The hamiltonian is $\hat{H} = \hat{h}_1 + \hat{h}_2 + j_0/r_{12}$. For integrals of the form $\int\cdots d\tau$ over the wavefunctions Ψ, which involve spin as well as space variables, interpret the integration as over both sets of variables, with the spin integration over the normalized spin state $\sigma\_(1,2)$ interpreted as

$$\int \sigma\_(1,2)^2\,d\tau = 1$$

Answer The 2×2 $\boldsymbol{H}$ and $\boldsymbol{S}$ matrices are

$$\boldsymbol{H} = \begin{pmatrix} H_{00} & H_{02}\\ H_{20} & H_{22}\end{pmatrix} \quad H_{MN} = \int \Psi_M \hat{H}\Psi_N\,d\tau$$

$$\boldsymbol{S} = \begin{pmatrix} S_{00} & S_{02}\\ S_{20} & S_{22}\end{pmatrix} \quad S_{MN} = \int \Psi_M\Psi_N\,d\tau$$

Note that the overlap integral is between the two-electron wavefunctions, not the overlap of individual atomic orbitals. The secular equation to solve to find E is

$$\begin{vmatrix} H_{00} - ES_{00} & H_{02} - ES_{02}\\ H_{20} - ES_{20} & H_{22} - ES_{22}\end{vmatrix} = 0$$

(Note that $S_{02} = S_{20}$ and $H_{02} = H_{20}$ due to hermiticity.)

The molecular orbitals ψ_a and ψ_b are orthogonal, so

$$\int \Psi_0\Psi_0 \mathrm{d}\tau = \int \overbrace{\psi_a(1)\psi_a(2)\sigma_-(1,2)}^{\psi_0}\overbrace{\psi_a(1)\psi_a(2)\sigma_-(1,2)}^{\psi_0}\mathrm{d}\tau$$

$$= \overbrace{\int \psi_a(1)^2 \mathrm{d}\tau_1}^{1}\overbrace{\int \psi_a(2)^2 \mathrm{d}\tau_2}^{1}\overbrace{\int \sigma_-(1,2)^2 \mathrm{d}\sigma}^{1} = 1$$

$$\int \Psi_2\Psi_0 \mathrm{d}\tau = \int \overbrace{\psi_b(1)\psi_b(2)\sigma_-(1,2)}^{\psi_2}\int\overbrace{\psi_a(1)\psi_a(2)\sigma_-(1,2)}^{\psi_0}\mathrm{d}\tau$$

$$= \overbrace{\int \psi_b(1)\psi_a(1)\mathrm{d}\tau_1}^{0}\overbrace{\int \psi_b(2)\psi_a(2)\mathrm{d}\tau_2}^{0}\overbrace{\int \sigma_-(1,2)^2 \mathrm{d}\sigma}^{1} = 0$$

and likewise for S_{02} and S_{22}. That is, $\boldsymbol{S}=\mathbf{1}$. The secular determinant is now easily rearranged into a quadratic equation for E with solutions

$$E = \tfrac{1}{2}(H_{00}+H_{22}) \pm \tfrac{1}{2}\left\{(H_{00}+H_{22})^2 - 4(H_{00}H_{22} - H_{02}^2)\right\}^{1/2}$$

$$= \tfrac{1}{2}(H_{00}+H_{22}) \pm \tfrac{1}{2}\left\{(H_{00}-H_{22})^2 + 4H_{02}^2\right\}^{1/2}$$

As usual, the problem boils down to an evaluation of various integrals that appear in the matrix elements.

To evaluate the H_{00} hamiltonian matrix elements, we note that

$$H_{00} = \int \Psi_0\left(\hat{h}_1 + \hat{h}_2 + \frac{j_0}{r_{12}}\right)\Psi_0 \mathrm{d}\tau$$

The first term in this integral (noting that the spin integration, as previously, gives 1) is:

$$\int \Psi_0 \hat{h}_1 \Psi_0 \mathrm{d}\tau = \int \psi_a(1)\psi_a(2)\hat{h}_1\psi_a(1)\psi_a(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$

$$= \overbrace{\int \psi_a(1)\hat{h}_1\psi_a(1)\mathrm{d}\tau_1}^{E_a}\overbrace{\int \psi_a(2)\psi_a(2)\mathrm{d}\tau_2}^{1} = E_a$$

The integral with $\hat{h}_2$ in place of $\hat{h}_1$ has the same value. For the electron–electron repulsion term,

$$j_0\int \Psi_0 \frac{1}{r_{12}}\Psi_0 \mathrm{d}\tau = j_0\int \psi_a(1)\psi_a(2)\frac{1}{r_{12}}\psi_a(1)\psi_a(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$

$$= \tfrac{1}{4}\left\{(\mathrm{AA}|\mathrm{AA}) + (\mathrm{AA}|\mathrm{AB}) + \cdots (\mathrm{BB}|\mathrm{BB})\right\}$$

Expressions of a similar kind can be developed for the other three elements of $\boldsymbol{H}$, so the optimum energy can be found by substituting these matrix elements of $\boldsymbol{H}$ into the solutions E. The coefficients in the CI expression for Ψ can then be found in the normal way by using the lower value of E and solving the secular equations.

Self-test 29.2 Establish the expression for H_{02}.

Answer: $H_{02} = \tfrac{1}{4}\left\{(\mathrm{AA}|\mathrm{AA}) - (\mathrm{AA}|\mathrm{AB}) + \cdots (\mathrm{BB}|\mathrm{BB})\right\}$

29.2 Many-body perturbation theory

The application of perturbation theory to a molecular system of interacting electrons and nuclei is called **many-body perturbation theory**. According to the presentation of perturbation theory in Topic 15 (see eqn 15.1, $\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$), the hamiltonian is expressed as a sum of a simple, 'model' hamiltonian, $\hat{H}^{(0)}$, and a perturbation, $\hat{H}^{(1)}$. Because we wish to find the correlation energy, a natural choice for the model hamiltonian is the sum of Fock operators of the HF-SCF method,

$$\hat{f}_i = \hat{h}_i + \sum_m \{2\hat{J}_m(i) - \hat{K}_m(i)\} \tag{29.2}$$

and for the perturbation it is the difference between this sum and the true many-electron hamiltonian. That is,

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} \qquad \text{with} \qquad \hat{H}^{(0)} = \sum_{i=1}^{N_\mathrm{e}} \hat{f}_i \tag{29.3a}$$

with

$$\hat{H} = \overbrace{-\frac{\hbar^2}{2m_\mathrm{e}}\sum_{i=1}^{N_\mathrm{e}}\nabla_i^2 - j_0\sum_{i=1}^{N_\mathrm{e}}\sum_{I=1}^{N_\mathrm{n}}\frac{Z_I}{r_{Ii}}}^{\sum_{i=1}^{N_\mathrm{e}}\hat{h}_i} + \frac{1}{2}j_0\sum_{i\neq j}^{N_\mathrm{e}}\frac{1}{r_{ij}} \tag{29.3b}$$

Because the core hamiltonian (the sum of the $\hat{h}_i$ in the Fock operator in eqn 29.2) cancels the one-electron terms in the full hamiltonian, the perturbation is the difference between the instantaneous interaction between the electrons (the blue term in eqn 29.3) and the average interaction (as represented by the operators J and K in the Fock operator). Thus, for electron 1,

$$\hat{H}^{(1)}(1) = \sum_i \frac{j_0}{r_{1i}} - \sum_m \{2J_m(1) - K_m(1)\} \tag{29.4}$$

where the first sum (the true interaction) is over all the electrons other than electron 1 itself and the second sum (the average interaction) is over all the occupied orbitals. This choice was first made by C. Møller and M.S. Plesset in 1934 and the method is called **Møller–Plesset perturbation theory** (MPPT). Applications of MPPT to molecular systems were not undertaken until the 1970s and the rise of sufficient computing power.

As usual in perturbation theory, the true wavefunction is written as a sum of the eigenfunction of the model hamiltonian and higher-order correction terms. The **correlation energy**, the difference between the true energy and the HF energy, is given by energy corrections that are second-order and higher. If we suppose that the true wavefunction of the system is given by a sum of CSFs like that in eqn 29.1, then

$$E_0^{(2)} = \sum_{M\neq 0} \frac{\left|\int \Psi_M \hat{H}^{(1)} \Psi_0 \mathrm{d}\tau\right|^2}{E_0^{(0)} - E_M^{(0)}} \qquad (29.5)$$

Møller–Plesset perturbation theory

According to **Brillouin's theorem**, only doubly excited Slater determinants have nonzero $\hat{H}^{(1)}$ matrix elements and hence only they make a contribution to $E_0^{(2)}$.[1] The identification of the second-order energy correction with the correlation energy is the basis of the MPPT method denoted MP2. The extension of MPPT to include third- and fourth-order energy corrections are denoted MP3 and MP4, respectively.

Example 29.2 Setting up Møller–Plesset perturbation theory

Use the MP2 procedure to set up an expression for the correlation energy in the model of H_2 that we have been developing.

Method According to Brillouin's theorem, and for our simple model of H_2 built from two basis orbitals, we write $\Psi = C_0\Psi_0 + C_2\Psi_2$ with, as before, $\Psi_0 = \psi_a(1)\psi_a(2)\sigma_-(1,2)$ and $\Psi_2 = \psi_b(1)\psi_b(2)\sigma_-(1,2)$. Formulate the integrals that appear in eqn 29.5.

Answer The only matrix element we need for the sum in eqn 29.5 is

$$\int \Psi_2 \hat{H}^{(1)} \Psi_0 \mathrm{d}\tau = j_0 \int \psi_b(1)\psi_b(2)\frac{1}{r_{12}}\psi_a(1)\psi_a(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$

(As before, integration of spin states has given 1.) All the integrals over terms based on J and K are zero because these are one-electron operators and so either $\psi_a(1)$ or $\psi_a(2)$ is left unchanged and its orthogonality to ψ_b ensures that the integral vanishes. We now expand each molecular orbital in terms of the basis functions χ_A and χ_B, and obtain

$$\int \Psi_2 \hat{H}^{(1)} \Psi_0 \mathrm{d}\tau = \frac{1}{2}\{(AA|AA) - (BA|AA) + \cdots + (BB|BB)\}$$

On using symmetries like $(AA|AB) = (AA|BA)$ and $(AA|AB) = (BB|BA)$, this expression simplifies to

$$\int \Psi_2 \hat{H}^{(1)} \Psi_0 \mathrm{d}\tau = \frac{1}{2}\{(AA|AA) - (AA|BB)\}$$

It follows that the second-order estimate of the correlation energy is

$$E_0^{(2)} = \frac{\frac{1}{4}\{(AA|AA) - (AA|BB)\}^2}{E_0^{(0)} - E_M^{(0)}} = \frac{\{(AA|AA) - (AA|BB)\}^2}{8(\varepsilon_a - \varepsilon_b)}$$

The term $(AA|AA) - (AA|BB)$ is the difference in repulsion energy between both electrons being confined to one atom and each being on a different atom.

Self-test 29.3 Demonstrate the validity of the last remark.

Checklist of concepts

☐ 1. **Electron correlation** is the tendency of electrons to stay apart in order to minimize their mutual repulsion.

☐ 2. **Virtual orbitals** are molecular orbitals that are unoccupied in the HF ground-state electronic wavefunction.

☐ 3. A **singly excited determinant** is formed by transferring an electron from an occupied orbital to a virtual orbital, a **doubly excited determinant** by transferring two electrons, and so on.

☐ 4. Each of the Slater determinants (including the HF wavefunction) is a **configuration state function** (CSF).

☐ 5. **Configuration interaction** (CI) expresses the exact electronic wavefunction as a linear combination of configuration state functions.

☐ 6. Configuration interaction and **Møller–Plesset perturbation theory** are two popular *ab initio* methods that accommodate electron correlation.

☐ 7. **Full CI** uses molecular orbitals built from a finite basis set and allows for all possible excited determinants.

☐ 8. The **correlation energy** is the difference between the true energy and the energy calculated by the Hartree–Fock procedure.

☐ 9. **Many-body perturbation theory** is the application of perturbation theory to a molecular system of interacting electrons and nuclei.

☐ 10. **Møller–Plesset perturbation theory** (MPPT) uses the sum of the Fock operators from the HF method as the simple, model hamiltonian.

☐ 11. According to **Brillouin's theorem**, only doubly excited determinants contribute to the second-order energy correction.

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[1] For details, see our *Molecular quantum mechanics*, Oxford University Press (2011).

Checklist of equations

Property	Equation	Comment	Equation number
Configuration interaction	$\Psi = C_0\Psi_0($$) + C_1\Psi_1($$) + C_2\Psi_2($$) + \cdots$		29.1
Møller–Plesset perturbation theory	$\hat{H}^{(1)}(1) = \sum_i j_0/r_{1i} - \sum_m \{2J_m(1) - K_m(1)\}.$		29.4
Correlation energy in MPPT	$E_0^{(2)} = \sum_{M \neq 0} \left\| \int \Psi_M \hat{H}^{(1)} \Psi_0 \mathrm{d}\tau \right\|^2 \Big/ \left(E_0^{(0)} - E_M^{(0)}\right).$	MP2	29.5

TOPIC 30

Density functional theory

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➤ Why do you need to know this material?

Density functional theory is currently a highly popular method for the calculation of electronic structure, and it is important to know the general features of the procedure.

➤ What is the key idea?

The energy of a molecule can be calculated from the electron density.

➤ What do you need to know already?

You need to be aware of the structure of the hamiltonian for a polyatomic molecule (Topic 27).

A technique that has gained considerable ground in recent years to become one of the most widely used procedures for the calculation of molecular structure is **density functional theory** (DFT). Its advantages include less demanding computational effort, less computer time, and—in some cases, particularly for d-metal complexes—better agreement with experimental values than is obtained from Hartree–Fock based methods.

30.1 The Kohn–Sham equations

The central focus of DFT is the electron probability density, ρ. The 'functional' part of the name comes from the fact that the energy of the molecule is a function of the electron density and the electron density is itself a function of the positions of the electrons, $\rho(\boldsymbol{r})$. In mathematics a function of a function is called a *functional*, and in this specific case we write the energy as the **functional** $E[\rho]$. We have encountered a functional elsewhere but did not use this terminology: the expectation value of the hamiltonian is the energy expressed as a functional of the wavefunction, for a single value of the energy, $E[\psi]$, is associated with each function ψ. An important point to note is that because $E[\psi]$ is an integral of $\psi\hat{H}\psi$ over all space, it has contributions from the whole range of values of ψ.

Simply from the structure of the hamiltonian in Topic 27 (eqn 27.1),

$$\hat{H} = \overbrace{-\frac{\hbar^2}{2m_e}\sum_{i=1}^{N_e}\nabla_i^2}^{\text{Kinetic energy of electrons}} \overbrace{-\sum_{i=1}^{N_e}\sum_{I=1}^{N_n}\frac{Z_I e^2}{4\pi\varepsilon_0 r_{Ii}}}^{\text{Their attraction to all the nuclei}} + \overbrace{\tfrac{1}{2}\sum_{i\neq j}^{N_e}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}}^{\text{Their mutual repulsion}} \qquad \text{The hamiltonian} \qquad (30.1)$$

we can suspect that the energy of a molecule can be expressed as contributions from the kinetic energy, the electron–nuclear interaction, and the electron–electron interaction. The first two contributions depend on the electron density distribution. The electron–electron interaction is likely to depend on the same quantity, but we have to be prepared for there to be a modification of the classical electron–electron interaction due to electron exchange (the contribution which in Hartree–Fock theory is expressed by K). That the exchange contribution can be expressed in terms of the electron density is not at all obvious, but in 1964 P. Hohenberg and W. Kohn were able to prove that the exact ground-state energy of an N_e-electron molecule is uniquely determined by the electron probability density. They showed that it is possible to write

$$E[\rho] = E_{\text{classical}}[\rho] + E_{\text{XC}}[\rho] \tag{30.2}$$

Energy functional

where $E_{\text{classical}}[\rho]$ is the sum of the contributions of kinetic energy, electron–nucleus interactions, and the classical electron–electron potential energy, and $E_{\text{XC}}[\rho]$ is the **exchange–correlation energy**. This term takes into account all the non-classical electron–electron effects due to spin and applies small corrections to the kinetic energy part of $E_{\text{classical}}$ that arise from electron–electron interactions. The **Hohenberg–Kohn theorem** guarantees the existence of $E_{\text{XC}}[\rho]$ but—like so many existence theorems in mathematics—gives no clue about how it should be calculated.

The first step in the implementation of this approach is to calculate the electron density. The relevant equations were deduced by W. Kohn and L.J. Sham in 1965, who showed that ρ can be expressed as a contribution from each electron present in the molecule, and written

$$\rho(\boldsymbol{r}) = \sum_{i=1}^{N_e} |\psi_i(\boldsymbol{r})|^2 \tag{30.3}$$

Electron density

The function ψ_i is called a **Kohn–Sham orbital** and is a solution of the **Kohn–Sham equation**, which closely resembles the form of the Schrödinger equation (on which it is based). For a two-electron system,

$$\begin{aligned}\hat{h}_1\psi_i(1) + j_0\int \frac{\rho(2)}{r_{12}}\mathrm{d}\tau_2\,\psi_i(1) + V_{\text{XC}}(1)\psi_i(1)\\ = \varepsilon_i\psi_i(1)\end{aligned} \tag{30.4}$$

Kohn–Sham equation

The first term is the usual core term, the second term is the classical interaction between electron 1 and electron 2, and the third term takes exchange effects into account and is called the **exchange–correlation potential**. The ε_i are the Kohn–Sham orbital energies.

30.2 The exchange–correlation energy

The exchange–correlation potential plays a central role in DFT and can be calculated once we know the exchange–correlation energy $E_{\text{XC}}[\rho]$ by forming the following 'functional derivative':

$$V_{\text{XC}}(\boldsymbol{r}) = \frac{\delta E_{\text{XC}}[\rho]}{\delta\rho} \tag{30.5}$$

Exchange–correlation potential

A functional derivative is defined like an ordinary derivative, but we have to remember that $E_{\text{XC}}[\rho]$ is a quantity that gets its value from the entire range of values of $\rho(\boldsymbol{r})$, not just from a single point. Thus, when $\boldsymbol{r}$ undergoes a small change, $\mathrm{d}\boldsymbol{r}$, the density changes by $\delta\rho$ to $\rho(\boldsymbol{r}+\mathrm{d}\boldsymbol{r})$ at each point and $E_{\text{XC}}[\rho]$ undergoes a change that is the sum (integral) of all such changes:

$$\delta E_{\text{XC}}[\rho] = \int \frac{\delta E_{\text{XC}}[\rho]}{\delta\rho}\delta\rho\mathrm{d}\boldsymbol{r} = \int V_{\text{XC}}(\boldsymbol{r})\delta\rho\mathrm{d}\boldsymbol{r} \tag{30.6}$$

Note that V_{XC} is an ordinary function of $\boldsymbol{r}$, not a functional: it is the local contribution to the integral that defines the global dependence of $E_{\text{XC}}[\rho]$ on $\delta\rho$ throughout the range of integration. This procedure is clarified and illustrated in Example 30.1.

(a) The exchange–correlation potential

The greatest challenge in density functional theory is to find an accurate expression for the exchange–correlation energy. One widely used but approximate form for $E_{\text{XC}}[\rho]$ is based on the model of a uniform electron gas, a hypothetical electrically neutral system in which electrons move in a space of continuous and uniform distribution of positive charge. For a uniform electron gas, the exchange–correlation energy can be written as the sum of an exchange contribution and a correlation contribution. The latter is a complicated functional that is beyond the scope of this Topic; we ignore it here. The following example shows how to infer the exchange–correlation potential for the exchange contribution.

Example 30.1 Deriving an exchange–correlation potential

The exchange–correlation energy for a uniform electron gas is[1]

$$E_{\text{XC}}[\rho] = A\int \rho^{4/3}\mathrm{d}\boldsymbol{r} \qquad A = -\tfrac{9}{8}\left(\frac{3}{\pi}\right)^{1/2} j_0$$

with, as usual, $j_0 = e^2/4\pi\varepsilon_0$. Deduce the corresponding exchange–correlation potential.

Method Identify how the functional $E_{\text{XC}}[\rho]$ changes when the density changes from $\rho(\boldsymbol{r})$ to $\rho(\boldsymbol{r}) + \delta\rho(\boldsymbol{r})$ at each point (Fig. 30.1), and then use a Taylor series (*Mathematical background* 1) to expand the integrand. Compare the result with eqn 30.6 to identify $V_{\text{XC}}(\boldsymbol{r})$.

Answer When the density changes from $\rho(\boldsymbol{r})$ to $\rho(\boldsymbol{r}) + \delta\rho(\boldsymbol{r})$ the functional changes from $E_{\text{XC}}[\rho]$ to $E_{\text{XC}}[\rho+\delta\rho]$:

$$E_{\text{XC}}[\rho+\delta\rho] = A\int (\rho+\delta\rho)^{4/3}\mathrm{d}\boldsymbol{r}$$

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[1] For the origin of this term, see our *Molecular quantum mechanics*, Oxford University Press (2011).

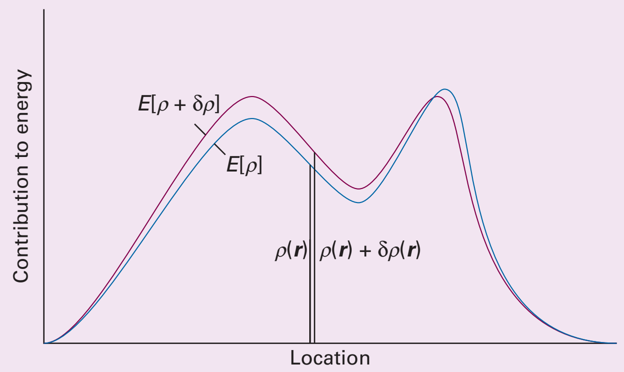

Figure 30.1 The change in the exchange–correlation energy functional from $E_{XC}[\rho]$ to $E_{XC}[\rho+\delta\rho]$ (the area under each curve) as the density changes from ρ to $\rho+\delta\rho$ at each point $\mathbf{r}$.

Expand the integrand in a Taylor series in the vicinity of ρ:

$$(\rho+\delta\rho)^{4/3}=\rho^{4/3}+\overbrace{\left(\frac{\mathrm{d}(\rho+\delta\rho)^{4/3}}{\mathrm{d}\rho}\right)_{\delta\rho=0}}^{\frac{4}{3}\rho^{1/3}}\delta\rho+\cdots$$

$$=\rho^{4/3}+\tfrac{4}{3}\rho^{1/3}\delta\rho+\cdots$$

We discard terms of order $\delta\rho^2$ and higher, and so obtain

$$E_{XC}[\rho+\delta\rho]=A\int(\rho^{4/3}+\tfrac{4}{3}\rho^{1/3}\,\delta\rho)\mathrm{d}\mathbf{r}$$
$$=E_{XC}[\rho]+\tfrac{4}{3}A\int\rho^{1/3}\delta\rho\mathrm{d}\mathbf{r}$$

Therefore, the differential δE_{XC} of the functional (the difference $E_{XC}[\rho+\delta\rho]-E_{XC}[\rho]$ that depends linearly on $\delta\rho$) is

$$\delta E_{XC}[\rho]=\overbrace{\tfrac{4}{3}A\int\rho^{1/3}\,\delta\rho\mathrm{d}\mathbf{r}}^{\int V_{XC}(\mathbf{r})\delta\rho\mathrm{d}\mathbf{r}}$$

and therefore

$$V_{XC}(\mathbf{r})=\frac{4}{3}A\rho^{1/3}=-\frac{3}{2}\left(\frac{3}{\pi}\right)^{1/2}j_0\rho(\mathbf{r})^{1/3} \qquad (30.7)$$

Self-test 30.1 Find the exchange–correlation potential if the exchange–correlation energy is given by $E_{XC}[\rho]=B\int\rho(\mathbf{r})^2\mathrm{d}\mathbf{r}$.

Answer: $V_{XC}(\mathbf{r})=2B\rho(\mathbf{r})$

(b) Solution of the equations

The Kohn–Sham equations must be solved iteratively and self-consistently (Fig. 30.2). First, we guess the electron density; it is common to use a superposition of atomic electron probability densities. Second, the exchange–correlation potential is calculated by assuming an approximate form of the dependence of the exchange–correlation energy on the electron density and evaluating the functional derivative. Next, the Kohn–Sham equations are solved to obtain an initial set of Kohn–Sham orbitals. This set of orbitals is used to obtain a better approximation to the electron probability density (from eqn 30.3) and the process is repeated until the density remains constant to within some specified tolerance. The electronic energy is then computed by using eqn 30.2.

As is the case for the Hartree–Fock one-electron wavefunctions, the Kohn–Sham orbitals can be expanded using a set of N_b basis functions; solving eqn 30.4 then amounts to finding the coefficients in the expansion. Various basis functions, including Slater-type orbitals (STO) and Gaussian-type orbitals (GTO), can be used (Topic 27). Whereas Hartree–Fock methods have computational times that scale as N_b^4, DFT methods scale as N_b^3. Therefore, DFT methods are computationally more efficient, though not necessary more accurate, than HF methods.

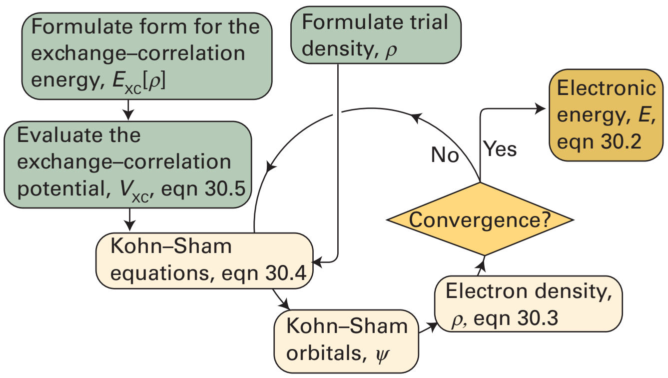

Figure 30.2 The iteration procedure for solving the Kohn–Sham equations in density functional theory.

Example 30.2 Applying the DFT method

Demonstrate how to apply DFT to molecular hydrogen.

Method Begin by assuming that the electron density is a sum of atomic electron densities arising from the presence of electrons in the atomic orbitals χ_A and χ_B (which may be STOs or GTOs), and write $\rho(r)=|\chi_A|^2+|\chi_B|^2$ for each electron. For the exchange–correlation energy, E_{XC}, use the form appropriate to a uniform electron gas and the corresponding exchange–correlation potential derived in Example 30.1.

Answer The Kohn–Sham orbital for the molecule is a solution of

$$\hat{h}_1\psi_a(1) + j_0\int\frac{\rho(2)}{r_{12}}\mathrm{d}\tau_2\psi_a(1) + \tfrac{4}{3}A\rho(1)^{1/3}\psi_a(1) = \varepsilon_a\psi_a(1)$$

Now insert the $\rho(r_1)$ and $\rho(r_2)$ we have assumed, $\rho(r) = |\chi_\mathrm{A}|^2 + |\chi_\mathrm{B}|^2$, and solve this equation numerically for ψ_a. Once we have that orbital, we replace our original guess at the electron density by $\rho(r) = |\psi_a(r)|^2$. This density is then substituted back into the Kohn–Sham equation to obtain an improved function $\psi_a(r)$ and the process repeated until the density and exchange–correlation energy are unchanged to within a specified tolerance on successive iterations.

When convergence of the iterations has been achieved, the electronic energy (eqn 30.2) is calculated from

$$E[\rho] = 2\int\psi_a(\boldsymbol{r})\hat{h}_1\psi_a(\boldsymbol{r})\mathrm{d}\boldsymbol{r} + j_0\int\frac{\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)}{r_{12}}\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2 - \frac{9}{8}\left(\frac{3}{\pi}\right)^{1/2} j_0\int\rho(\boldsymbol{r})^{4/3}\mathrm{d}\boldsymbol{r}$$

where the first term is the sum of the energies of the two electrons in the field of the two nuclei, the second term is the electron–electron repulsion, and the final term includes the correction due to non-classical electron–electron effects.

Self-test 30.2 What would the final term be if the exchange–correlation potential were that deduced in Self-test 30.1?

Answer: $B\int\rho(\boldsymbol{r})^2\,\mathrm{d}\boldsymbol{r}$

Checklist of concepts

☐ **1.** In **density functional theory** (DFT), the electronic energy is written as a functional of the electron probability density.

☐ **2.** The **Hohenberg–Kohn theorem** guarantees that the exact ground-state energy of a molecule is uniquely determined by the electron probability density.

☐ **3.** The **exchange–correlation energy** takes into account non-classical electron–electron effects.

☐ **4.** The electron density is computed from the **Kohn–Sham orbitals**, the solutions to the **Kohn–Sham equations**. The latter equations are solved self-consistently.

☐ **5.** The **exchange–correlation potential** is the functional derivative of the exchange–correlation energy.

☐ **6.** One commonly used but approximate form for the exchange–correlation energy is based on the model of an electron gas.

Checklist of equations

Property	Equation	Comment	Equation number
Energy	$E[\rho] = E_\mathrm{classical}[\rho] + E_\mathrm{XC}[\rho]$		30.2
Electron density	$\rho(\boldsymbol{r}) = \sum_{i=1}^{N_\mathrm{e}}\lvert\psi_i(\boldsymbol{r})\rvert^2$	Definition	30.3
Kohn–Sham equations	$\hat{h}_1\psi_i(1) + j_0\int(\rho(2)/r_{12})\mathrm{d}\tau_2\psi_i(1) + V_\mathrm{XC}(1)\psi_i(1) = \varepsilon_i\psi_i(1)$	Solve numerically and iteratively	30.4
Exchange–correlation potential	$V_\mathrm{XC}(\boldsymbol{r}) = \delta E_\mathrm{XC}[\rho]/\delta\rho$	Definition; a functional derivative	30.5
	$V_\mathrm{XC}(\boldsymbol{r}) = -\frac{3}{2}(3/\pi)^{1/2}\,j_0\rho(\boldsymbol{r})^{1/3}$	Electron-gas model	30.7

Focus 6 on Molecular structure

Topic 22 Valence-bond theory

Discussion questions

22.1 Discuss the role of the Born–Oppenheimer approximation in the calculation of a molecular potential energy curve or surface.

22.2 Why are promotion and hybridization invoked in valence-bond theory?

22.3 Describe the various types of hybrid orbitals and how they are used to describe the bonding in alkanes, alkenes, and alkynes. How does hybridization explain that in allene, $CH_2{=}C{=}CH_2$, the two CH_2 groups lie in perpendicular planes?

22.4 Why is spin pairing so common a feature of bond formation (in the context of valence-bond theory)?

22.5 What are the consequences of resonance?

22.6 Write the Lewis structure of the peroxynitrite ion, $ONOO^-$. Label each atom with its state of hybridization and specify the composition of each of the different types of bond.

Exercises

22.1(a) Write the valence-bond wavefunction for the single bond in HF.
22.1(b) Write the valence-bond wavefunction for the triple bond in N_2.

22.2(a) Write the valence-bond wavefunction for the resonance hybrid $HF \leftrightarrow H^+F^- \leftrightarrow H^-F^+$ (allow for different contributions of each structure).
22.2(b) Write the valence-bond wavefunction for the resonance hybrid $N_2 \leftrightarrow N^+N^- \leftrightarrow N^{2-}N^{2+} \leftrightarrow$ structures of similar energy.

22.3(a) Describe the structure of a P_2 molecule in valence-bond terms. Why is P_4 a more stable form of molecular phosphorus?
22.3(b) Describe the structures of SO_2 and SO_3 in terms of valence-bond theory.

22.4(a) Describe the bonding in 1,3-butadiene using hybrid orbitals.
22.4(b) Describe the bonding in 1,3-pentadiene using hybrid orbitals.

22.5(a) Show that the linear combinations $h_1 = s + p_x + p_y + p_z$ and $h_2 = s - p_x - p_y + p_z$ are mutually orthogonal.
22.5(b) Show that the linear combinations $h_1 = (\sin\chi)s + (\cos\chi)p$ and $h_2 = (\cos\chi)s - (\sin\chi)p$ are mutually orthogonal for all values of the angle χ.

22.6(a) Normalize the sp^2 hybrid orbital $h = s + 2^{1/2}p$ given that the s and p orbitals are each normalized to 1.
22.6(b) Normalize the linear combinations in Exercise 22.5(b) given that the s and p orbitals are each normalized to 1.

Problems

22.1 An sp^2 hybrid orbital that lies in the xy plane and makes an angle of 120° to the x-axis has the form

$$\psi = \frac{1}{3^{1/2}}\left(s - \frac{1}{2^{1/2}}p_x + \frac{3^{1/2}}{2^{1/2}}p_y\right)$$

Use hydrogenic atomic orbitals to write the explicit form of the hybrid orbital. Show that it has its maximum amplitude in the direction specified.

22.2 Confirm that the hybrid orbitals in eqn 22.7 make angles of 120° to each other.

22.3 Show that if two equivalent hybrid orbitals of the form sp^λ make an angle θ to each other, then $\lambda = -1/\cos\theta$. Plot a graph of λ against θ and confirm that $\theta = 180°$ when $\lambda = 1$ and $\theta = 120°$ when $\lambda = 2$.

Topic 23 The principles of molecular orbital theory

Discussion questions

23.1 What feature of molecular orbital theory is responsible for bond formation?

23.2 Why is spin pairing so common a feature of bond formation (in the context of molecular orbital theory)?

Exercises

23.1(a) Normalize the molecular orbital $\psi = \psi_A + \lambda\psi_B$ in terms of the parameter λ and the overlap integral S.

23.1(b) A better description of the molecule in Exercise 23.1(a) might be obtained by including more orbitals on each atom in the linear combination. Normalize the molecular orbital $\psi = \psi_A + \lambda\psi_B + \lambda'\psi'_B$ in terms of the parameters λ and λ' and the appropriate overlap integrals S, where ψ_B and ψ'_B are mutually orthogonal orbitals on atom B.

23.2(a) Suppose that a molecular orbital has the (unnormalized) form $0.145A + 0.844B$. Find a linear combination of the orbitals A and B that is orthogonal to this combination and determine the normalization constants of both combinations using $S = 0.250$.

23.2(b) Suppose that a molecular orbital has the (unnormalized) form $0.727A + 0.144B$. Find a linear combination of the orbitals A and B that is orthogonal to this combination and determine the normalization constants of both combinations using $S = 0.117$.

23.3(a) The energy of H_2^+ with internuclear separation R is given by eqn 23.4. The values of the contributions are given below. Plot the molecular potential energy curve and find the bond dissociation energy (in electronvolts) and the equilibrium bond length.

R/a_0	0	1	2	3	4
j/E_h	1.000	0.729	0.472	0.330	0.250
k/E_h	1.000	0.736	0.406	0.199	0.092
S	1.000	0.858	0.587	0.349	0.189

where $E_h = 27.2\,\text{eV}$, $a_0 = 52.9\,\text{pm}$, and $E_{H1s} = -\frac{1}{2}E_h$.

23.3(b) The same data as in Exercise 23.3(a) may be used to calculate the molecular potential energy curve for the antibonding orbital, which is given by eqn 23.7. Plot the curve.

23.4(a) Identify the g or u character of bonding and antibonding π orbitals formed by side-by-side overlap of p atomic orbitals.

23.4(b) Identify the g or u character of bonding and antibonding δ orbitals formed by face-to-face overlap of d atomic orbitals.

Problems

23.1 Calculate the (molar) energy of electrostatic repulsion between two hydrogen nuclei at the separation in H_2 (74.1 pm). The result is the energy that must be overcome by the attraction from the electrons that form the bond. Does the gravitational attraction between them play any significant role? *Hint*: The gravitational potential energy of two masses is equal to $-Gm_1m_2/r$.

23.2 Imagine a small electron-sensitive probe of volume 1.00 pm^3 inserted into an H_2^+ molecule ion in its ground state. Calculate the probability that it will register the presence of an electron at the following positions: (a) at nucleus A, (b) at nucleus B, (c) halfway between A and B, (c) at a point 20 pm along the bond from A and 10 pm perpendicularly. Do the same for the molecule ion the instant after the electron has been excited into the antibonding LCAO-MO.

23.3 Derive eqns 23.4 and 23.7 by working with the normalized LCAO-MOs for the H_2^+ molecule-ion. Proceed by evaluating the expectation value of the hamiltonian for the ion. Make use of the fact that A and B each individually satisfy the Schrödinger equation for an isolated H atom.

23.4 Examine whether occupation of the bonding orbital with one electron (as calculated in the preceding problem) has a greater or lesser bonding effect than occupation of the antibonding orbital with one electron. Is that true at all internuclear separations?

23.5‡ The LCAO-MO approach described in the text can be used to introduce numerical methods needed in quantum chemistry. In this problem we evaluate the overlap, Coulomb, and resonance integrals numerically and compare the results with the analytical equations (eqns 23.5). (a) Use the LCAO-MO wavefunction and the H_2^+ hamiltonian to derive equations for the relevant integrals, and use mathematical software or an electronic spreadsheet to evaluate the overlap, Coulomb, and resonance integrals numerically, and the total energy for the $1s\sigma_g$ MO in the range $a_0 < R < 4a_0$. Compare the results obtained by numerical integration with results obtained analytically. (b) Use the results of the numerical integrations to draw a graph of the total energy, $E(R)$, and determine the minimum of total energy, the equilibrium internuclear distance, and the dissociation energy (D_e).

23.6(a) Calculate the total amplitude of the normalized bonding and antibonding LCAO-MOs that may be formed from two H1s orbitals at a separation of $2a_0 = 106$ pm. Plot the two amplitudes for positions along the molecular axis both inside and outside the internuclear region. (b) Plot the probability densities of the two orbitals. Then form the *difference density*, the difference between ψ^2 and $\frac{1}{2}(\psi_A^2 + \psi_B^2)$.

Topic 24 Homonuclear diatomic molecules

Discussion questions

24.1 Draw diagrams to show the various orientations in which a p orbital and a d orbital on adjacent atoms may form bonding and antibonding molecular orbitals.

24.2 Outline the rules of the building-up principle for homonuclear diatomic molecules.

24.3 What is the role of the Born–Oppenheimer approximation in molecular orbital theory?

24.4 What is the justification for treating s and p atomic-orbital contributions to molecular orbitals separately?

24.5 To what extent can orbital overlap be related to bond strength?

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‡ These problems were supplied by Charles Trapp and Carmen Giunta.

Exercises

24.1(a) Give the ground-state electron configurations and bond orders of (a) Li_2, (b) Be_2, and (c) C_2.
24.1(b) Give the ground-state electron configurations of (a) F_2^-, (b) N_2, and (c) O_2^{2-}.

24.2(a) From the ground-state electron configurations of B_2 and C_2, predict which molecule should have the greater bond dissociation energy.
24.2(b) From the ground-state electron configurations of Li_2 and Be_2, predict which molecule should have the greater bond dissociation energy.

24.3(a) Which has the higher dissociation energy, F_2 or F_2^+ ?
24.3(b) Arrange the species O_2^+, O_2, O_2^-, O_2^{2-} in order of increasing bond length.

24.4(a) Evaluate the bond order of each Period 2 homonuclear diatomic.
24.4(b) Evaluate the bond order of each Period 2 homonuclear diatomic cation, X_2^+, and anion, X_2^-.

24.5(a) For each of the species in Exercise 24.3(b), specify which molecular orbital is the HOMO.
24.5(b) For each of the species in Exercise 24.3(b), specify which molecular orbital is the LUMO.

24.6(a) What is the speed of a photoelectron ejected from an orbital of ionization energy 12.0 eV by a photon of radiation of wavelength 100 nm?
24.6(b) What is the speed of a photoelectron ejected from a molecule with radiation of energy 21 eV and known to come from an orbital of ionization energy 12 eV?

24.7(a) The overlap integral between two hydrogenic 1s orbitals on nuclei separated by a distance R is given by eqn 24.4. At what separation is $S = 0.20$ for (i) H_2, (ii) He_2?
24.7(b) The overlap integral between two hydrogenic 2s orbitals on nuclei separated by a distance R is given by the expression in *Brief illustration* 24.2. At what separation is $S = 0.20$ for (i) H_2, (ii) He_2?

Problems

24.1 Sketch how the overlap between a 1s orbital and a 2p orbital directed towards it can be expected to depend on their separation. The overlap integral between an H1s orbital and an H2p orbital directed towards it on nuclei separated by a distance R is $S = (R/a_0)\{1+(R/a_0)+\frac{1}{3}(R/a_0)^2\}e^{-R/a_o}$. Plot this function, and find the separation for which the overlap is a maximum.

24.2‡ Use the $2p_x$ and $2p_z$ hydrogenic atomic orbitals to construct simple LCAO descriptions of 2pσ and 2pπ molecular orbitals. (a) Make a probability density plot, and both surface and contour plots of the *xz*-plane amplitudes of the $2p_z\sigma$ and $2p_z\sigma^*$ molecular orbitals. (b) Make surface and contour plots of the *xz*-plane amplitudes of the $2p_x\pi$ and $2p_x\pi^*$ molecular orbitals. Include plots for both an internuclear distance, R, of $10a_0$ and $3a_0$, where $a_0 = 52.9$ pm. Interpret the graphs, and explain why this graphical information is useful.

24.3 Show, if overlap is ignored, (a) that any molecular orbital expressed as a linear combination of two atomic orbitals may be written in the form $\psi = \psi_A \cos\theta + \psi_B \sin\theta$, where θ is a parameter that varies between 0 and $\frac{1}{2}\pi$, and (b) that if ψ_A and ψ_B are orthogonal and normalized to 1, then ψ is also normalized to 1. (c) To what values of θ do the bonding and antibonding orbitals in a homonuclear diatomic molecule correspond?

24.4 In a particular photoelectron spectrum using 21.21 eV photons, electrons were ejected with kinetic energies of 11.01 eV, 8.23 eV, and 5.22 eV. Sketch the molecular orbital energy level diagram for the species, showing the ionization energies of the three identifiable orbitals.

24.5 Show that overlap integral between two hydrogenic 2s orbitals is given by

$$S(2s,2s) = \left\{1 + \frac{ZR}{2a_0} + \frac{1}{12}\left(\frac{ZR}{a_0}\right)^2 + \frac{1}{240}\left(\frac{ZR}{a_0}\right)^4\right\}e^{-ZR/2a_0}$$

Topic 25 Heteronuclear diatomic molecules

Discussion questions

25.1 Describe the Pauling and Mulliken electronegativity scales. Why should they be approximately in step?

25.2 Why do both ionization energy and electron affinity play a role in estimating the energy of an atomic orbital to use in a molecular structure calculation?

25.3 Discuss the steps involved in the calculation of the energy of a system by using the variation principle. Are any assumptions involved?

25.4 What is the physical significance of the Coulomb and resonance integrals?

25.5 Discuss how the properties of carbon explain the bonding features that make it an ideal biological building block.

Exercises

25.1(a) Give the ground-state electron configurations of (a) CO, (b) NO, and (c) CN^-.
25.1(b) Give the ground-state electron configurations of (a) XeF, (b) PN, and (c) SO^-.

25.2(a) Sketch the molecular orbital energy level diagram for XeF and deduce its ground-state electron configuration. Is XeF likely to have a shorter bond length than XeF^+?
25.2(b) Sketch the molecular orbital energy level diagram for IF and deduce its ground-state electron configuration. Is IF likely to have a shorter bond length than IF^- or IF^+?

25.3(a) Use the electron configurations of NO^- and NO^+ to predict which is likely to have the shorter bond length.
25.3(b) Use the electron configurations of SO^- and SO^+ to predict which is likely to have the shorter bond length.

25.4(a) A reasonably reliable conversion between the Mulliken and Pauling electronegativity scales is given by eqn 25.4. Use Table 25.1 to assess how good the conversion formula is for Period 2 elements.

25.4(b) A reasonably reliable conversion between the Mulliken and Pauling electronegativity scales is given by eqn 25.4. Use Table 25.1 to assess how good the conversion formula is for Period 3 elements.

25.5(a) Estimate the orbital energies to use in a calculation of the molecular orbitals of HCl. For data, see Tables 20.2 and 20.3.

25.5(b) Estimate the orbital energies to use in a calculation of the molecular orbitals of HBr. For data, see Tables 20.2 and 20.3.

25.6(a) Use the values derived in Exercise 25.5(a) to estimate the molecular orbital energies in HCl; use $S=0$.

25.6(b) Use the values derived in Exercise 25.5(b) to estimate the molecular orbital energies in HBr; use $S=0$.

25.7(a) Now repeat Exercise 25.6(a), but with $S=0.20$.

25.7(b) Now repeat Exercise 25.6(b), but with $S=0.20$.

Problems

25.1 Equation 25.8c follows from eqn 25.8a by making the approximation $|\alpha_B - \alpha_A| >> 2|\beta|$ and setting $S=0$. Explore the consequences of not setting $S=0$.

25.2 Suppose that a molecular orbital of a heteronuclear diatomic molecule is built from the orbital basis *A*, *B*, and *C*, where *B* and *C* are both on one atom (they can be envisaged as F2s and F2p in HF, for instance). Set up the secular equations for the optimum values of the coefficients and the corresponding secular determinant.

25.3 Continue the preceding problem by setting $\alpha_A = -7.2$ eV, $\alpha_B = -10.4$ eV, $\alpha_C = -8.4$ eV, $\beta_{AB} = -1.0$ eV, $\beta_{AC} = -0.8$ eV, and calculate the orbital energies and coefficients with (i) both $S=0$, (ii) both $S=0.2$.

25.4 As a variation of the preceding problem explore the consequences of increasing the energy separation of the *B* and *C* orbitals (use $S=0$ for this stage of the calculation). Are you justified in ignoring orbital *C* at any stage?

Topic 26 Polyatomic molecules

Discussion questions

26.1 Discuss the scope, consequences, and limitations of the approximations on which the Hückel method is based.

26.2 Distinguish between delocalization energy, π-electron binding energy, and π-bond formation energy. Explain how each concept is employed.

Exercises

26.1(a) Write down the secular determinants for (a) linear H_3, (b) cyclic H_3 within the Hückel approximation.

26.1(b) Write down the secular determinants for (a) linear H_4, (b) cyclic H_4 within the Hückel approximation.

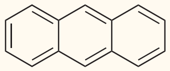
26.2(a) Predict the electron configurations of (a) the benzene anion, (b) the benzene cation. Estimate the π-electron binding energy in each case.

26.2(b) Predict the electron configurations of (a) the allyl radical, (b) the cyclobutadiene cation. Estimate the π-electron binding energy in each case.

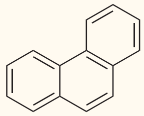
26.3(a) Compute the delocalization energy and π-bond formation energy of (a) the benzene anion, (b) the benzene cation.

26.3(b) Compute the delocalization energy and π-bond formation energy of (a) the allyl radical, (b) the cyclobutadiene cation.

26.4(a) Write down the secular determinants for (a) anthracene (**1**), (b) phenanthrene (**2**) within the Hückel approximation and using the C2p orbitals as the basis set.

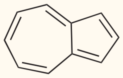


1 Anthracene

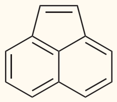


2 Phenanthrene

26.4(b) Write down the secular determinants for (a) azulene (**3**), (b) acenaphthalene (**4**) within the Hückel approximation and using the C2p orbitals as the basis set.



3 Azulene



4 Acenaphthalene

26.5(a) Use mathematical software to estimate the π-electron binding energy of (a) anthracene (**1**), (b) phenanthrene (**2**) within the Hückel approximation.

26.5(b) Use mathematical software to estimate the π-electron binding energy of (a) azulene (**3**), (b) acenaphthalene (**4**) within the Hückel approximation.

Problems

26.1 Set up and solve the Hückel secular equations for the π electrons of CO_3^{2-}. Express the energies in terms of the Coulomb integrals α_O and α_C and the resonance integral β. Determine the delocalization energy of the ion.

26.2 For a linear conjugated polyene with each of N carbon atoms contributing an electron in a 2p orbital, the energies E_k of the resulting π molecular orbitals are given by

$$E_k = \alpha + 2\beta\cos\frac{k\pi}{N+1} \qquad k = 1, 2, 3, \ldots N$$

(a) Use this expression to determine a reasonable empirical estimate of the resonance integral β for the homologous series consisting of ethene, butadiene, hexatriene, and octatetraene, given that $\pi^* \leftarrow \pi$ ultraviolet absorptions from the HOMO to the LUMO occur at 61 500, 46 080, 39 750, and 32 900 cm^{-1}, respectively. (b) Calculate the π-electron delocalization energy, $E_{\text{deloc}} = E_\pi - n(\alpha + \beta)$, of octatetraene, where E_π is the total π-electron binding energy and n is the total number of π electrons. (c) In the context of this Hückel model, the π molecular orbitals are written as linear combinations of the carbon 2p orbitals. The coefficient of the jth atomic orbital in the kth molecular orbital is given by

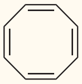
$$c_{kj} = \left(\frac{2}{N+1}\right)^{1/2}\sin\frac{jk\pi}{N+1} \qquad j = 1, 2, 3, \ldots, N$$

Determine the values of the coefficients of each of the six 2p orbitals in each of the six π molecular orbitals of hexatriene. Match each set of coefficients (that is, each molecular orbital) with a value of the energy calculated with the expression given in part (a) of the molecular orbital. Comment on trends that relate the energy of a molecular orbital with its 'shape', which can be inferred from the magnitudes and signs of the coefficients in the linear combination that describes the molecular orbital.

26.3 For monocyclic conjugated polyenes (such as cyclobutadiene and benzene) with each of N carbon atoms contributing an electron in a 2p orbital, simple Hückel theory gives the following expression for the energies E_k of the resulting π molecular orbitals:

$$E_k = \alpha + 2\beta\cos\frac{2k\pi}{N} \quad k = 0, \pm1, \ldots \pm N/2 \text{ for } N \text{ even}$$
$$k = 0, \pm1, \ldots \pm(N-1)/2 \text{ for } N \text{ odd}$$

(a) Calculate the energies of the π molecular orbitals of benzene and cyclooctatetraene (**5**). Comment on the presence or absence of degenerate energy levels. (b) Calculate and compare the delocalization energies of benzene (using the expression above) and hexatriene. What do you conclude from your results? (c) Calculate and compare the delocalization energies of cyclooctatetraene and octatetraene. Are your conclusions for this pair of molecules the same as for the pair of molecules investigated in part (b)?



5 Cyclooctatetraene

26.4 Set up the secular determinants for the homologous series consisting of ethene, butadiene, hexatriene, and octatetraene and diagonalize them by using mathematical software. Use your results to show that the π molecular orbitals of linear polyenes obey the following rules:

- The π molecular orbital with lowest energy is delocalized over all carbon atoms in the chain.
- The number of nodal planes between C2p orbitals increases with the energy of the π molecular orbital.

26.5 Set up the secular determinants for cyclobutadiene, benzene, and cyclooctatetraene and diagonalize them by using mathematical software. Use your results to show that the π molecular orbitals of monocyclic polyenes with an even number of carbon atoms follow a pattern in which:

- The π molecular orbitals of lowest and highest energy are non-degenerate.
- The remaining π molecular orbitals exist as degenerate pairs.

26.6 Electronic excitation of a molecule may weaken or strengthen some bonds because bonding and antibonding characteristics differ between the HOMO and the LUMO. For example, a carbon–carbon bond in a linear polyene may have bonding character in the HOMO and antibonding character in the LUMO. Therefore, promotion of an electron from the HOMO to the LUMO weakens this carbon–carbon bond in the excited electronic state, relative to the ground electronic state. Consult Figs 26.2 and 26.4 and discuss in detail any changes in bond order that accompany the $\pi^* \leftarrow \pi$ ultraviolet absorptions in butadiene and benzene.

26.7‡ Prove that for an open chain of N conjugated carbons the characteristic polynomial of the secular determinant (the polynomial obtained by expanding the determinant), $P_N(x)$, where $x = (\alpha - \beta)/\beta$, obeys the recurrence relation $P_N = xP_{N-1} - P_{N-2}$, with $P_1 = x$ and $P_0 = 1$.

26.8 The standard potential of an electrode is a measure of the thermodynamic tendency of an atom, ion, or molecule to accept an electron (Topic 77). Studies indicate that there is a correlation between the LUMO energy and the standard potential of aromatic hydrocarbons. Do you expect the standard potential to increase or decrease as the LUMO energy decreases? Explain your answer.

26.9‡ In Exercise 26.1(a) you are invited to set up the Hückel secular determinant for linear and cyclic H_3. The same secular determinant applies to the molecular ions H_3^+ and D_3^+. The molecular ion H_3^+ was discovered as long ago as 1912 by J.J. Thomson but its equilateral triangular structure was confirmed by M.J. Gaillard, et al. much more recently (*Phys. Rev.* **A17**, 1797 (1978)). The molecular ion H_3^+ is the simplest polyatomic hydrogen species with a confirmed existence and plays an important role in chemical reactions occurring in interstellar clouds that may lead to the formation of water, carbon monoxide, and ethanol. The H_3^+ ion has also been found in the atmospheres of Jupiter, Saturn, and Uranus. (a) Solve the Hückel secular equations for the energies of the H_3 system in terms of the parameters α and β, draw an energy level diagram for the orbitals, and determine the binding energies of H_3^+, H_3, and H_3^-. (b) Accurate quantum mechanical calculations by G.D. Carney and R.N. Porter (*J. Chem. Phys.* **65**, 3547 (1976)) give the dissociation energy for the process $H_3^+ \rightarrow H + H + H^+$ as 849 kJ mol^{-1}. From this information and data in Table 24.2, calculate the enthalpy of the reaction $H^+(g) + H_2(g) \rightarrow H_3^+(g)$. (c) From your equations and the information given, calculate a value for the resonance integral β in H_3^+. Then go on to calculate the binding energies of the other H_3 species in (a).

26.10‡ There is some indication that other hydrogen ring compounds and ions in addition to H_3 and D_3 species may play a role in interstellar chemistry. According to J.S. Wright and G.A. DiLabio (*J. Phys. Chem.* **96**, 10793 (1992)), H_5^-, H_6, and H_7^+ are particularly stable whereas H_4 and H_5^+ are not. Confirm these statements using Hückel calculations.

Topic 27 Self-consistent fields

Discussion questions

27.1 Describe the physical significance of each of the terms that appears in the Fock operator.

27.2 Outline the computational steps used in the Hartree–Fock self-consistent field approach to electronic structure calculations.

27.3 Explain how the Roothaan equations arise in the Hartree–Fock method. What additional approximations do they represent?

27.4 Explain why the use of Gaussian-type orbitals is generally preferred over the use of Slater-type orbitals in basis sets.

27.5 Describe why the Slater determinant provides a useful representation of electron configurations of many-electron atoms. Why is it an approximation to the true wavefunction?

27.6 Discuss the role of basis-set functions in electronic structure calculations. What are some commonly used basis sets?

Exercises

27.1(a) Write the expression for the potential energy contribution to the electronic hamiltonian for LiH.
27.1(b) Write the expression for the potential energy contribution to the electronic hamiltonian for BeH_2.

27.2(a) Write the electronic hamiltonian for HeH^+.
27.2(b) Write the electronic hamiltonian for LiH^{2+}.

27.3(a) Write the Slater determinant for the ground state of HeH^+.
27.3(b) Write the Slater determinant for the ground state of LiH^{2+}.

27.4(a) Write the Hartree–Fock equation for HeH^+.
27.4(b) Write the Hartree–Fock equation for LiH^{2+}.

27.5(a) Set up the Roothaan equations for HeH^+ and establish the simultaneous equations corresponding to the Roothaan equations. Adopt a basis set of two real normalized functions, one centred on H and one on He; denote the molecular orbitals by ψ_a and ψ_b.
27.5(b) Set up the Roothaan equations for LiH^{2+} and establish the simultaneous equations corresponding to the Roothaan equations. Adopt a basis set of two real normalized functions, one centred on H and one on Li; denote the molecular orbitals by ψ_a and ψ_b.

27.6(a) Construct the elements F_{AA} and F_{AB} for the species HeH^+ and express them in terms of the notation in eqn 27.14.
27.6(b) Construct the elements F_{AA} and F_{AB} for the species LiH^{2+} and express them in terms of the notation in eqn 27.14.

27.7(a) Identify all of the four-centre, two-electron integrals that are equal to (AA|AB).
27.7(b) Identify all of the four-centre, two-electron integrals that are equal to (BB|BA).

27.8(a) How many basis functions are needed in an electronic structure calculation on CH_3Cl using a minimal basis set?
27.8(b) How many basis functions are needed in an electronic structure calculation on CH_2Cl_2 using a minimal basis set?

27.9(a) What is the general mathematical form of a p-type Gaussian?
27.9(b) What is the general mathematical form of a d-type Gaussian?

27.10(a) A one-dimensional Gaussian (in x) has the form $e^{-\alpha x^2}$ or $x^n e^{-\alpha x^2}$; one-dimensional Gaussians in y and z have similar forms. Show that the s-type Gaussian (see eqn 27.16) can be written as a product of three one-dimensional Gaussians.
27.10(b) A one-dimensional Gaussian (in x) has the form $e^{-\alpha x^2}$ or $x^n e^{-\alpha x^2}$; one-dimensional Gaussians in y and z have similar forms. Show that a p-type Gaussian (see eqn 27.16) can be written as a product of three one-dimensional Gaussians.

27.11(a) Show that the product of s-type Gaussians on He and H in HeH^+ is a Gaussian at an intermediate position. Note that the Gaussians have different exponents.
27.11(b) Show that the product of s-type Gaussians on Li and H in LiH^{2+} is a Gaussian at an intermediate position. Note that the Gaussians have different exponents.

Problems

One of the following problems requires the use of commercially available software. Use versions that are available with this text or the software recommended by your instructor.

27.1 Using appropriate electronic structure software and basis sets of your or your instructor's choosing, perform Hartree–Fock self-consistent field calculations for the ground electronic states of H_2 and F_2. Determine ground-state energies and equilibrium geometries. Compare computed equilibrium bond lengths to experimental values.

27.2 A useful property of determinants is that interchanging any two rows or columns changes their sign and therefore that if any two rows or columns are identical, then the determinant vanishes. Use this property to show that (a) the wavefunction (expressed as a Slater determinant) is antisymmetric under particle exchange, (b) no two electrons can occupy the same orbital with the same spin.

27.3 Show that the Slater determinant in eqn 27.2a is normalized assuming that the spinorbitals from which it is constructed are orthogonal and normalized.

27.4 It is often necessary during the course of an electronic structure calculation to take derivatives of the basis functions with respect to nuclear coordinates. Show that the derivative of an s-type Gaussian with respect to x yields a p-type Gaussian and that the derivative of a p-type Gaussian (of the form $x\,e^{-\alpha r^2}$) yields a sum of s- and d-type Gaussians (which are proportional to functions such as $e^{-\alpha r^2}$ and $xye^{-\alpha r^2}$ and its analogues, respectively).

27.5 Consider a four-centre integral in an electronic structure calculation on NH_3 involving s-type Gaussian functions centred on each atomic nucleus. Show that the four-centre, two-electron integral reduces to an integral over two different centres.

27.6 (a) In a continuation of Exercise 27.5(a) for HeH^+, proceed to determine the energies of the two molecular orbitals as well as the relation between the two coefficients for ψ_a and the relation between the two coefficients for ψ_b. (b) Repeat for LiH^{2+} (in a continuation of Exercise 27.5(b)).

27.7 (a) Continuing the Hartree–Fock calculation on HeH^+ in Problem 27.6(a), give the expressions for all four of the elements of the Fock matrix in terms of four-centre, two-electron integrals; the latter are defined in eqn 27.14. (b) Repeat for LiH^{2+} (in a continuation of Problem 27.6(b).)

Topic 28 Semi-empirical methods

Discussion questions

28.1 Why is Hückel molecular orbital theory considered a semi-empirical method?

28.2 Describe some of the common semi-empirical methods.

Exercises

28.1(a) Identify the quadratic equation for the coefficient of the basis function centred on H in HeH^+ starting from the Fock matrix and making the Hückel approximations.

28.1(b) Identify the quadratic equation for the coefficient of the basis function centred on H in LiH^{2+} starting from the Fock matrix and making the Hückel approximations.

28.2(a) Identify the two-electron integrals that are set to zero in the semi-empirical method known as (a) CNDO, (b) INDO.

28.2(b) Identify the two-electron integrals that are set to zero in in the semi-empirical method known as NDDO.

Problems

Some of the following problems require the use of commercially available software. Use versions that are available with this text or the software recommended by your instructor.

28.1 Use an appropriate semi-empirical method to compute the equilibrium bond lengths and standard enthalpies of formation of (a) ethanol, C_2H_5OH, (b) 1,4-dichlorobenzene, $C_6H_4Cl_2$. Compare to experimental values and suggest reasons for any discrepancies.

28.2 Molecular electronic structure methods may be used to estimate the standard enthalpy of formation of molecules in the gas phase. (a) Use a semi-empirical method of your choice to calculate the standard enthalpies of formation of ethene, butadiene, hexatriene, and octatetraene in the gas phase. (b) Consult a database of thermochemical data, and, for each molecule in part (a), calculate the difference between the calculated and experimental values of the standard enthalpy of formation. (c) A good thermochemical database will also report the uncertainty in the experimental value of the standard enthalpy of formation. Compare experimental uncertainties with the relative errors calculated in part (b) and discuss the reliability of your chosen semi-empirical method for the estimation of thermochemical properties of linear polyenes.

28.3 (a) Using the expressions for the four elements of the Fock matrix for HeH^+ determined in Problem 27.7(a), show how these expressions simplify if the CNDO semi-empirical method is used. (b) Repeat for LiH^{2+}, beginning with the expressions determined in Problem 27.7(b).

28.4 (a) In a continuation of Problem 27.6(a), use Hückel molecular orbital theory to express the energies of the molecular orbitals in terms of α and β. (b) Repeat for LiH^{2+} (in a continuation of Problem 27.6(b)).

Topic 29 *Ab initio* methods

Discussion questions

29.1 Discuss what is meant by a virtual orbital, a singly excited determinant, and a doubly excited determinant.

29.2 Describe some computational limitations of the configuration interaction method.

29.3 Describe the choice of the hamiltonians $\hat{H}^{(0)}$ and $\hat{H}^{(1)}$ in MPPT.

29.4 Discuss the importance of Brillouin's theorem in electronic structure calculations.

Exercises

29.1(a) In a Hartree–Fock calculation on the silicon atom using 20 basis-set functions, how many of the molecular orbitals generated would be unoccupied and could be used as virtual orbitals in a configuration interaction calculation?

29.1(b) In a Hartree–Fock calculation on the sulfur atom using 20 basis-set functions, how many of the molecular orbitals generated would be unoccupied and could be used as virtual orbitals in a configuration interaction calculation?

29.2(a) Give an example of a singly excited determinant in a CI calculation of H_2.

29.2(b) Give an example of a doubly excited determinant in a CI calculation of H_2.

29.3(a) Use eqn 29.1 to write the expression for the ground-state wavefunction in a CI calculation on HeH^+ involving the ground-state determinant and a singly excited determinant.

29.3(b) Use eqn 29.1 to write the expression for the ground-state wavefunction in a CI calculation on LiH^{2+} involving the ground-state and a doubly excited determinant.

29.4(a) The second-order energy correction (eqn 29.5) in MPPT arises from the doubly excited determinant (the $M=2$ term). Derive an expression for the integral that appears in the numerator of eqn 29.5 in terms of the integrals (AB|CD) for HeH^+.

29.4(b) The second-order energy correction (eqn 29.5) in MPPT arises from the doubly excited determinant (the $M=2$ term). Derive an expression for the integral that appears in the numerator of eqn 29.5 in terms of the integrals (AB|CD) for LiH^{2+}.

Problems

29.1‡ Luo, et al. (*J. Chem. Phys.* **98**, 3564 (1993)) reported experimental observation of He_2, a species that had escaped detection for a long time. The observation required temperatures in the neighbourhood of 1 mK. Perform configuration interaction and MPPT electronic structure calculations and compute the equilibrium bond length R_e of the dimer as well as the energy of the dimer at R_e relative to the separated He + He atomic limit. (High-level, accurate computational studies suggest that the well depth for He_2 is about 0.0151 zJ at a distance R_e of about 297 pm.)

29.2 In a configuration interaction calculation on the excited ${}^3\Sigma_u^+$ electronic state of H_2, which of the following Slater determinants can contribute to the excited-state wavefunction?

(a) $\left|1\sigma_g^\alpha 1\sigma_u^\alpha\right|$ (b) $\left|1\sigma_g^\alpha 1\pi_u^\alpha\right|$

(c) $\left|1\sigma_u^\alpha 1\pi_g^\beta\right|$ (d) $\left|1\sigma_g^\beta 2\sigma_u^\beta\right|$

(e) $\left|1\pi_u^\alpha 1\pi_g^\alpha\right|$ (f) $\left|1\pi_u^\beta 2\pi_u^\beta\right|$

29.3 Use MPPT to obtain an expression for the ground-state wavefunction corrected to first order in the perturbation.

29.4 (a) Show why configuration interaction gives an improved ground-state wavefunction for HeH^+ compared to the Hartree–Fock ground-state wavefunction. Use a minimal basis set and ignore overlap. Follow along the lines of the argument presented in *Brief illustration* 29.1 but recognize the complication introduced by the fact that HeH^+ does not have inversion symmetry. (b) Repeat for LiH^{2+}.

29.5 In Example 29.1, the secular equation for a CI calculation on molecular hydrogen using the ground-state Slater determinant and the doubly excited determinant was presented as well as the expression for one of the hamiltonian matrix elements. Develop similar expressions for the remaining hamiltonian matrix elements.

29.6 Show that in MPPT first-order energy corrections do not contribute to the correlation energy.

29.7 Prove Brillouin's theorem, which states that the hamiltonian matrix elements between the ground-state Hartree–Fock Slater determinant and singly excited determinants are zero.

29.8 Derive an expression for the second-order estimate of the correlation energy for H_2 if, in a CI calculation using a minimal basis set, the overlap between the two basis-set functions is not ignored but set equal to a constant S.

Topic 30 Density functional theory

Discussion questions

30.1 Describe some of the advantages of density functional theory compared to other Hartree–Fock based methods.

30.2 Discuss what is meant by a 'functional'.

30.3 Describe the contributions to the energy functional $E[\rho]$.

30.4 Discuss what is meant by a uniform electron gas and how it is used in DFT.

Exercises

30.1(a) Which of the following are functionals? (a) $\mathrm{d}(x^3)/\mathrm{d}x$; (b) $\mathrm{d}(x^3)/\mathrm{d}x$ evaluated at $x=1$; (c) $\int x^3\mathrm{d}x$; (d) $\int_1^3 x^3\mathrm{d}x$?

30.1(b) Which of the following are functionals? (a) $\mathrm{d}(3x^2)/\mathrm{d}x$; (b) $\mathrm{d}(3x^2)/\mathrm{d}x$ evaluated at $x=4$; (c) $\int 3x^2\mathrm{d}x$; (d) $\int_1^3 3x^2\mathrm{d}x$?

30.2(a) Using eqn 30.3, write the expression for the electron density in terms of the Kohn–Sham orbitals in a DFT calculation on LiH.

30.2(b) Using eqn 30.3, write the expression for the electron density in terms of the Kohn–Sham orbitals in a DFT calculation on BeH_2.

30.3(a) Write the two Kohn–Sham equations for the Kohn–Sham orbitals in a DFT calculation on HeH^+. Use the exchange–correlation potential of eqn 30.7.

30.3(b) Write the two Kohn–Sham equations for the Kohn–Sham orbitals in a DFT calculation on LiH^{2+}. Use the exchange–correlation potential of eqn 30.7.

Problem

30.1 Find the DFT exchange–correlation potential if the exchange–correlation energy is given by $\int C\rho^{5/3}\mathrm{d}\boldsymbol{r}$.

Integrated activities

F6.1 State and compare the approximations on which the valence-bond and molecular orbital theories are based.

F6.2 Use concepts of molecular orbital theory to describe the chemical reactivity of O_2, N_2, and NO.

F6.3 Explain why the Hartree–Fock formalism does not account for electron correlation but the methods of configuration interaction and many-body perturbation theory do.

F6.4 Distinguish between semi-empirical, *ab initio*, and density functional theory methods of electronic structure determination.

F6.5 Is DFT a semi-empirical method? Justify your answer.

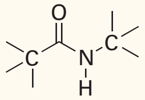
F6.6 Which of the molecules N_2, NO, O_2, C_2, F_2, and CN would you expect to be stabilized by (a) the addition of an electron to form AB^-, (b) the removal of an electron to form AB^+?

F6.7 State the parities of the six π orbitals of benzene.

F6.8 The languages of valence-bond theory and molecular orbital theory are commonly combined when discussing unsaturated organic compounds. Construct the molecular orbital energy level diagram of ethene on the basis that the molecule is formed from the appropriately hybridized CH_2 or CH fragments. Repeat for ethyne (acetylene).

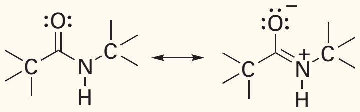
F6.9 Molecular orbital calculations based on semi-empirical, *ab initio*, and DFT methods describe the spectroscopic properties of conjugated molecules better than simple Hückel theory. (a) Use the computational method of your choice (semi-empirical, *ab initio*, or density functional) to calculate the energy separation between the HOMO and LUMO of ethene, butadiene, hexatriene, and octatetraene. (b) Plot the HOMO–LUMO energy separations against the experimental frequencies for $\pi^* \leftarrow \pi$ ultraviolet absorptions for these molecules (61 500, 46 080, 39 750, and 32 900 $\mathrm{cm^{-1}}$, respectively). Use mathematical software to find the polynomial equation that best fits the data. (b) Use your polynomial fit from part (b) to estimate the wavenumber and wavelength of the $\pi^* \leftarrow \pi$ ultraviolet absorption of decapentaene from the calculated HOMO–LUMO energy separation. (c) Discuss why the calibration procedure of part (b) is necessary.

F6.10 Here we develop a molecular orbital theory treatment of the peptide group (**6**), which links amino acids in proteins, and establish the features that stabilize its planar conformation.



6 Peptide group

(a) It will be familiar from introductory chemistry that valence-bond theory explains the planar conformation by invoking delocalization of the π bond over the oxygen, carbon, and nitrogen atoms by resonance:



It follows that we can model the peptide group using molecular orbital theory by making LCAO-MOs from 2p orbitals perpendicular to the plane defined by the O, C, and N atoms. The three combinations have the form

$$\psi_1 = a\psi_O + b\psi_C + c\psi_N \quad \psi_2 = d\psi_O - e\psi_N \quad \psi_3 = f\psi_O - g\psi_C + h\psi_N$$

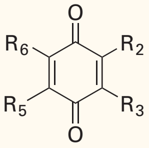
where the coefficients *a* to *h* are all positive. Sketch the orbitals ψ_1, ψ_2, and ψ_3 and characterize them as bonding, nonbonding, or antibonding molecular orbitals. In a nonbonding molecular orbital, a pair of electrons resides in an orbital confined largely to one atom and not appreciably involved in bond formation. (b) Show that this treatment is consistent only with a planar conformation of the peptide link. (c) Draw a diagram showing the relative energies of these molecular orbitals and determine the occupancy of the orbitals. *Hint*: Convince yourself that there are four electrons to be distributed among the molecular orbitals. (d) Now consider a non-planar conformation of the peptide link, in which the O2p and C2p orbitals are perpendicular to the plane defined by the O, C, and N atoms, but the N2p orbital lies on that plane. The LCAO-MOs are given by

$$\psi_4 = a\psi_O + b\psi_C \quad \psi_5 = e\psi_N \quad \psi_6 = f\psi_O - g\psi_C$$

Just as before, sketch these molecular orbitals and characterize them as bonding, nonbonding, or antibonding. Also, draw an energy level diagram and determine the occupancy of the orbitals. (e) Why is this arrangement of atomic orbitals consistent with a non-planar conformation for the peptide link? (f) Does the bonding MO associated with the planar conformation have the same energy as the bonding MO associated with the non-planar conformation? If not, which bonding MO is lower in energy? Repeat the analysis for the nonbonding and antibonding molecular orbitals. (g) Use your results from parts (a)–(f) to construct arguments that support the planar model for the peptide link.

F6.11 Molecular orbital calculations may be used to predict trends in the standard potentials of conjugated molecules, such as the quinones and flavins that are involved in biological electron transfer reactions. It is commonly assumed that decreasing the energy of the LUMO enhances the ability of a molecule to accept an electron into the LUMO, with an accompanying increase in the value of the molecule's standard potential. Furthermore, a number of studies indicate that there is a linear correlation between the LUMO energy and the reduction potential of aromatic hydrocarbons. (a) The standard potentials at pH = 7 for the one-electron reduction of methyl-substituted 1,4-benzoquinones (**7**) to their respective semiquinone radical anions are:

R_2	R_3	R_5	R_6	$E^{\ominus}/\mathrm{V}$
H	H	H	H	0.078
CH_3	H	H	H	0.023
CH_3	H	CH_3	H	−0.067
CH_3	CH_3	CH_3	H	−0.165
CH_3	CH_3	CH_3	CH_3	−0.260



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(a) Using the computational method of your choice (semi-empirical, *ab initio*, or density functional theory), calculate E_{LUMO}, the energy of the LUMO of each substituted 1,4-benzoquinone, and plot E_{LUMO} against $E^{\ominus}$. Do your calculations support a linear relation between E_{LUMO} and $E^{\ominus}$? (b) The 1,4-benzoquinone for which $R_2=R_3=CH_3$ and $R_5=R_6=OCH_3$ is a suitable model of ubiquinone, a component of the respiratory electron-transport chain. Determine E_{LUMO} of this quinone and then use your results from part (a) to estimate its standard potential. (c) The 1,4-benzoquinone for which $R_2=R_3=R_5=CH_3$ and $R_6=H$ is a suitable model of plastoquinone, a component of the photosynthetic electron-transport chain. Determine E_{LUMO} of this quinone and then use your results from part (a) to estimate its standard potential. Is plastoquinone expected to be a better or worse oxidizing agent than ubiquinone?

F6.12 Use appropriate electronic structure software and basis sets of your or your instructor's choosing to perform electronic structure calculations for the ground electronic states of H_2 and F_2 using (a) MP2; (b) DFT; (c) CI including ground-state, singly excited, and doubly excited Slater determinants. Determine ground-state energies and equilibrium geometries. Compare computed equilibrium bond lengths to experimental values.

F6.13 The variation principle can be used to formulate the wavefunctions of electrons in atoms as well as molecules. Suppose that the function $\psi_{\text{trial}} = N(\alpha)\mathrm{e}^{-\alpha r^2}$, with $N(\alpha)$ the normalization constant and α an adjustable parameter, is used as a trial wavefunction for the 1s orbital of the hydrogen atom. Show that

$$E(\alpha)=\frac{3\alpha\hbar^2}{2\mu}-2e^2\left(\frac{2\alpha}{\pi}\right)^{1/2}$$

where e is the fundamental charge and μ is the reduced mass for the H atom. What is the minimum energy associated with this trial wavefunction?

F6.14 In 'free electron molecular orbital' (FEMO) theory, the electrons in a conjugated molecule are treated as independent particles in a box of length L. Sketch the form of the two occupied orbitals in butadiene predicted by this model and predict the minimum excitation energy of the molecule. The conjugated tetraene $CH_2=CHCH=CHCH=CHCH=CH_2$ can be treated as a box of length $8R$, where $R \approx 140$ pm (as in this case, an extra half bond-length is often added at each end of the box). Calculate the minimum excitation energy of the molecule and sketch the HOMO and LUMO. Estimate the colour a sample of the compound is likely to appear in white light.

F6.15 An important quantity in nuclear magnetic resonance spectroscopy (Topics 47 – 49) and which should be familiar from ^{13}C-NMR spectra of organic molecules, is the chemical shift; this experimentally determined quantity is influenced by the details of the electronic structure near the ^{13}C nucleus of interest. Consider the following series of molecules: benzene, methylbenzene, trifluoromethylbenzene, benzonitrile, and nitrobenzene in which the substituents *para* to the C atom of interest are H, CH_3, CF_3, CN, and NO_2, respectively. (a) Use the computational method of your choice to calculate the net charge at the C atom *para* to these substituents in the series of organic molecules given above. (b) It is found empirically that the ^{13}C chemical shift of the *para* C atom increases in the order: methylbenzene, benzene, trifluoromethylbenzene, benzonitrile, nitrobenzene. Is there a correlation between the behaviour of the ^{13}C chemical shift and the computed net charge on the ^{13}C atom? (This problem is revisited in Focus 10, Problem F10.1.)

F6.16 Use mathematical software, a spreadsheet, or the *Living graphs* (labelled $^{\text{LG}}$) on the website of this book for the following exercises:

(a) Plot the amplitude of the bonding molecular orbital in a hydrogen molecule-ion in a plane containing the two nuclei for different values of the internuclear distance. Point to the features of the 1σ orbital that lead to bonding.

(b) Plot the amplitude of the antibonding molecular orbital in a hydrogen molecule-ion in a plane containing the two nuclei for different values of the internuclear distance. Point to the features of the 2σ orbital that lead to antibonding.

Mathematical background 5 Matrices

A **matrix** is an array of numbers that are generalizations of ordinary numbers. We shall consider only square matrices, which have the numbers arranged in the same number of rows and columns. By using matrices, we can manipulate large numbers of ordinary numbers simultaneously. A **determinant** is a particular combination of the numbers that appear in a matrix and is used to manipulate the matrix.

Matrices may be combined together by addition or multiplication according to generalizations of the rules for ordinary numbers. Although we describe below the key algebraic procedures involving matrices, it is important to note that most numerical matrix manipulations are now carried out with mathematical software. You are encouraged to use such software, if it is available to you.

MB5.1 Definitions

Consider a square matrix $\boldsymbol{M}$ of n^2 numbers arranged in n columns and n rows. These n^2 numbers are the **elements** of the matrix, and may be specified by stating the row, r, and column, c, at which they occur. Each element is therefore denoted M_{rc}. A **diagonal matrix** is a matrix in which the only nonzero elements lie on the major diagonal (the diagonal from M_{11} to M_{nn}). Thus, the matrix

$$\boldsymbol{D}=\begin{pmatrix}1 & 0 & 0\\ 0 & 2 & 0\\ 0 & 0 & 1\end{pmatrix}$$

is a 3×3 diagonal square matrix. The condition may be written

$$M_{rc}=m_r\delta_{rc} \qquad \text{(MB5.1)}$$

where δ_{rc} is the **Kronecker delta**, which is equal to 1 for $r=c$ and to 0 for $r\neq c$. In the above example, $m_1=1$, $m_2=2$, and $m_3=1$. The **unit matrix**, **1** (and occasionally **I**), is a special case of a diagonal matrix in which all nonzero elements are 1.

The **transpose** of a matrix $\boldsymbol{M}$ is denoted $\boldsymbol{M}^{\mathrm{T}}$ and is defined by

$$M^T_{mn}=M_{nm} \qquad \text{Transpose} \quad \text{(MB5.2)}$$

That is, the element in row n, column m of the original matrix becomes the element in row m, column n of the transpose (in effect, the elements are reflected across the diagonal). The **determinant**, $|\boldsymbol{M}|$, of the matrix $\boldsymbol{M}$ is a number arising from a specific procedure for taking sums and differences of products of matrix elements. For example, a 2×2 determinant is evaluated as

$$\begin{vmatrix}a & b\\ c & d\end{vmatrix}=ad-bc \qquad \text{2×2 Determinant} \quad \text{(MB5.3a)}$$

and a 3×3 determinant is evaluated by expanding it as a sum of 2×2 determinants:

$$\begin{vmatrix}a & b & c\\ d & e & f\\ g & h & i\end{vmatrix}=a\begin{vmatrix}e & f\\ h & i\end{vmatrix}-b\begin{vmatrix}d & f\\ g & i\end{vmatrix}+c\begin{vmatrix}d & e\\ g & h\end{vmatrix} \qquad \text{3×3 Determinant} \quad \text{(MB5.3b)}$$
$$=a(ei-fh)-b(di-fg)+c(dh-eg)$$

Note the sign change in alternate columns (b occurs with a negative sign in the expansion). An important property of a determinant is that if any two rows or any two columns are interchanged, then the determinant changes sign.

Brief illustration MB5.1 Matrix manipulations

The following grid illustrates the features so far:

Matrix	Transpose	Determinant
$\boldsymbol{M}$	$\boldsymbol{M}^{\mathrm{T}}$	$\lvert\boldsymbol{M}\rvert$
$\begin{pmatrix}1 & 2\\ 3 & 4\end{pmatrix}$	$\begin{pmatrix}1 & 3\\ 2 & 4\end{pmatrix}$	$\begin{vmatrix}1 & 2\\ 3 & 4\end{vmatrix}=1\times4-2\times3=-2$

MB5.2 Matrix addition and multiplication

Two matrices $\boldsymbol{M}$ and $\boldsymbol{N}$ may be added to give the sum $\boldsymbol{S}=\boldsymbol{M}+\boldsymbol{N}$, according to the rule

$$S_{rc}=M_{rc}+N_{rc} \qquad \text{Matrix addition} \quad \text{(MB5.4)}$$

That is, corresponding elements are added. Two matrices may also be multiplied to give the product $\boldsymbol{P}=\boldsymbol{MN}$ according to the rule

$$P_{rc}=\sum_n M_{rn}N_{nc} \qquad \text{Matrix multiplication} \quad \text{(MB5.5)}$$

These procedures are illustrated in Fig. MB5.1. It should be noticed that in general $\boldsymbol{MN}\neq\boldsymbol{NM}$, and matrix multiplication is in general non-commutative (that is, it depends on the order of multiplication).

Brief illustration MB5.2 Matrix addition and multiplication

Consider the matrices

$$\boldsymbol{M}=\begin{pmatrix}1 & 2\\ 3 & 4\end{pmatrix} \quad \text{and} \quad \boldsymbol{N}=\begin{pmatrix}5 & 6\\ 7 & 8\end{pmatrix}$$

Their sum is

$$S=\begin{pmatrix}1 & 2\\ 3 & 4\end{pmatrix}+\begin{pmatrix}5 & 6\\ 7 & 8\end{pmatrix}=\begin{pmatrix}6 & 8\\ 10 & 12\end{pmatrix}$$

and their product is

$$P=\begin{pmatrix}1 & 2\\ 3 & 4\end{pmatrix}\begin{pmatrix}5 & 6\\ 7 & 8\end{pmatrix}=\begin{pmatrix}1\times5+2\times7 & 1\times6+2\times8\\ 3\times5+4\times7 & 3\times6+4\times8\end{pmatrix}=\begin{pmatrix}19 & 22\\ 43 & 50\end{pmatrix}$$

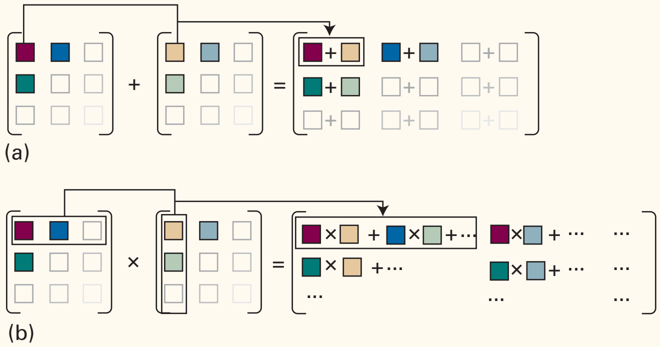


Figure MB5.1 A diagrammatic representation of (a) matrix addition, (b) matrix multiplication.

The **inverse** of a matrix M is denoted M^{-1}, and is defined so that

$$MM^{-1}=M^{-1}M=1 \qquad \text{Inverse} \qquad \text{(MB5.6)}$$

The inverse of a matrix is best constructed by using mathematical software, and the tedious analytical approach is rarely necessary.

Brief illustration MB5.3 Inversion

Mathematical software gives the following inversion of M:

Matrix	Inverse
M	M^{-1}
$\begin{pmatrix}1 & 2\\ 3 & 4\end{pmatrix}$	$\begin{pmatrix}-2 & 1\\ \frac{3}{2} & -\frac{1}{2}\end{pmatrix}$

MB5.3 Eigenvalue equations

An **eigenvalue equation** is an equation of the form

$$Mx=\lambda x \qquad \text{Eigenvalue equation} \qquad \text{(MB5.7a)}$$

where M is a square matrix with n rows and n columns, λ is a constant, the **eigenvalue**, and x is the **eigenvector**, an $n\times1$ (column) matrix that satisfies the conditions of the eigenvalue equation and has the form:

$$x=\begin{pmatrix}x_1\\ x_2\\ \vdots\\ x_n\end{pmatrix}$$

In general, there are n eigenvalues $\lambda^{(i)}$, $i=1, 2, \ldots, n$, and n corresponding eigenvectors $x^{(i)}$. We write eqn MB5.7a as (noting that $1x=x$)

$$(M-\lambda 1)x=0 \qquad \text{(MB5.7b)}$$

Equation MB5.7b has a solution only if the determinant $|M-\lambda 1|$ of the coefficients of the matrix $M-\lambda 1$ is zero. It follows that the n eigenvalues may be found from the solution of the **secular equation**:

$$|M-\lambda 1|=0 \qquad \text{(MB5.8)}$$

If the inverse of the matrix $M-\lambda 1$ exists, then, from eqn MB5.7b, $(M-\lambda 1)^{-1}(M-\lambda 1)x=x=0$, a trivial solution. For a nontrivial solution, $(M-\lambda 1)^{-1}$ must not exist, which is the case if eqn MB5.8 holds.

Brief illustration MB5.4 Simultaneous equations

Once again we use the matrix M in *Brief illustration* MB5.1, and write eqn MB5.7 as

$$\begin{pmatrix}1 & 2\\ 3 & 4\end{pmatrix}\begin{pmatrix}x_1\\ x_2\end{pmatrix}=\lambda\begin{pmatrix}x_1\\ x_2\end{pmatrix} \text{ rearranged into } \begin{pmatrix}1-\lambda & 2\\ 3 & 4-\lambda\end{pmatrix}\begin{pmatrix}x_1\\ x_2\end{pmatrix}=0$$

From the rules of matrix multiplication, the latter form expands into

$$\begin{pmatrix}(1-\lambda)x_1+2x_2\\ 3x_1+(4-\lambda)x_2\end{pmatrix}=0$$

which is simply a statement of the two simultaneous equations

$$(1-\lambda)x_1+2x_2=0 \quad \text{and} \quad 3x_1+(4-\lambda)x_2=0$$

The condition for these two equations to have solutions is

$$|M-\lambda 1|=\begin{vmatrix}1-\lambda & 2\\ 3 & 4-\lambda\end{vmatrix}=(1-\lambda)(4-\lambda)-6=0$$

This condition corresponds to the quadratic equation

$$\lambda^2-5\lambda-2=0$$

with solutions $\lambda=+5.372$ and $\lambda=-0.372$, the two eigenvalues of the original equation.

The n eigenvalues found by solving the secular equations are used to find the corresponding eigenvectors. To do so, we begin by considering an $n\times n$ matrix X which will be formed from the eigenvectors corresponding to all the eigenvalues. Thus, if the eigenvalues are λ_1, λ_2, … and the corresponding eigenvectors are

$$\boldsymbol{x}^{(1)}=\begin{pmatrix}x_1^{(1)}\\x_2^{(1)}\\\vdots\\x_n^{(1)}\end{pmatrix}\quad \boldsymbol{x}^{(2)}=\begin{pmatrix}x_1^{(2)}\\x_2^{(2)}\\\vdots\\x_n^{(2)}\end{pmatrix}\quad\cdots\ \boldsymbol{x}^{(n)}=\begin{pmatrix}x_1^{(n)}\\x_2^{(n)}\\\vdots\\x_n^{(n)}\end{pmatrix} \tag{MB5.9a}$$

the matrix X is

$$\boldsymbol{X}=(\boldsymbol{x}^{(1)}\ \boldsymbol{x}^{(2)}\cdots\boldsymbol{x}^{(n)})=\begin{pmatrix}x_1^{(1)}&x_1^{(2)}&\cdots&x_1^{(n)}\\x_2^{(1)}&x_2^{(2)}&\cdots&x_2^{(n)}\\\vdots&\vdots&&\vdots\\x_n^{(1)}&x_n^{(2)}&\cdots&x_n^{(n)}\end{pmatrix} \tag{MB5.9b}$$

Similarly, we form an $n\times n$ matrix $\boldsymbol{\Lambda}$ with the eigenvalues λ along the diagonal and zeroes elsewhere:

$$\boldsymbol{\Lambda}=\begin{pmatrix}\lambda_1&0&\cdots&0\\0&\lambda_2&\cdots&0\\\vdots&\vdots&&\vdots\\0&0&\cdots&\lambda_n\end{pmatrix} \tag{MB5.10}$$

Now all the eigenvalue equations $\boldsymbol{M}x^{(i)}=\lambda_i x^{(i)}$ may be combined into the single matrix equation

$$\boldsymbol{MX}=\boldsymbol{X\Lambda} \tag{MB5.11}$$

Brief illustration MB5.5 Eigenvalue equations

In *Brief illustration* MB5.4 we established that if $\boldsymbol{M}=\begin{pmatrix}1&2\\3&4\end{pmatrix}$ then $\lambda_1=+5.372$ and $\lambda_2=-0.372$, with eigenvectors $\boldsymbol{x}^{(1)}=\begin{pmatrix}x_1^{(1)}\\x_2^{(1)}\end{pmatrix}$ and $\boldsymbol{x}^{(2)}=\begin{pmatrix}x_1^{(2)}\\x_2^{(2)}\end{pmatrix}$. We form

$$\boldsymbol{X}=\begin{pmatrix}x_1^{(1)}&x_1^{(2)}\\x_2^{(1)}&x_2^{(2)}\end{pmatrix}\qquad \boldsymbol{\Lambda}=\begin{pmatrix}5.372&0\\0&-0.372\end{pmatrix}$$

The expression $\boldsymbol{MX}=\boldsymbol{X\Lambda}$ becomes

$$\begin{pmatrix}1&2\\3&4\end{pmatrix}\begin{pmatrix}x_1^{(1)}&x_1^{(2)}\\x_2^{(1)}&x_2^{(2)}\end{pmatrix}=\begin{pmatrix}x_1^{(1)}&x_1^{(2)}\\x_2^{(1)}&x_2^{(2)}\end{pmatrix}\begin{pmatrix}5.372&0\\0&-0.372\end{pmatrix}$$

which expands to

$$\begin{pmatrix}x_1^{(1)}+2x_2^{(1)}&x_1^{(2)}+2x_2^{(2)}\\3x_1^{(1)}+4x_2^{(1)}&3x_1^{(2)}+4x_2^{(2)}\end{pmatrix}=\begin{pmatrix}5.372x_1^{(1)}&-0.372x_1^{(2)}\\5.372x_2^{(1)}&-0.372x_2^{(2)}\end{pmatrix}$$

This is a compact way of writing the four equations

$$\begin{aligned}x_1^{(1)}+2x_2^{(1)}&=5.372x_1^{(1)} & x_1^{(2)}+2x_2^{(2)}&=-0.372x_1^{(2)}\\3x_1^{(1)}+4x_2^{(1)}&=5.372x_2^{(1)} & 3x_1^{(2)}+4x_2^{(2)}&=-0.372x_2^{(2)}\end{aligned}$$

corresponding to the two original simultaneous equations and their two roots.

Finally, we form X^{-1} from X and multiply eqn MB5.11 by it from the left:

$$\boldsymbol{X}^{-1}\boldsymbol{MX}=\boldsymbol{X}^{-1}\boldsymbol{X\Lambda}=\boldsymbol{\Lambda} \tag{MB5.12}$$

A structure of the form $X^{-1}MX$ is called a **similarity transformation**. In this case the similarity transformation $X^{-1}MX$ makes M diagonal (because $\boldsymbol{\Lambda}$ is diagonal). It follows that if the matrix X that causes $X^{-1}MX$ to be diagonal is known, then the problem is solved: the diagonal matrix so produced has the eigenvalues as its only nonzero elements, and the matrix X used to bring about the transformation has the corresponding eigenvectors as its columns. As will be appreciated once again, the solutions of eigenvalue equations are best found by using mathematical software.

Brief illustration MB5.6 Similarity transformation

To apply the similarity transformation, eqn MB5.12, to the matrix $\begin{pmatrix}1&2\\3&4\end{pmatrix}$ from *Brief illustration* MB5.1 it is best to use mathematical software to find the form of X. The result is

$$\boldsymbol{X}=\begin{pmatrix}0.416&0.825\\0.909&-0.566\end{pmatrix}\qquad \boldsymbol{X}^{-1}=\begin{pmatrix}0.574&0.837\\0.922&-0.422\end{pmatrix}$$

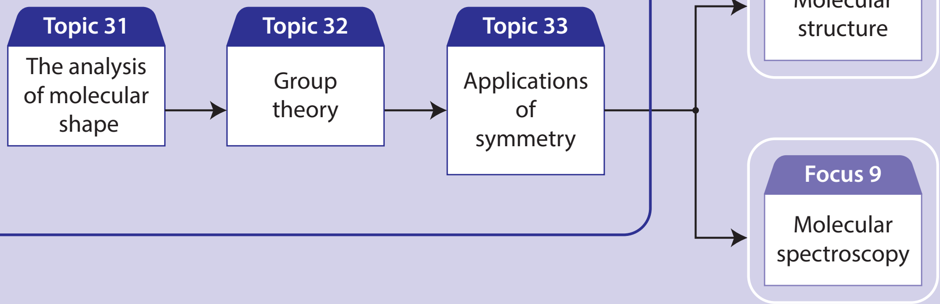
This result can be verified by carrying out the multiplication

$$\begin{aligned}\boldsymbol{X}^{-1}\boldsymbol{MX}&=\begin{pmatrix}0.574&0.837\\0.922&-0.422\end{pmatrix}\begin{pmatrix}1&2\\3&4\end{pmatrix}\begin{pmatrix}0.416&0.825\\0.909&-0.566\end{pmatrix}\\&=\begin{pmatrix}5.372&0\\0&-0.372\end{pmatrix}\end{aligned}$$

The result is indeed the diagonal matrix $\boldsymbol{\Lambda}$ calculated in *Brief illustration* MB5.4. It follows that the eigenvectors $\boldsymbol{x}^{(1)}$ and $\boldsymbol{x}^{(2)}$ are

$$\boldsymbol{x}^{(1)}=\begin{pmatrix}0.416\\0.909\end{pmatrix}\qquad \boldsymbol{x}^{(2)}=\begin{pmatrix}0.825\\-0.566\end{pmatrix}$$

FOCUS 7 ON Molecular symmetry



Many conclusions can be drawn without doing any calculation by taking note of the symmetry of a molecule. Calculations too can be simplified by seeing that the symmetry of a molecule implies that certain terms are necessarily zero. Symmetry arguments are used throughout the discussion of *Molecular structure* and *Molecular spectroscopy*. They are also used in the description of the structures of solids, but here we focus on individual molecules.

The first task is to identify the symmetries of a molecule (**Topic 31**). To do so, we introduce the concepts of 'symmetry operation' and 'symmetry element'. On doing so, we find that molecules can be classified according to the symmetries they possess and put into one of a number of symmetry groups. This classification is the first step in the application of symmetry arguments to molecules. We show that some conclusions about molecular properties (such as the existence of polarity and chirality) can be drawn directly from the group to which the molecule belongs.

The next stage is to realize that the symmetry operations obey the same relations that mathematicians use to define a 'group', and thus the study of symmetry is seen to be a part of 'group theory' (**Topic 32**). The recognition that symmetry is a part of group theory takes on great power when we show that symmetry operations can be represented by numbers (more specifically, matrices, arrays of numbers), for then the study of symmetry becomes quantitative. For most purposes in chemistry, the 'character table' is the most useful, and the concept is introduced in this Topic.

The calculation of molecular properties often depends on the existence of certain integrals: group theory provides powerful ways to conclude when these integrals necessarily vanish (**Topic 33**). It also provides ways to decide which atomic orbitals can contribute to the molecular orbitals discussed in the topics covered in *Molecular structure*.

TOPIC 31

The analysis of molecular shape

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➤ Why do you need to know this material?

Symmetry arguments can be used to make immediate assessments of the properties of molecules, and when expressed quantitatively (Topic 32) can be used to save a great deal of calculation.

➤ What is the key idea?

Molecules can be classified into groups according to their symmetry elements.

➤ What do you need to know already?

This Topic does not draw on others directly, but it will be useful to be aware of the shapes of a variety of simple molecules and ions encountered in introductory chemistry courses.

Some objects are 'more symmetrical' than others. A sphere is more symmetrical than a cube because it looks the same after it has been rotated through any angle about any diameter. A cube looks the same only if it is rotated through certain angles about specific axes, such as 90°, 180°, or 270° about an axis passing through the centres of any of its opposite faces (Fig. 31.1), or by 120° or 240° about an axis passing through any of its opposite corners. Similarly, an NH_3 molecule is 'more symmetrical' than an H_2O molecule because NH_3 looks the same after rotations of 120° or 240° about the axis shown in Fig. 31.2, whereas H_2O looks the same only after a rotation of 180°.

This Topic puts these intuitive notions on a more formal foundation. In it, we see that molecules can be grouped together according to their symmetry, with the tetrahedral species CH_4 and SO_4^{2-} in one group and the pyramidal species

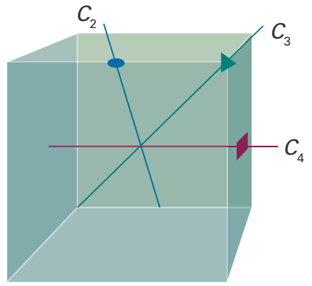


Figure 31.1 Some of the symmetry elements of a cube. The twofold, threefold, and fourfold axes are labelled with the conventional symbols.

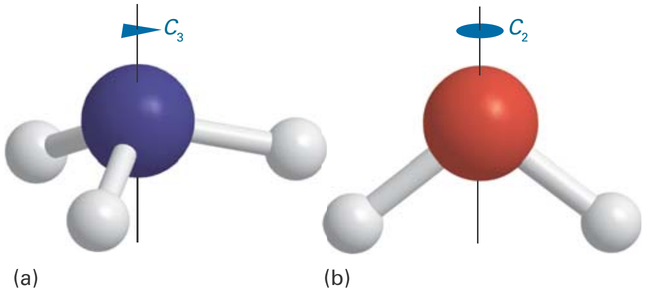


Figure 31.2 (a) An NH_3 molecule has a threefold (C_3) axis and (b) an H_2O molecule has a twofold (C_2) axis. Both have other symmetry elements too.

NH_3 and SO_3^{2-} in another. It turns out that molecules in the same group share certain physical properties, so powerful predictions can be made about whole series of molecules once we know the group to which they belong.

We have slipped in the term 'group' in its conventional sense. In fact, a group in mathematics has a precise formal significance and considerable power and gives rise to the name 'group theory' for the quantitative study of symmetry. This power is revealed in Topics 32 and 33.

31.1 Symmetry operations and symmetry elements

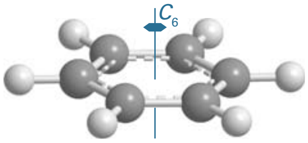
An action that leaves an object looking the same after it has been carried out is called a **symmetry operation**. Typical symmetry operations include rotations, reflections, and inversions. There is a corresponding **symmetry element** for each symmetry operation, which is the point, line, or plane with respect to which the symmetry operation is performed. For instance, a rotation (a symmetry operation) is carried out around an axis (the corresponding symmetry element). We shall see that we can classify molecules by identifying all their symmetry elements and grouping together molecules that possess the same set of symmetry elements. This procedure, for example, puts the trigonal pyramidal species NH_3 and SO_3^{2-} into one group and the angular species H_2O and SO_2 into another group.

In the following paragraphs we describe the operations and the corresponding elements; for convenience, they are collected in Table 31.1.

An ***n*-fold rotation** (the operation) about an ***n*-fold axis of symmetry**, C_n (the corresponding element), is a rotation through 360°/n. An H_2O molecule has one twofold axis, C_2. An NH_3 molecule has one threefold axis, C_3, with which is associated two symmetry operations, one being 120° rotation in a clockwise sense and the other 120° rotation in an anticlockwise sense. There is only one twofold rotation associated with a C_2 axis because clockwise and anticlockwise 180° rotations are identical. A pentagon has a C_5 axis, with two rotations (one clockwise, the other anticlockwise) through 72° associated with it. It also has an axis denoted C_5^2, corresponding to two successive C_5 rotations; there are two such operations, one through 144° in a clockwise sense and the other through 144° in an anticlockwise sense. A cube has three C_4 axes, four C_3 axes, and six C_2 axes. However, even this high symmetry is exceeded by a sphere, which possesses an infinite number of symmetry axes (along any diameter) of all possible integral values of n. If a molecule possesses several rotation axes, then the one (or more) with the greatest value of n is called the **principal axis**. The principal axis of a benzene molecule is the sixfold axis perpendicular to the hexagonal ring (**1**).

Table 31.1 Symmetry operations and symmetry elements

Symmetry operation	Symbol	Symmetry element
n-fold rotation	C_n	n-fold axis of rotation
Reflection	σ	Mirror plane
Inversion	i	Centre of symmetry
n-fold improper rotation	S_n	n-fold improper rotation axis
Identity	E	Entire object



1 Benzene, C_6H_6

A **reflection** (the operation) in a **mirror plane**, σ (the element), may contain the principal axis of a molecule or be perpendicular to it. If the plane contains the principal axis, it is called 'vertical' and denoted σ_v. An H_2O molecule has two vertical planes of symmetry (Fig. 31.3) and an NH_3 molecule has three. A vertical mirror plane that bisects the angle between two C_2 axes is called a 'dihedral plane' and is denoted σ_d (Fig. 31.4). When the plane of symmetry is perpendicular to the principal axis it is called 'horizontal' and denoted σ_h. A C_6H_6 molecule has a C_6 principal axis and a horizontal mirror plane (as well as several other symmetry elements).

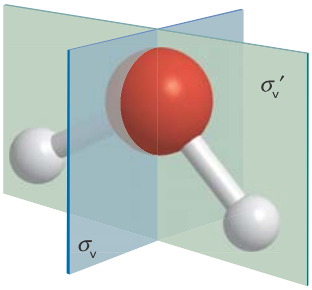


Figure 31.3 An H_2O molecule has two mirror planes. They are both vertical (that is, contain the principal axis), so are denoted σ_v and σ_v'.

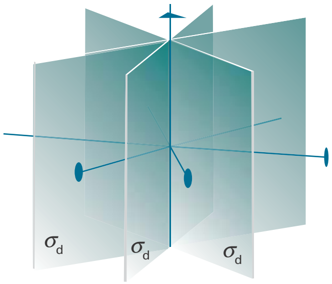


Figure 31.4 Dihedral mirror planes (σ_d) bisect the C_2 axes perpendicular to the principal axis.

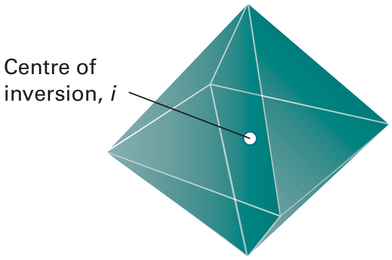


Figure 31.5 A regular octahedron has a centre of inversion (i).

In an **inversion** (the operation) through a **centre of symmetry**, i (the element), we imagine taking each point in a molecule, moving it to the centre of the molecule, and then moving it out the same distance on the other side; that is, the point (x, y, z) is taken into the point ($-x$, $-y$, $-z$). Neither an H_2O molecule nor an NH_3 molecule has a centre of inversion, but a sphere and a cube do have one. A C_6H_6 molecule does have a centre of inversion, and so does a regular octahedron (Fig. 31.5); a regular tetrahedron and a CH_4 molecule do not.

An ***n*-fold improper rotation** (the operation) about an ***n*-fold axis of improper rotation** or an ***n*-fold improper rotation axis**, S_n (the symmetry element), is composed of two successive transformations. The first component is a rotation through 360°/n, and the second is a reflection through a plane perpendicular to the axis of that rotation. A CH_4 molecule has three S_4 axes (Fig. 31.6).

The **identity**, E, consists of doing nothing; the corresponding symmetry element is the entire object. Because every molecule is indistinguishable from itself if nothing is done to it, every object possesses at least the identity element. One reason for including the identity is that some molecules have only this symmetry element (**2**).

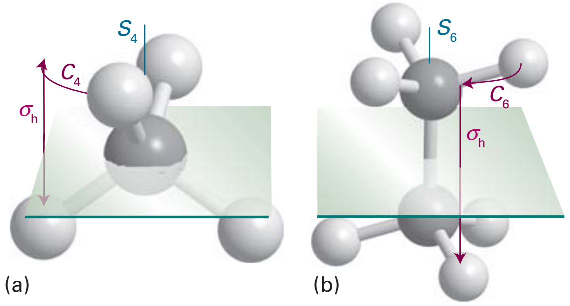
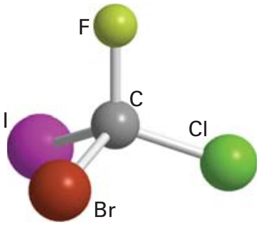


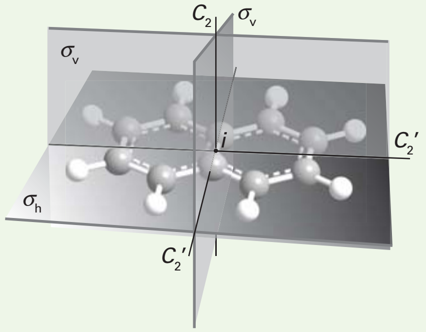
Figure 31.6 (a) A CH_4 molecule has a fourfold improper rotation axis (S_4): the molecule is indistinguishable after a 90° rotation followed by a reflection across the horizontal plane, but neither operation alone is a symmetry operation. (b) The staggered form of ethane has an S_6 axis composed of a 60° rotation followed by a reflection.



2 CBrClFI

Brief illustration 31.1 Symmetry elements

To identify the symmetry elements of a naphthalene molecule (**3**) we first note that, like all molecules, it has the identity element, E. There is one twofold axis of rotation, C_2, perpendicular to the plane and two others, C_2', lying in the plane. There is a mirror plane in the plane of the molecule, σ_h, and two perpendicular planes, σ_v, containing the C_2 rotation axis. There is also a centre of inversion, i, at the midpoint of the molecule. Note that some of these elements are implied by others: the centre of inversion, for instance, is implied by the joint presence of a σ_v plane and a C_2' axis.



3 Naphthalene, $C_{10}H_8$

Self-test 31.1 Identify the symmetry elements of an SF_6 molecule.

Answer: E, $3S_4$, $3C_4$, $6C_2$, $4S_6$, $4C_3$, $3\sigma_h$, $6\sigma_d$, i

31.2 The symmetry classification of molecules

The classification of objects according to symmetry elements corresponding to operations that leave at least one common point unchanged gives rise to the **point groups**. There are five kinds of symmetry operation (and five kinds of symmetry element) of this kind (see Table 31.1). When we consider crystals (Topic 37), we meet symmetries arising from translation

Table 31.2 The notation for point groups

C_i	$\bar{1}$										
C_s	m										
C_1	1	C_2	2	C_3	3	C_4	4	C_6	6		
		C_{2v}	$2mm$	C_{3v}	$3m$	C_{4v}	$4mm$	C_{6v}	$6mm$		
		C_{2h}	$2/m$	C_{3h}	$\bar{6}$	C_{4h}	$4/m$	C_{6h}	$6/m$		
		D_2	222	D_3	32	D_4	422	D_6	622		
		D_{2h}	mmm	D_{3h}	$\bar{6}2m$	D_{4h}	$4/mmm$	D_{6h}	$6/mmm$		
		D_{2d}	$\bar{4}2m$	D_{3d}	$\bar{3}m$	S_4	$\bar{4}/m$	S_6	$\bar{3}$		
T	23	T_d	$\bar{4}3m$	T_h	$m3$						
O	432	O_h	$m3m$								

In the International system (or Hermann–Mauguin system) for point groups, a number *n* denotes the presence of an *n*-fold axis and *m* denotes a mirror plane. A slash (/) indicates that the mirror plane is perpendicular to the symmetry axis. It is important to distinguish symmetry elements of the same type but of different classes, as in 4/*mmm*, in which there are three classes of mirror plane. A bar over a number indicates that the element is combined with an inversion. The only groups listed here are the so-called 'crystallographic point groups'.

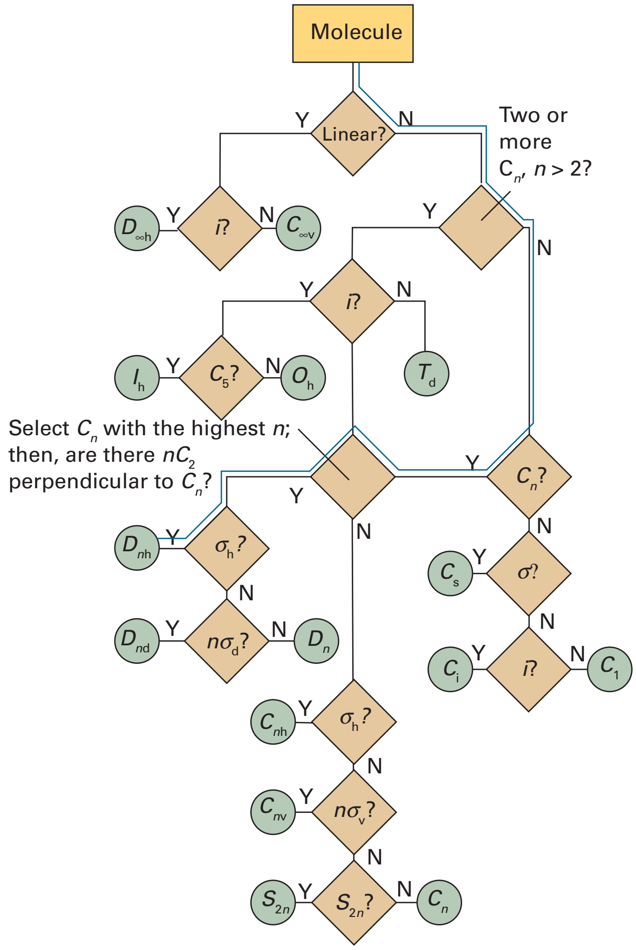


Figure 31.7 A flow diagram for determining the point group of a molecule. Start at the top and answer the question posed in each diamond (Y = yes, N = no).

through space. These more extensive groups are called **space groups**.

To classify molecules according to their symmetries, we list their symmetry elements and collect together molecules with the same list of elements. The name of the group to which a molecule belongs is determined by the symmetry elements it possesses. There are two systems of notation (Table 31.2). The **Schoenflies system** (in which a name looks like C_{4v}) is more common for the discussion of individual molecules, and the **Hermann–Mauguin system** or **International system** (in which a name looks like 4*mm*) is used almost exclusively in the discussion of crystal symmetry. The identification of a molecule's point group according to the Schoenflies system is simplified by referring to the flow diagram in Fig. 31.7 and the shapes shown in Fig. 31.8.

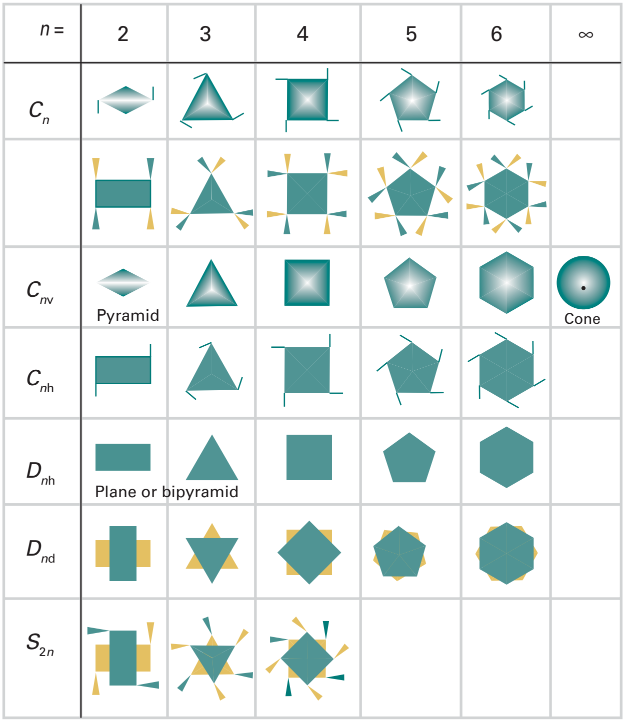
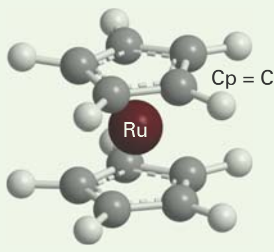


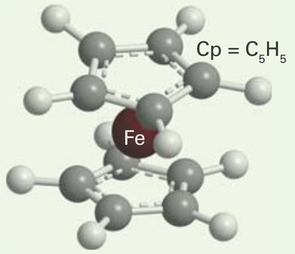
Figure 31.8 A summary of the shapes corresponding to different point groups. The group to which a molecule belongs can often be identified from this diagram without going through the formal procedure in Fig. 31.7.

Brief illustration 31.2 Symmetry classification

To identify the point group to which a ruthenocene molecule (**4**) belongs we use the flow diagram in Fig. 31.7. The path to trace is shown by a blue line; it ends at D_{nh}. Because the molecule has a fivefold axis, it belongs to the group D_{5h}. If the rings were staggered, as they are in an excited state of ferrocene that lies 4 kJ mol^{-1} above the ground state (**5**), the horizontal reflection plane would be absent, but dihedral planes would be present.



4 Ruthenocene, $Ru(Cp)_2$



5 Ferrocene, $Fe(Cp)_2$ (excited state)

Self-test 31.2 Classify the pentagonal antiprismatic excited state of ferrocene (**5**).

Answer: D_{5d}

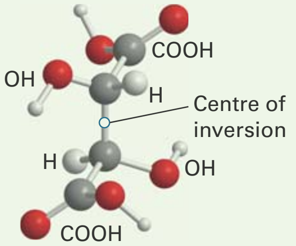
(a) The groups C_1, C_i, and C_s

A molecule belongs to the group C_1 if it has no element other than the identity. It belongs to C_i if it has the identity and the inversion alone, and to C_s if it has the identity and a mirror plane alone.

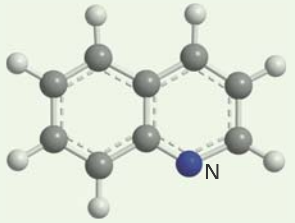
Name	Elements
C_1	E
C_i	E, i
C_s	E, σ

Brief illustration 31.3 C_1, C_i, and C_s

The CBrClFI molecule (**2**) has only the identity element, and so belongs to the group C_1. *meso*-Tartaric acid (**6**) has the identity and inversion elements, and so belongs to the group C_i. Quinoline (**7**) has the elements (E, σ), and so belongs to the group C_s.



6 Meso-tartaric acid, HOOCCH(OH)CH(OH)COOH



7 Quinoline, C_9H_7N

Self-test 31.3 Identify the group to which the molecule (**8**) belongs.

8

Answer: C_{2v}

(b) The groups C_n, C_{nv}, and C_{nh}

A molecule belongs to the group C_n if it possesses an n-fold axis. Note that symbol C_n is now playing a triple role: as the label of a symmetry element, a symmetry operation, and a group. If in addition to the identity and a C_n axis a molecule has n vertical mirror planes σ_v, then it belongs to the group C_{nv}. Objects that in addition to the identity and an n-fold principal axis also have a horizontal mirror plane σ_h belong to the group C_{nh}. The presence of certain symmetry elements may be implied by the presence of others: thus, in C_{2h} the elements C_2 and σ_h jointly imply the presence of a centre of inversion (Fig. 31.9).

Name	Elements
C_n	E, C_n
C_{nv}	$E, C_n, n\sigma_v$
C_{nh}	E, C_n, σ_h

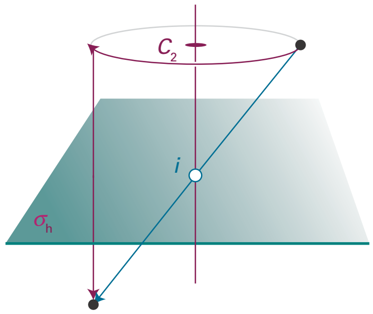
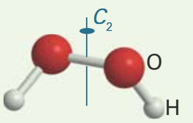


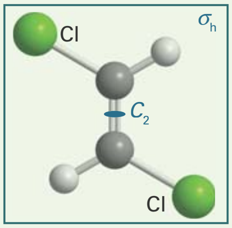
Figure 31.9 The presence of a twofold axis and a horizontal mirror plane jointly imply the presence of a centre of inversion in the molecule.

Brief illustration 31.4 C_n, C_{nv}, and C_{nh}

An H_2O_2 molecule (**9**) has the symmetry elements E and C_2, so it belongs to the group C_2. An H_2O molecule has the symmetry elements E, C_2, and $2\sigma_v$, so it belongs to the group C_{2v}. An NH_3 molecule has the elements E, C_3, and $3\sigma_v$, so it belongs to the group C_{3v}. A heteronuclear diatomic molecule such as HCl belongs to the group $C_{\infty v}$ because rotations around the axis by any angle and reflections in all the infinite number of planes that contain the axis are symmetry operations. Other members of the group $C_{\infty v}$ include the linear OCS molecule and a cone. The molecule *trans*-CHCl=CHCl (**10**) has the elements E, C_2, and σ_h, so belongs to the group C_{2h}.

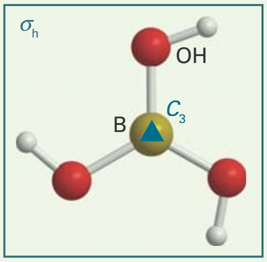


9 Hydrogen peroxide, H_2O_2



10 *trans*-CHCl=CHCl

Self-test 31.4 Identify the group to which the molecule $B(OH)_3$ in the conformation shown in (**11**) belongs.



11 $B(OH)_3$

Answer: C_{3h}

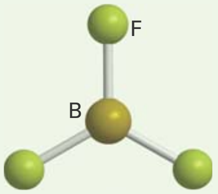
(c) The groups D_n, D_{nh}, and D_{nd}

We see from Fig. 31.7 that a molecule that has an n-fold principal axis and n twofold axes perpendicular to C_n belongs to the group D_n. A molecule belongs to D_{nh} if it also possesses a horizontal mirror plane. $D_{\infty h}$ is also the group of the linear OCO and HCCH molecules and of a uniform cylinder. A molecule belongs to the group D_{nd} if in addition to the elements of D_n it possesses n dihedral mirror planes σ_d.

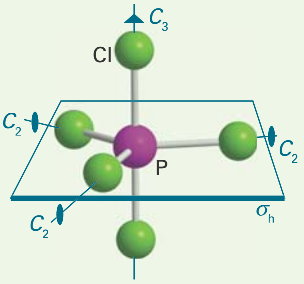
Name	Elements
D_n	E, C_n, nC_2'
D_{nh}	E, C_n, nC_2', σ_h
D_{nd}	$E, C_n, nC_2', n\sigma_d$

Brief illustration 31.5 D_n, D_{nh}, and D_{nd}

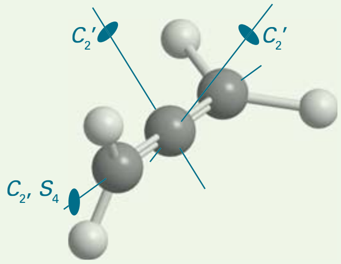
The planar trigonal BF_3 molecule has the elements E, C_3, $3C_2$, and σ_h (with one C_2 axis along each B–F bond), so it belongs to D_{3h} (**12**). The C_6H_6 molecule has the elements E, C_6, $3C_2$, $3C_2'$, and σ_h together with some others that these elements imply, so it belongs to D_{6h}. Three of the C_2 axes bisect C–C bonds and the other three pass through vertices of the hexagon formed by the carbon framework of the molecule, and the prime on $3C_2'$ indicates that the three C_2 axes are different from the other three C_2 axes. All homonuclear diatomic molecules, such as N_2, belong to the group $D_{\infty h}$ because all rotations around the axis are symmetry operations, as are end-to-end rotation and end-to-end reflection. Another example of a D_{nh} species is (**13**). The twisted, 90° allene (**14**) belongs to D_{2d}.



12 Boron trifluoride, BF_3

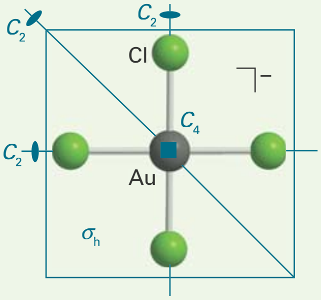


13 Phosphorus pentachloride, PCl_5 (D_{3h})

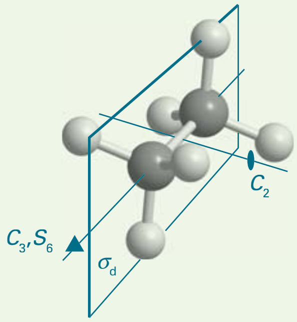


14 Allene, C_3H_4 (D_{2d})

Self-test 31.5 Identify the groups to which (a) the tetrachloridoaurate(III) ion (**15**) and (b) the staggered conformation of ethane (**16**) belong.



15 Tetrachloridoaurate(III) ion, $[AuCl_4]^-$



16 Ethane, C_2H_6

Answer: (a) D_{4h}, (b) D_{3d}

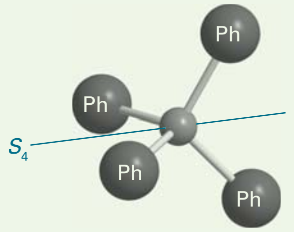
(d) The group S_n

Molecules that have not been classified into one of the groups mentioned so far, but which possess one S_n axis, belong to the group S_n. Note that the group S_2 is the same as C_i, so such a molecule will already have been classified as C_i.

Name	Elements
S_n	E, S_n, and groups not previously classified

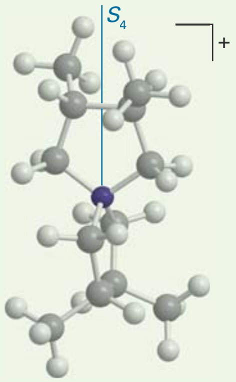
Brief illustration 31.6 S_n

Tetraphenylmethane belongs to the point group S_4 (**17**). Molecules belonging to S_n with $n>4$ are rare.



17 Tetraphenylmethane, $C(C_6H_5)_4$ (S_4)

Self-test 31.6 Identify the group to which the ion in (**18**) belongs.



18 $N(CH_2CH(CH_3)CH(CH_3)CH_2)_2^+$

Answer: S_4

(e) The cubic groups

A number of very important molecules possess more than one principal axis. Most belong to the **cubic groups** and in particular to the **tetrahedral groups** T, T_d, and T_h (Fig. 31.10a) or to the **octahedral groups** O and O_h (Fig. 31.10b). A few icosahedral (20-faced) molecules belonging to the **icosahedral group**, I (Fig. 31.10c), are also known. The groups T_d and O_h are the groups of the regular tetrahedron and the regular octahedron, respectively. If the object possesses the rotational symmetry of the tetrahedron or the octahedron, but none of their planes of reflection, then it belongs to the simpler groups T or O (Fig. 31.11). The group T_h is based on T but also contains a centre of inversion (Fig. 31.12).

Name	Elements
T	$E, 4C_3, 3C_2$
T_d	$E, 3C_2, 4C_3, 3S_4, 6\sigma_d$
T_h	$E, 3C_2, 4C_3, i, 4S_6, 3\sigma_h$
O	$E, 3C_4, 4C_3, 6C_2$
O_h	$E, 3S_4, 3C_4, 6C_2, 4S_6, 4C_3, 3\sigma_h, 6\sigma_d, i$
I	$E, 6C_5, 10C_3, 15C_2$
I_h	$E, 6S_{10}, 10S_6, 6C_5, 10C_3, 15C_2, 15\sigma, i$

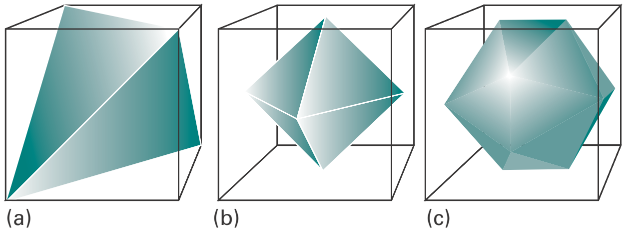


Figure 31.10 (a) Tetrahedral, (b) octahedral, and (c) icosahedral molecules are drawn in a way that shows their relation to a cube: they belong to the cubic groups T_d, O_h, and I_h, respectively.

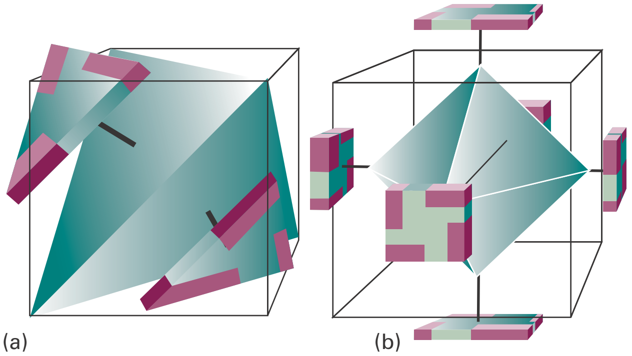


Figure 31.11 Shapes corresponding to the point groups (a) T and (b) O. The presence of the decorated slabs reduces the symmetry of the object from T_d and O_h, respectively.

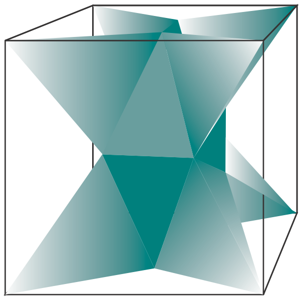
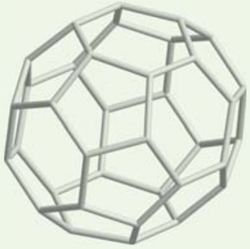


Figure 31.12 The shape of an object belonging to the group T_h.

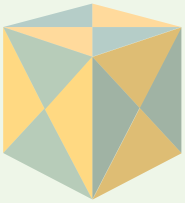
Brief illustration 31.7 The cubic groups

The molecules CH_4 and SF_6 belong, respectively, to the groups T_d and O_h. Molecules belonging to the icosahedral group I include some of the boranes and buckminsterfullerene, C_{60} (**19**). The shapes shown in Fig. 31.11 belong to the groups T and O, respectively.



19 Buckminsterfullerene, C_{60} (I)

Self-test 31.7 Identify the group to which the object shown in **20** belongs.



20

Answer: T_h

(f) The full rotation group

The **full rotation group**, R_3 (the 3 refers to rotation in three dimensions), consists of an infinite number of rotation axes with all possible values of n. A sphere and an atom belong to R_3, but no molecule does. Exploring the consequences of R_3 is a very important way of applying symmetry arguments to atoms, and is an alternative approach to the theory of orbital angular momentum.

Name	Elements
R_3	$E, \infty C_2, \infty C_3, \ldots$

31.3 Some immediate consequences of symmetry

Some statements about the properties of a molecule can be made as soon as its point group has been identified.

(a) Polarity

A **polar molecule** is one with a permanent electric dipole moment (HCl, O_3, and NH_3 are examples). If the molecule belongs to the group C_n with $n > 1$, it cannot possess a charge distribution with a dipole moment perpendicular to the symmetry axis because the symmetry of the molecule implies that any dipole that exists in one direction perpendicular to the axis is cancelled by an opposing dipole (Fig. 31.13a). For example, the perpendicular component of the dipole associated with one O–H bond in H_2O is cancelled by an equal but opposite component of the dipole of the second O–H bond, so any dipole that the molecule has must be parallel to the twofold symmetry axis. However, as the group makes no reference to operations relating the two ends of the molecule, a charge distribution may exist that results in a dipole along the axis (Fig. 31.13b), and H_2O has a dipole moment parallel to its twofold symmetry axis.

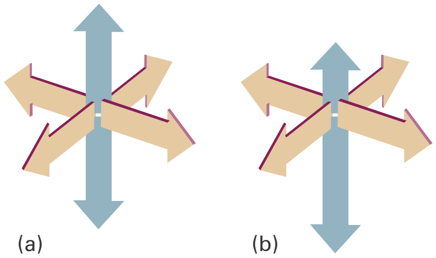


Figure 31.13 (a) A molecule with a C_n axis cannot have a dipole perpendicular to the axis, but (b) it may have one parallel to the axis. The arrows represent local contributions to the overall electric dipole, such as may arise from bonds between pairs of neighbouring atoms with different electronegativities.

The same remarks apply generally to the group C_{nv}, so molecules belonging to any of the C_{nv} groups may be polar. In all the other groups, such as C_{3h}, D, etc., there are symmetry operations that take one end of the molecule into the other. Therefore, as well as having no dipole perpendicular to the axis, such molecules can have none along the axis, for otherwise these additional operations would not be symmetry operations. We can conclude that *only molecules belonging to the groups C_n, C_{nv}, and C_s may have a permanent electric dipole moment.* For C_n and C_{nv}, that dipole moment must lie along the symmetry axis.

Brief illustration 31.8 Polar molecules

Ozone, O_3, which is angular and belongs to the group C_{2v}, may be polar (and is), but carbon dioxide, CO_2, which is linear and belongs to the group $D_{\infty h}$, is not.

Self-test 31.8 Is tetraphenylmethane polar?

Answer: No (S_4)

(b) Chirality

A **chiral molecule** (from the Greek word for 'hand') is a molecule that cannot be superimposed on its mirror image. An **achiral molecule** is a molecule that can be superimposed on its mirror image. Chiral molecules are **optically active** in the sense that they rotate the plane of polarized light. A chiral molecule

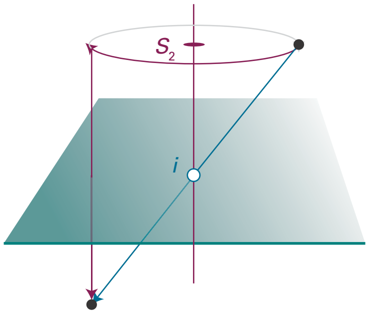


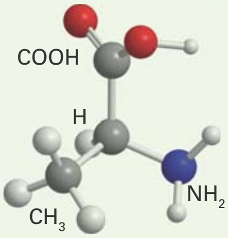
Figure 31.14 Some symmetry elements are implied by the other symmetry elements in a group. Any molecule containing an inversion also possesses at least an S_2 element because i and S_2 are equivalent.

and its mirror-image partner constitute an **enantiomeric pair** of isomers and rotate the plane of polarization in equal but opposite directions.

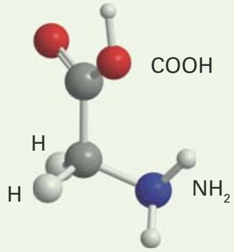
A *molecule may be chiral, and therefore optically active, only if it does not possess an axis of improper rotation*, S_n. We need to be aware that an S_n improper rotation axis may be present under a different name, and be implied by other symmetry elements that are present. For example, molecules belonging to the groups C_{nh} possess an S_n axis implicitly because they possess both C_n and σ_h, which are the two components of an improper rotation axis. Any molecule containing a centre of inversion, i, also possesses an S_2 axis, because i is equivalent to C_2 in conjunction with σ_h, and that combination of elements is S_2 (Fig. 31.14). It follows that all molecules with centres of inversion are achiral and hence optically inactive. Similarly, because $S_1 = \sigma$, it follows that any molecule with a mirror plane is achiral.

Brief illustration 31.9 Chiral molecules

A molecule may be chiral if it does not have a centre of inversion or a mirror plane, which is the case with the amino acid alanine (**21**), but not with glycine (**22**). However, a molecule may be achiral even though it does not have a centre of inversion. For example, the S_4 species (**18**) is achiral and optically inactive: though it lacks i (that is, S_2) it does have an S_4 axis.



21 L-Alanine, $NH_2CH(CH_3)COOH$



22 Glycine, NH_2CH_2COOH

Self-test 31.9 Is tetraphenylmethane chiral?

Answer: No (S_4)

Checklist of concepts

☐ 1. A **symmetry operation** is an action that leaves an object looking the same after it has been carried out; see Table 31.1.

☐ 2. A **symmetry element** is a point, line, or plane with respect to which a symmetry operation is performed; see Table 31.1.

☐ 3. The notation for **point groups** commonly used for molecules and solids is summarized in Table 31.2.

☐ 4. To be **polar**, a molecule must belong to C_n, C_{nv}, or C_s (and have no higher symmetry).

☐ 5. A molecule may be **chiral** only if it does not possess an axis of improper rotation, S_n.

TOPIC 32

Group theory

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➤ Why do you need to know this material?

Group theory puts qualitative ideas about symmetry on to a systematic basis that can be applied to a wide variety of calculations; it is used to draw conclusions that might not be immediately obvious and as a result can greatly simplify calculations. It is also the basis of the labelling of atomic and molecular orbitals that is used throughout chemistry.

➤ What is the key idea?

Symmetry operations may be represented by the effect of matrices acting on a basis.

➤ What do you need to know already?

You need to know about the types of symmetry operation and element introduced in Topic 31. This discussion draws heavily on matrix algebra, especially matrix multiplication, as set out in *Mathematical background* 5.

The systematic discussion of symmetry is called **group theory**. Much of group theory is a summary of common sense about the symmetries of objects. However, because group theory is systematic, its rules can be applied in a straightforward, mechanical way. In most cases the theory gives a simple, direct method for arriving at useful conclusions with the minimum of calculation, and this is the aspect we stress here. In some cases, though, they lead to unexpected results.

32.1 The elements of group theory

A **group** in mathematics is a collection of transformations that satisfy four criteria. Thus, if we write the transformations as R, R', … (which we can think of as reflections, rotations, and so on, of the kind introduced in Topic 31), then they form a group if:

1. One of the transformations is the identity (that is: 'do nothing').
2. For every transformation R, the inverse transformation R^{-1} is included in the collection so that the combination RR^{-1} (the transformation R^{-1} followed by R) is equivalent to the identity.
3. The combination RR' (the transformation R' followed by R) is equivalent to a single member of the collection of transformations.
4. The combination $R(R'R'')$, the transformation $(R'R'')$ followed by R, is equivalent to $(RR')R''$, the transformation R'' followed by (RR').

There is one potentially very confusing point that needs to be clarified at the outset. The entities that make up a group are its 'elements'. In chemistry, these elements are almost always symmetry operations. However, as explained in Topic 31, we distinguish 'symmetry operations' from 'symmetry elements', the axes, planes, and so on with respect to which the operation is carried out. Finally, there is a third use of the word 'element', to denote the number lying in a particular location in a matrix. Be very careful to distinguish *element* (of a group), *symmetry element*, and *matrix element*.

Example 32.1 Showing that symmetry operations form a group

Show that the symmetry operations of the group C_{2v} fulfil the criteria for being a group in the mathematical sense.

Method We need to show that combinations of the operations match the criteria set out above. The operations are set out in Topic 31.

Answer Criterion 1 is fulfilled because the collection of symmetry operations includes the identity E. Criterion 2 is fulfilled because in each case the inverse of an operation is the operation itself. Thus two twofold rotations are equivalent to the identity: $C_2C_2 = E$ and likewise for the two reflections and the identity itself. Criterion 3 is fulfilled, because in each case one operation followed by another is the same as one of the four symmetry operations. For instance, a twofold rotation C_2 followed by the reflection σ_v' is the same as the single reflection σ_v (Fig. 32.1). Thus: $\sigma_v' C_2 = \sigma_v$. The following group multiplication table for the point group can be constructed similarly, where the entries are the product symmetry operations RR':

$R\downarrow\ R'\rightarrow$	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

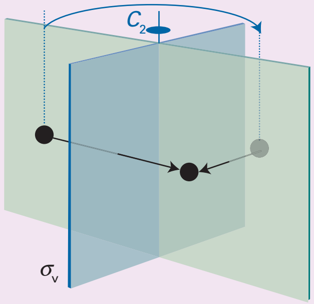


Figure 32.1 A twofold rotation C_2 followed by the reflection σ_v' is the same as the single reflection σ_v.

Criterion 4 is fulfilled, as it is immaterial how the operations are grouped together.

Self-test 32.1 Confirm that the operations of the group C_{3v}, which are illustrated in Fig. 32.2, form a group.

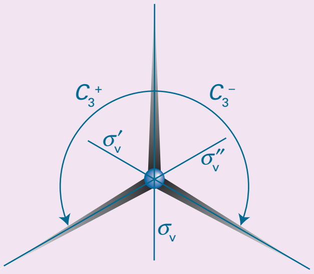


Figure 32.2 The symmetry operations of the group C_{3v}.

Answer: Criteria are fulfilled

Symmetry operations fall into the same **class** if they are of the same type (for example, rotations) and can be transformed into one another by a symmetry operation of the group. The two threefold rotations in C_{3v} (namely C_3^+ and C_3^-) belong to the same class because one can be converted into the other by a reflection (see Fig. 32.2); the three reflections all belong to the same class because each can be rotated into another by a threefold rotation. The formal definition of a class is that two operations R and R' belong to the same class if there is a member S of the group such that

$$R' = S^{-1}RS \qquad \text{Membership of a class} \qquad (32.1)$$

where S^{-1} is the inverse of S.

Brief illustration 32.1 Classes

To show that C_3^+ and C_3^- belong to the same class in C_{3v} (which intuitively we know to be the case), take $S = \sigma_v$. The reciprocal of a reflection is the reflection itself, so $\sigma_v^{-1} = \sigma_v$. It follows that

$$\sigma_v^{-1}C_3^+\sigma_v = \sigma_v C_3^+\sigma_v = \sigma_v\sigma_v' = C_3^-$$

Therefore, C_3^+ and C_3^- are related by an equation of the form of eqn 32.1 and hence belong to the same class.

Self-test 32.2 Show that the two reflections of the group C_{2v} fall into different classes.

32.2 Matrix representations

Group theory takes on great power when the notional ideas presented so far are expressed in terms of collections of numbers in the form of matrices.

(a) Representatives of operations

Consider the set of three p orbitals shown on the C_{2v} SO_2 molecule in Fig. 32.3. Under the reflection operation σ_v, the change $(p_S,p_B,p_A) \leftarrow (p_S,p_A,p_B)$ takes place. We can express this transformation by using matrix multiplication (*Mathematical background* 5):

$$(p_S,p_B,p_A)=(p_S,p_A,p_B)\overbrace{\begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix}}^{\boldsymbol{D}(\sigma_v)}=(p_S,p_A,p_B)\boldsymbol{D}(\sigma_v) \qquad (32.2)$$

The matrix $\boldsymbol{D}(\sigma_v)$ is called a **representative** of the operation σ_v. Representatives take different forms according to the **basis**, the set of orbitals that has been adopted. In this case, the basis is (p_S,p_A,p_B).

Brief illustration 32.2 Representatives

We use the same technique to find matrices that reproduce the other symmetry operations. For instance, C_2 has the effect $(-p_S,-p_B,-p_A) \leftarrow (p_S,p_A,p_B)$, and its representative is

$$\boldsymbol{D}(C_2)=\begin{pmatrix}-1&0&0\\0&0&-1\\0&-1&0\end{pmatrix}$$

The effect of σ'_v is $(-p_S,-p_A,-p_B) \leftarrow (p_S,p_A,p_B)$, and its representative is

$$\boldsymbol{D}(\sigma'_v)=\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&-1\end{pmatrix}$$

The identity operation has no effect on the basis, so its representative is the 3×3 unit matrix:

$$\boldsymbol{D}(E)=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}$$

Self-test 32.3 Find the representative of the C_2 operation of an H_2O molecule for the basis $(H1s_A,H1s_B)$.

Answer: $\boldsymbol{D}(C_2)=\begin{pmatrix}0&1\\1&0\end{pmatrix}$

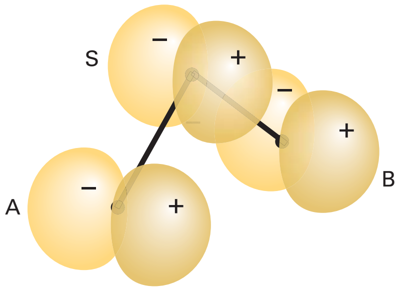


Figure 32.3 The three p_x orbitals that are used to illustrate the construction of a matrix representation in a C_{2v} molecule (SO_2).

(b) The representation of a group

The set of matrices that represents *all* the operations of the group is called a **matrix representation**, Γ (uppercase gamma), of the group for the basis that has been chosen. The **dimensionality** of a representation is the number of rows (or columns) of each of its matrix representatives. An n-dimensional representation is denoted $\Gamma^{(n)}$; The matrices of a representation multiply together in the same way as the operations they represent. Thus, if for any two operations R and R' we know that $RR'=R''$, then $\boldsymbol{D}(R)\boldsymbol{D}(R')=\boldsymbol{D}(R'')$ for a given basis.

Brief illustration 32.3 Matrix representations

In the group C_{2v}, a twofold rotation followed by a reflection in a mirror plane is equivalent to a reflection in the second mirror plane: specifically, $\sigma'_v C_2=\sigma_v$. When we use the representatives specified in *Brief illustration* 32.2, we find

$$\boldsymbol{D}(\sigma'_v)\boldsymbol{D}(C_2)=\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&-1\end{pmatrix}\begin{pmatrix}-1&0&0\\0&0&-1\\0&-1&0\end{pmatrix}$$
$$=\begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix}=\boldsymbol{D}(\sigma_v)$$

This multiplication reproduces the group multiplication. The same is true of all pairs of representative multiplications, so the four matrices form a representation of the group.

Self-test 32.4 Confirm the result that $\sigma_v\sigma'_v=C_2$ by using the matrix representatives developed here.

The discovery of a matrix representation of the group means that we have found a link between symbolic manipulations of operations and algebraic manipulations of numbers.

(c) Irreducible representations

Inspection of the representatives of the group C_{2v} shows that they are all of **block-diagonal form**:

$$\boldsymbol{D}=\begin{pmatrix}\blacksquare & & \\ & \blacksquare & \blacksquare \\ & \blacksquare & \blacksquare\end{pmatrix} \tag{32.3}$$

Block-diagonal form

The block-diagonal form of the representatives shows us that the symmetry operations of C_{2v} never mix p_S with the other two functions. Consequently, the basis can be cut into two parts, one consisting of p_S alone and the other of (p_A,p_B). It is readily verified that the p_S orbital itself is a basis for the one-dimensional representation

$$\boldsymbol{D}(E)=1 \quad \boldsymbol{D}(C_2)=-1 \quad \boldsymbol{D}(\sigma_v)=1 \quad \boldsymbol{D}(\sigma_v')=-1$$

which we shall call $\Gamma^{(1)}$. The remaining two basis functions are a basis for the two-dimensional representation $\Gamma^{(2)}$:

$$\boldsymbol{D}(E)=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} \quad \boldsymbol{D}(C_2)=\begin{pmatrix}0 & -1\\ -1 & 0\end{pmatrix}$$
$$\boldsymbol{D}(\sigma_v)=\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} \quad \boldsymbol{D}(\sigma_v')=\begin{pmatrix}-1 & 0\\ 0 & -1\end{pmatrix}$$

These matrices are the same as those of the original three-dimensional representation, except for the loss of the first row and column. We say that the original three-dimensional representation has been **reduced** to the 'direct sum' of a one-dimensional representation 'spanned' by p_S, and a two-dimensional representation spanned by (p_A,p_B). This reduction is consistent with the common-sense view that the central orbital plays a role different from the other two. We denote the reduction symbolically by writing

$$\Gamma^{(3)}=\Gamma^{(1)}+\Gamma^{(2)} \tag{32.4}$$

Direct sum

The one-dimensional representation $\Gamma^{(1)}$ cannot be reduced any further, and is called an **irreducible representation** of the group (an 'irrep').

Example 32.2 Reducing a representation

Demonstrate that the two-dimensional representation $\Gamma^{(2)}$ is reducible for the basis (p_A,p_B) in the group C_{2v} by switching attention to the linear combinations $p_1=p_A+p_B$ and $p_2=p_A-p_B$. These combinations are sketched in Fig. 32.4.

Method The representatives in the new basis can be constructed from the old by noting, for example, that under σ_v, $(p_B,p_A)\leftarrow(p_A,p_B)$.

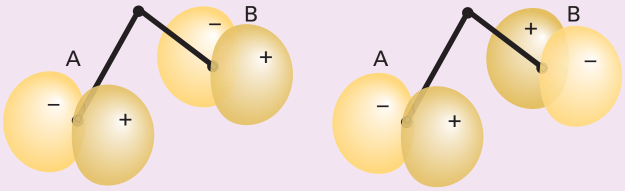


Figure 32.4 Two linear combinations of the basis orbitals shown in Fig. 32.3. The two combinations each span a one-dimensional irreducible representation and their symmetry species are different.

Answer Under σ_v, $p_B+p_A\leftarrow p_A+p_B$ and $p_B-p_A\leftarrow p_A-p_B$; therefore, under σ_v, $(p_1,-p_2)\leftarrow(p_1,p_2)$. Similar analysis for the other symmetry operations results in the following representatives in the new basis (p_1,p_2):

$$\boldsymbol{D}(E)=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} \quad \boldsymbol{D}(C_2)=\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix}$$
$$\boldsymbol{D}(\sigma_v)=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} \quad \boldsymbol{D}(\sigma_v')=\begin{pmatrix}-1 & 0\\ 0 & -1\end{pmatrix}$$

The new representatives are all in block-diagonal form, and the two combinations are not mixed with each other by any operation of the group. The reduction of $\Gamma^{(2)}$ has been reduced to the sum of two one-dimensional representations. Thus, p_1 spans

$$\boldsymbol{D}(E)=1 \quad \boldsymbol{D}(C_2)=-1 \quad \boldsymbol{D}(\sigma_v)=1 \quad \boldsymbol{D}(\sigma_v')=-1$$

which is the same one-dimensional representation as that spanned by p_S, and p_2 spans

$$\boldsymbol{D}(E)=1 \quad \boldsymbol{D}(C_2)=1 \quad \boldsymbol{D}(\sigma_v)=-1 \quad \boldsymbol{D}(\sigma_v')=-1$$

which is a different one-dimensional representation; we denote these two representations $\Gamma^{(1)}$ and $\Gamma^{(1)\prime}$, respectively. At this stage we have reduced the original representation as follows:

$$\Gamma^{(3)}=\Gamma^{(1)}+\Gamma^{(1)}+\Gamma^{(1)\prime}$$

Self-test 32.5 Consider the H_2O molecule and focus on the two H1s orbitals. Is the two-dimensional representation on the basis $(H1s_A,H1s_B)$ reducible?

Answer: Yes; adopt $H1s_A+H1s_B$, $H1s_A-H1s_B$.

(d) Characters and symmetry species

The **character**, χ (chi), of an operation in a particular matrix representation is the sum of the diagonal elements of the representative of that operation. Thus, in the original basis we are using, the characters of the representatives are

R	E	C_2	σ_v	σ_v'
$D(R)$	$\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}$	$\begin{pmatrix}-1&0&0\\0&0&-1\\0&-1&0\end{pmatrix}$	$\begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix}$	$\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&-1\end{pmatrix}$
$\chi(R)$	3	−1	1	−3

The characters of one-dimensional representatives are just the representatives themselves. The sum of the characters of the reduced representation is unchanged by the reduction:

R	E	C_2	σ_v	σ_v'
$\chi(R)$ for $\Gamma^{(1)}$	1	−1	1	−1
$\chi(R)$ for $\Gamma^{(1)}$	1	−1	1	−1
$\chi(R)$ for $\Gamma^{(1)\prime}$	1	1	−1	−1
Sum:	3	−1	1	−3

At this point we have found two irreducible representations of the group C_{2v}. Although the notation $\Gamma^{(n)}$ can be used for general representations, it is common in chemical applications of group theory to use the labels A, B, E, and T to denote the **symmetry species** of the representation:

A: one-dimensional representation, character +1 under the principal rotation

B: one-dimensional representation, character −1 under the principal rotation

E: two-dimensional irreducible representation

T: three-dimensional irreducible representation

Subscripts are used to distinguish the irreducible representations if there is more than one of the same type: A_1 is reserved for the representation with character +1 for all operations. All the irreducible representations of C_{2v} are one-dimensional, and the table above is labelled as follows:

Symmetry species	E	C_2	σ_v	σ_v'
B_1	1	−1	1	−1
B_1	1	−1	1	−1
A_2	1	1	−1	−1

Are these the only irreducible representations of the group C_{2v}? There is in fact only one more species of irreducible representations of this group, for a surprising theorem of group theory states that

$$\text{Number of symmetry species} = \text{number of classes} \qquad (32.5)$$

Number of species

In C_{2v}, for instance, there are four classes (four columns in the table of characters), so there are only four species of irreducible representation. The character table in Table 32.1 therefore shows the characters of all the irreducible representations of this group. Another powerful result relates the sum of the dimensions, d_i, of all the symmetry species $\Gamma^{(i)}$ to the **order** of the group, the total number of symmetry operations, h:

$$\sum_{\text{Species } i} d_i^2 = h \qquad (32.6)$$

Dimensionality and order

Brief illustration 32.4 Symmetry species

There are three classes of operation in the group C_{3v} (E,C_3,σ_v: we don't need to know the number in each class), so there are three symmetry species (they turn out to be A_1, A_2, and E). The order of the group is 6 (we now need to know that the elements of the group (that is, the symmetry operations) are (E,$2C_3$,$3\sigma_v$), for $h=6$), so if we already knew that two of the symmetry species are one-dimensional, we could infer that the remaining irreducible representation is two-dimensional (E) from $1^2+1^2+d^2=6$.

Self-test 32.6 How many symmetry species are there for the group T_d, with elements (E,$8C_3$,$3C_2$,$6\sigma_d$,$6S_4$)? Can you infer their dimensionalities?

Answer: five species; 2A+E+2T, $2\times(1)^2+1\times(2)^2+2\times(3)^2=24=h$

32.3 Character tables

The tables we have been constructing are called **character tables** and from now on move to the centre of the discussion. The columns of a character table are labelled with the symmetry operations of the group. For instance, for the group C_{3v} the columns are headed E, C_3, and σ_v (Table 32.2). The numbers multiplying each operation are the numbers of members of each class. The rows under the labels for the operations summarize the symmetry properties of the orbitals. They are labelled with the symmetry species.

Table 32.1* The C_{2v} character table

C_{2v}, $2mm$	E	C_2	σ_v	σ_v'	$h=4$	
A_1	1	1	1	1	z	z^2, y^2, x^2
A_2	1	1	−1	−1		xy
B_1	1	−1	1	−1	x	zx
B_2	1	−1	−1	1	y	yz

* More character tables are given in the *Resource section*.

Table 32.2* The C_{3v} character table

C_{3v}, $3m$	E	$2C_3$	$3\sigma_v$	$h = 6$	
A_1	1	1	1	z	z^2, x^2+y^2
A_2	1	1	−1		
E	2	−1	0	(x, y)	$(xy, x^2-y^2), (yz, zx)$

* More character tables are given in the *Resource section*.

(a) Character tables and orbital degeneracy

The character of the identity operation E tells us the degeneracy of the orbitals. Thus, in a C_{3v} molecule, any orbital with a symmetry label A_1 or A_2 is non-degenerate. Any doubly degenerate pair of orbitals in C_{3v} must be labelled E because, in this group, only E symmetry species have characters greater than 1. (Take care to distinguish the identity operation E (italic, a column heading) from the symmetry label E (roman, a row label).)

Because there are no characters greater than 2 in the column headed E in C_{3v}, we know that there can be no triply degenerate orbitals in a C_{3v} molecule. This last point is a powerful result of group theory, for it means that with a glance at the character table of a molecule, we can state the maximum possible degeneracy of its orbitals.

Example 32.3 Using a character table to judge degeneracy

Can a trigonal planar molecule such as BF_3 have triply degenerate orbitals? What is the minimum number of atoms from which a molecule can be built that does display triple degeneracy?

Method First identify the point group, and then refer to the corresponding character table in the *Resource section*. The maximum number in the column headed by the identity E is the maximum orbital degeneracy possible in a molecule of that point group. For the second part, consider the shapes that can be built from two, three, etc. atoms, and decide which number can be used to form a molecule that can have orbitals of symmetry species T.

Answer Trigonal planar molecules belong to the point group D_{3h}. Reference to the character table for this group shows that the maximum degeneracy is 2, as no character exceeds 2 in the column headed E. Therefore, the orbitals cannot be triply degenerate. A tetrahedral molecule (symmetry group T) has an irreducible representation with a T symmetry species. The minimum number of atoms needed to build such a molecule is four (as in P_4, for instance).

Self-test 32.7 A buckminsterfullerene molecule, C_{60} (19 of Topic 31), belongs to the icosahedral point group. What is the maximum possible degree of degeneracy of its orbitals?

Answer: 5

(b) The symmetry species of atomic orbitals

The characters in the rows labelled A and B and in the columns headed by symmetry operations other than the identity E indicate the behaviour of an orbital under the corresponding operations: a +1 indicates that an orbital is unchanged, and a −1 indicates that it changes sign. It follows that we can identify the symmetry label of the orbital by comparing the changes that occur to an orbital under each operation, and then comparing the resulting +1 or −1 with the entries in a row of the character table for the point group concerned. By convention, irreducible representations are labelled with uppercase Roman letters (such as A_1 and E) and the orbitals to which they apply are labelled with the lowercase equivalents (so an orbital of symmetry species A_1 is called an a_1 orbital). Examples of each type of orbital are shown in Fig. 32.5.

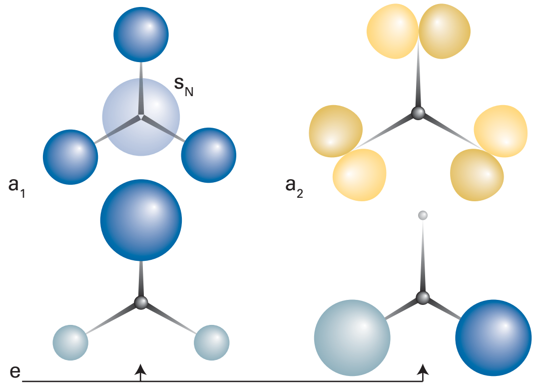


Figure 32.5 Typical linear combinations of orbitals in a C_{3v} molecule.

Brief illustration 32.5 Symmetry species of atomic orbitals

Consider the $O2p_x$ orbital in H_2O (the x-axis is perpendicular to the molecular plane; the y-axis is parallel to the H–H direction; the z-axis bisects the HOH angle). Because H_2O belongs to the point group C_{2v}, we know by referring to the C_{2v} character table (Table 32.1) that the labels available for the orbitals are a_1, a_2, b_1, and b_2. We can decide the appropriate label for $O2p_x$ by noting that under a 180° rotation (C_2) the orbital changes sign (Fig. 32.6), so it must be either B_1 or B_2, as only these two symmetry

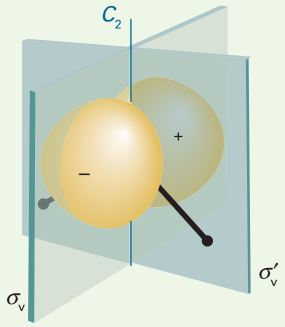


Figure 32.6 A p_x orbital on the central atom of a C_{2v} molecule and the symmetry elements of the group.

types have character –1 under C_2. The O2p_x orbital also changes sign under the reflection σ'_v; which identifies it as B_1. As we shall see, any molecular orbital built from this atomic orbital will also be a b_1 orbital. Similarly, O2p_y changes sign under C_2 but not under σ'_v; therefore, it can contribute to b_2 orbitals.

Self-test 32.8 Identify the symmetry species of d orbitals on the central atom of a square-planar (D_{4h}) complex.

Answer: $A_{1g}+B_{1g}+B_{2g}+E_g$

For the rows labelled E or T (which refer to the behaviour of sets of doubly and triply degenerate orbitals, respectively), the characters in a row of the table are the sums of the characters summarizing the behaviour of the individual orbitals in the basis. Thus, if one member of a doubly degenerate pair remains unchanged under a symmetry operation but the other changes sign (Fig. 32.7), then the entry is reported as $\chi = 1 - 1 = 0$. Care must be exercised with these characters because the transformations of orbitals can be quite complicated; nevertheless, the sums of the individual characters are integers.

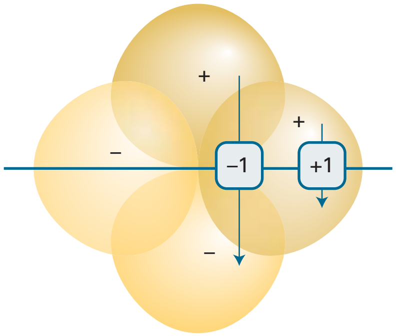


Figure 32.7 The two orbitals shown here have different properties under reflection through the mirror plane: one changes sign (character –1), the other does not (character +1).

The behaviour of s, p, and d orbitals on a central atom under the symmetry operations of the molecule is so important that the symmetry species of these orbitals are generally indicated in a character table. To make these allocations, we look at the symmetry species of x, y, and z, which appear on the right-hand side of the character table. Thus, the position of z in Table 32.2 shows that p_z (which is proportional to $zf(r)$) has symmetry species A_1 in C_{3v}, whereas p_x and p_y (which are proportional to $xf(r)$ and $yf(r)$, respectively) are jointly of E symmetry. In technical terms, we say that p_x and p_y jointly **span** an irreducible representation of symmetry species E. An s orbital on the central atom always spans the fully symmetrical irreducible representation (typically labelled A_1 but sometimes A'_1) of a group as it is unchanged under all symmetry operations.

The five d orbitals of a shell are represented by xy for d_{xy}, etc., and are also listed on the right of the character table. We can see at a glance that in C_{3v}, d_{xy} and $d_{x^2-y^2}$ on a central atom jointly belong to E and hence form a doubly degenerate pair.

(c) The symmetry species of linear combinations of orbitals

So far, we have dealt with the symmetry classification of individual orbitals. The same technique may be applied to linear combinations of orbitals on atoms that are related by symmetry transformations of the molecule, such as the linear combinations p_1 and p_2 of Example 32.2 and the combination $\psi_1 = \psi_A + \psi_B + \psi_C$ of the three H1s orbitals in the C_{3v} molecule NH_3 (Fig. 32.8). This latter combination remains unchanged under a C_3 rotation and under any of the three vertical reflections of the group, so its characters are

$$\chi(E)=1 \quad \chi(C_3)=1 \quad \chi(\sigma_v)=1$$

Comparison with the C_{3v} character table shows that ψ_1 is of symmetry species A_1, and therefore that it contributes to a_1 molecular orbitals in NH_3.

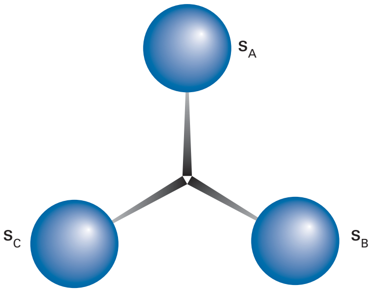


Figure 32.8 The three H1s orbitals used to construct linear combinations in a C_{3v} molecule such as NH_3.

Example 32.4 Identifying the symmetry species of orbitals

Identify the symmetry species of the orbital $\psi = \psi_A - \psi_B$ in a C_{2v} NO_2 molecule, where ψ_A is an O2p_x orbital on one O atom and ψ_B that on the other O atom.

Method The negative sign in ψ indicates that the sign of ψ_B is opposite to that of ψ_A. We need to consider how the combination changes under each operation of the group, and then write the character as +1, −1, or 0 as specified above. Then we compare the resulting characters with each row in the character table for the point group, and hence identify the symmetry species.

Answer The combination is shown in Fig. 32.9. Under C_2, ψ changes into itself, implying a character of +1. Under the reflection σ_v, both orbitals change sign, so $\psi \to -\psi$, implying a character of −1. Under σ_v', $\psi \to -\psi$, so the character for this operation is also −1. The characters are therefore

$$\chi(E)=1 \quad \chi(C_2)=1 \quad \chi(\sigma_v)=-1 \quad \chi(\sigma_v')=-1$$

These values match the characters of the A_2 symmetry species, so ψ can contribute to an a_2 orbital.

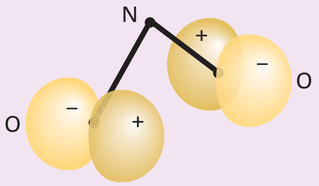
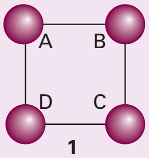


Figure 32.9 One linear combination of O2p_x orbitals in the C_{2v} NO_2 molecule.

Self-test 32.9 Consider $PtCl_4^-$, in which the Cl ligands form a square planar array of point group D_{4h} (**1**). Identify the symmetry type of the combination $\psi_A - \psi_B + \psi_C - \psi_D$.



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Answer: B_{2g}

Checklist of concepts

☐ 1. A **group** in mathematics is a collection of transformations that satisfy the four criteria set out at the start of the Topic.

☐ 2. A **matrix representative** is a matrix that represents the effect of an operation on a basis.

☐ 3. The **character** is the sum of the diagonal elements of a matrix representative of an operation.

☐ 4. A **matrix representation** is the collection of matrix representatives for the operations in the group.

☐ 5. A **character table** consists of entries showing the characters of all the irreducible representations of a group.

☐ 6. A **symmetry species** is a label for an irreducible representation of a group.

☐ 7. The character of the identity operation *E* is the degeneracy of the orbitals that form a basis for an irreducible representation of a group.

Checklist of equations

Property	Equation	Comment	Equation number
Class membership	$R' = S^{-1}RS$	All elements members of the group; R and R' in same class	32.1
Number of species rule	Number of symmetry species = number of classes		32.5
Character and order	$\sum_{\text{Species } i} d_i^2 = h$	h is the order of the group	32.6

TOPIC 33

Applications of symmetry

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➤ Why do you need to know this material?

This Topic explains how the concepts introduced in Topics 31 and 32 are put to use. The arguments here are essential for understanding how molecular orbitals are constructed and underlie the whole of spectroscopy.

➤ What is the key idea?

An integral is invariant under symmetry transformations of a molecule.

➤ What do you need to know already?

This Topic develops the material that began in Topic 31, where the symmetry classification of molecules is introduced on the basis of their symmetry elements, and draws heavily on the properties of characters and character tables described in Topic 32.

Group theory shows its power when brought to bear on a variety of problems in chemistry, among them the construction of molecular orbitals and the formulation of spectroscopic selection rules. This Topic describes these two applications after establishing a general result relating to integrals. In Topics 6 and 7 it is explained how integrals ('matrix elements') are central to the formulation of quantum mechanics, and knowing with very little calculation that various integrals are necessarily zero can save a great deal of calculational effort as well as adding to insight about the origin of properties.

33.1 Vanishing integrals

An integral, which we shall denote I, in one dimension is equal to the area beneath the curve. In higher dimensions, it is equal to volume and various generalizations of volume. The key point is that the value of the area, volume, etc., is independent of the orientation of the axes used to express the function being integrated, the 'integrand' (Fig. 33.1). In group theory we express this point by saying that *I is invariant under any symmetry operation*, and that each symmetry operation brings about the trivial transformation $I \rightarrow I$.

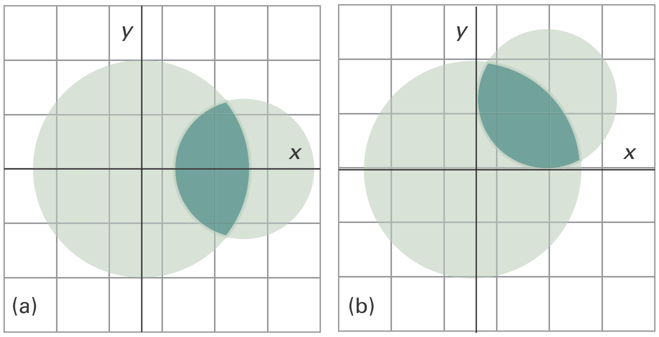


Figure 33.1 The value of an integral I (for example, an area) is independent of the coordinate system used to evaluate it: the dark shaded regions have the same area in (a) and (b). That is, I is a basis of a representation of symmetry species A_1 (or its equivalent).

(a) Integrals over the product of two functions

Suppose we had to evaluate the integral

$$I=\int f_1 f_2 \mathrm{d}\tau \qquad (33.1)$$

where f_1 and f_2 are functions and the integration is over all space. For example, f_1 might be an atomic orbital A on one atom and f_2 an atomic orbital B on another atom, in which case I would be their overlap integral (denoted S). If we knew that the integral is zero, we could say at once that a molecular orbital does not result from (A,B) overlap in that molecule. We shall now see that the character tables introduced in Topic 32 provide a quick way of judging whether an integral is necessarily zero.

The volume element $\mathrm{d}\tau$ is invariant under any symmetry operation. It follows that the integral is nonzero only if the integrand itself, the product f_1f_2, is unchanged by any symmetry operation of the molecular point group. If the integrand changed sign under a symmetry operation, the integral would be the sum of equal and opposite contributions, and hence would be zero. It follows that the only contribution to a nonzero integral comes from functions for which under any symmetry operation of the molecular point group $f_1f_2 \rightarrow f_1f_2$, and hence for which the characters of the operations are all equal to +1. Therefore, for I not to be zero, *the integrand f_1f_2 must have symmetry species A_1* (or its equivalent in the specific molecular point group).

The following procedure is used to deduce the symmetry species spanned by the product f_1f_2 and hence to see whether it does indeed span A_1:

- Identify the symmetry species of the individual functions f_1 and f_2 by reference to the character table for the molecular point group in question and write their characters in two rows in the same order as in the table.
- Multiply the two numbers in each column, writing the results in the same order.
- Inspect the row so produced, and see if it can be expressed as a sum of characters from each column of the group. The integral must be zero if this sum does not use A_1.

A shortcut that works when f_1 and f_2 are bases for irreducible representations of a group is to note their symmetry species; if they are different (B_1 and A_2, for instance), then the integral of their product must vanish; if they are the same (both B_1, for instance), then the integral may be nonzero.

It is important to note that group theory is specific about when an integral must be zero, but integrals that it allows to be nonzero may be zero for reasons unrelated to symmetry. For example, the N—H distance in ammonia may be so great that the (s_1,s_N) overlap integral, where s_1 is the combination $s_A+s_B+s_C$ of the three H1s atomic orbitals, is zero simply because the orbitals are so far apart.

Example 33.1 Deciding if an integral must be zero 1

May the integral of the function $f=xy$ be nonzero when evaluated over a region the shape of an equilateral triangle centred on the origin (Fig. 33.2)?

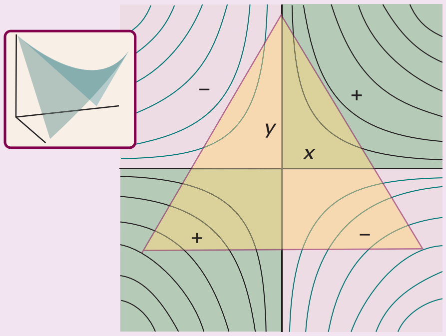


Figure 33.2 The integral of the function $f=xy$ over the tinted region is zero. In this case, the result is obvious by inspection, but group theory can be used to establish similar results in less obvious cases. The insert shows the shape of the function in three dimensions.

Method First, note that an integral over a single function f is included in the previous discussion if we take $f_1=f$ and $f_2=1$ in eqn 33.1. Therefore, we need to judge whether f alone belongs to the symmetry species A_1 (or its equivalent) in the point group of the system. To decide, we identify the point group and then examine the character table to see whether f belongs to A_1 (or its equivalent).

Answer An equilateral triangle has the point-group symmetry D_{3h}. If we refer to the character table of the group, we see that xy is a member of a basis that spans the irreducible representation E'. Therefore, its integral must be zero, because the integrand has no component that spans A_1'.

Self-test 33.1 Can the function x^2+y^2 have a nonzero integral when integrated over a regular pentagon centred on the origin?

Answer: Yes (Fig. 33.3)

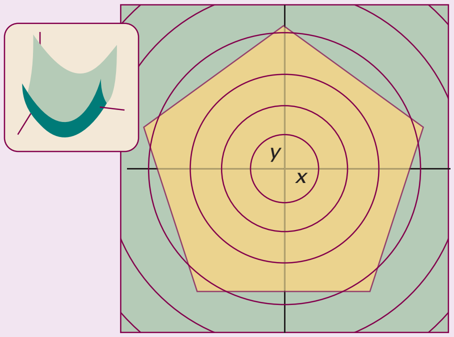


Figure 33.3 The integration of a function over a pentagonal region. The insert shows the shape of the function in three dimensions.

(b) Decomposition of a direct product

In many cases, the product of functions f_1 and f_2 spans a sum of irreducible representations. For instance, in C_{2v} we may find the characters 2,0,0,–2 when we multiply the characters of f_1 and f_2 together. In this case, we note that these characters are the sum of the characters for A_2 and B_1:

	E	C_{2v}	σ_v	σ'_v
A_2	1	1	−1	−1
B_1	1	−1	1	−1
A_2+B_1	2	0	0	−2

To summarize this result we write the symbolic expression $A_2\times B_1=A_2+B_1$, which is called the **decomposition of a direct product**. This expression is symbolic. The × and + signs in this expression are not ordinary multiplication and addition signs: formally, they denote technical procedures with matrices called a 'direct product' and a 'direct sum'. Because the sum on the right does not include a component that is a basis for an irreducible representation of symmetry species A_1, we can conclude that the integral of $f_1 f_2$ over all space is zero in a C_{2v} molecule.

Whereas the decomposition of the characters 2,0,0,–2 can be done by inspection in this simple case, in other cases and more complex groups the decomposition is often far from obvious. For example, if we found the characters 8,–2,–6,4, it might not be obvious that the sum contains A_1. Group theory, however, provides a systematic way of using the characters of the representation spanned by a product to find the symmetry species of the irreducible representations. The formal recipe is

$$n(\Gamma)=\frac{1}{h}\sum_R \chi^{(\Gamma)}(R)\chi(R) \qquad \text{Decomposition of direct product} \tag{33.2}$$

We implement this expression as follows:

- Write down a table with columns headed by the symmetry operations, R, of the group. Include a column for every operation, not just the classes.
- In the first row write down the characters of the representation we want to analyse; these are the $\chi(R)$.
- In the second row, write down the characters of the irreducible representation Γ we are interested in; these are the $\chi^{(\Gamma)}(R)$.
- Multiply the two rows together, add the products together, and divide by the order of the group, h.

The resulting number, $n(\Gamma)$, is the number of times Γ occurs in the decomposition.

Brief illustration 33.1 Decomposition of a direct product

To find whether A_1 does indeed occur in the product with characters 8, −2, −6,4 in C_{2v}, we draw up the following table:

	E	C_{2v}	σ_v	σ'_v	$h=4$ (the order of the group)
f_1f_2	8	−2	−6	4	(the characters of the product)
A_1	1	1	1	1	(the symmetry species we are interested in)
	8	−2	−6	4	(the product of the two sets of characters)

The sum of the numbers in the last line is 4; when that number is divided by the order of the group, we get 1, so A_1 occurs once in the decomposition. When the procedure is repeated for all four symmetry species, we find that $f_1 f_2$ spans $A_1+2A_2+5B_2$.

Self-test 33.2 Does A_2 occur among the symmetry species of the irreducible representations spanned by a product with characters 7,–3,–1,5 in the group C_{2v}?

Answer: No

(c) Integrals over products of three functions

Integrals of the form

$$I=\int f_1 f_2 f_3 \mathrm{d}\tau \tag{33.3}$$

are also common in quantum mechanics for they include matrix elements of operators (Topic 7), and it is important to know when they are necessarily zero. As for integrals over two functions, for I to be nonzero, *the product $f_1 f_2 f_3$ must span A_1 (or its equivalent) or contain a component that spans A_1*. To test whether this is so, the characters of all three functions are multiplied together in the same way as in the rules set out above.

Example 33.2 Deciding if an integral must be zero 2

Does the integral $\int(3\mathrm{d}_{z^2})x(3\mathrm{d}_{xy})\mathrm{d}\tau$ vanish in a C_{2v} molecule?

Method We must refer to the C_{2v} character table (Table 32.1) and the characters of the irreducible representations spanned by $3z^2-r^2$ (the form of the d_{z^2} orbital), x, and xy; then we can use the procedure set out above (with one more row of multiplication).

Answer We draw up the following table:

	E	C_2	σ_v	σ'_v	
$f_3=\mathrm{d}_{xy}$	1	1	−1	−1	A_2
$f_2=x$	1	−1	1	−1	B_1
$f_1=\mathrm{d}_{z^2}$	1	1	1	1	A_1
$f_1 f_2 f_3$	1	−1	−1	1	

The characters are those of B_2. Therefore, the integral is necessarily zero.

Self-test 33.3 Does the integral $\int(2p_x)(2p_y)(2p_z)d\tau$ necessarily vanish in an octahedral environment?

Answer: No

33.2 Applications to orbitals

The rules we have outlined let us decide which atomic orbitals may have nonzero overlap in a molecule. It is also very useful to have a set of procedures to construct linear combinations of atomic orbitals to have a certain symmetry, and thus to know in advance whether or not they will have nonzero overlap with other orbitals.

(a) Orbital overlap

An overlap integral, S, between two sets of atomic orbitals ψ_1 and ψ_2 is

$$S=\int\psi_2^*\psi_1 d\tau \qquad \text{Overlap integral} \qquad (33.4)$$

and clearly has the same form as eqn 33.1. It follows from that discussion that *only orbitals of the same symmetry species may have nonzero overlap* ($S\neq 0$), so only orbitals of the same symmetry species form bonding and antibonding combinations. It is explained in Topic 23 that the selection of atomic orbitals that had mutual nonzero overlap is the central and initial step in the construction of molecular orbitals by the LCAO procedure. We are therefore at the point of contact between group theory and the material introduced in that Topic.

Example 33.3 Determining which orbitals can contribute to bonding

The four H1s orbitals of methane span A_1+T_2. With which of the C atomic orbitals can they overlap? What bonding pattern would be possible if the C atom had d orbitals available?

Method Refer to the T_d character table (in the *Resource section*) and look for s, p, and d orbitals spanning A_1 or T_2.

Answer An s orbital spans A_1, so it may have nonzero overlap with the A_1 combination of H1s orbitals. The C2p orbitals span T_2, so they may have nonzero overlap with the T_2 combination. The d_{xy}, d_{yz}, and d_{zx} orbitals span T_2, so they may overlap the same combination. Neither of the other two d orbitals span A_1 (they span E), so they remain nonbonding orbitals. It follows that in methane there are (C2s,H1s)-overlap a_1 orbitals and (C2p,H1s)-overlap t_2 orbitals. The C3d orbitals might contribute to the latter. The lowest energy configuration is probably $a_1^2t_2^6$, with all bonding orbitals occupied.

Self-test 33.4 Consider the octahedral SF_6 molecule, with the bonding arising from overlap of S orbitals and a 2p orbital on each F directed towards the central S atom. The latter spans $A_{1g}+E_g+T_{1u}$. What s orbitals have nonzero overlap? Suggest what the ground-state configuration is likely to be.

Answer: 3s(A_{1g}), 3p(T_{1u}), 3d(E_g); $a_{1g}^2t_{1u}^6e_g^4$

(b) Symmetry-adapted linear combinations

In the discussion of the molecular orbitals of NH_3 (Topic 32) we encounter molecular orbitals of the form $\psi=c_1s_N+c_2(s_A+s_B+s_C)$, where s_N is an N2s atomic orbital and s_A, s_B, and s_C are H1s orbitals. The s_N orbital has nonzero overlap with the combination of H1s orbitals as the latter has matching symmetry. The combination of H1s orbitals is an example of a **symmetry-adapted linear combination** (SALC), which are orbitals constructed from equivalent atoms and having a specified symmetry. Group theory also provides machinery that takes an arbitrary **basis**, or set of atomic orbitals (s_A, etc.), as input and generates combinations of the specified symmetry. As illustrated by the example of NH_3, SALCs are the building blocks of LCAO molecular orbitals and their construction is the first step in any molecular orbital treatment of molecules.

The technique for building SALCs is derived by using the full power of group theory and involves the use of a **projection operator**, $P^{(\Gamma)}$, an operator that takes one of the basis orbitals and generates from it—projects from it—a SALC of the symmetry species Γ:

$$P^{(\Gamma)}=\frac{1}{h}\sum_R \chi^{(\Gamma)}(R)R \qquad \text{Projection operator} \qquad (33.5)$$

To implement this rule, do the following:

- Write each basis orbital at the head of a column and in successive rows show the effect of each operation R on each orbital. Treat each operation individually.
- Multiply each member of the column by the character, $\chi^{(\Gamma)}(R)$, of the corresponding operation.
- Add together all the orbitals in each column with the factors as determined in the second step.
- Divide the sum by the order of the group, h.

We now form the overall molecular orbital by forming a linear combination of all the SALCs of the specified symmetry species. In this case, therefore, the a_1 molecular orbital is $\psi = c_N s_N + c_1 s_1$, as specified above. This is as far as group theory can take us. The coefficients are found by solving the Schrödinger equation; they do not come directly from the symmetry of the system.

Example 33.4 Constructing symmetry-adapted orbitals

Construct symmetry-adapted linear combinations of H1s orbitals for NH_3.

Method Identify the point group of the molecule and have available its character table. Then apply the projection-operator technique.

Answer From the (s_N, s_A, s_B, s_C) basis in NH_3 we form the following table, with each row showing the effect of the operator shown on the left:

	s_N	s_A	s_B	s_C
E	s_N	s_A	s_B	s_C
C_3^+	s_N	s_B	s_C	s_A
C_3^-	s_N	s_C	s_A	s_B
σ_v	s_N	s_A	s_C	s_B
σ_v'	s_N	s_B	s_A	s_C
σ_v''	s_N	s_C	s_B	s_A

To generate the A_1 combination, we take the characters for A_1 (1,1,1,1,1,1); then the second and third rules lead to $\psi \propto s_N + s_N + \ldots = 6s_N$. The order of the group (the number of elements) is 6, so the combination of A_1 symmetry that can be generated from s_N is s_N itself. Applying the same technique to the column under s_A gives

$$\psi = \tfrac{1}{6}(s_A + s_B + s_C + s_A + s_B + s_C) = \tfrac{1}{3}(s_A + s_B + s_C)$$

The same combination is built from the other two columns, so they give no further information. The combination we have just formed is the one we see above and denote s_1 (apart from the numerical factor).

Self-test 33.5 Generate the symmetry-adapted linear combinations of the H1s orbitals in H_2O.

Answer: $H1s_A + H1s_B$, $H1s_A - H1s_B$

We run into a problem when we try to generate an SALC of symmetry species E, because, for representations of dimension 2 or more, the rules generate sums of SALCs. This problem can be illustrated as follows. In C_{3v}, the E characters are 2, −1, −1, 0, 0, 0, so the column under s_N gives

$$\psi = \tfrac{1}{6}(2s_N - s_N - s_N + 0 + 0 + 0) = 0$$

The other columns give

$$\tfrac{1}{6}(2s_A - s_B - s_C) \qquad \tfrac{1}{6}(2s_B - s_A - s_C) \qquad \tfrac{1}{6}(2s_C - s_B - s_A)$$

However, any one of these three expressions can be expressed as a sum of the other two (they are not 'linearly independent'). The difference of the second and third gives $\tfrac{1}{2}(s_B - s_C)$, and this combination and the first, $\tfrac{1}{6}(2s_A - s_B - s_C)$ are the two (now linearly independent) SALCs we have used in the discussion of e orbitals.

33.3 Selection rules

It is explained in Topic 16 and developed further in Topic 45 that the intensity of a spectral line arising from a molecular transition between some initial state with wavefunction ψ_i and a final state with wavefunction ψ_f depends on the (electric) transition dipole moment, $\boldsymbol{\mu}_\text{fi}$. The z-component of this vector is defined through

$$\mu_{z,\text{fi}} = -e\int \psi_\text{f}^* z \psi_\text{i}\,\text{d}\tau \qquad \text{Transition dipole moment} \qquad (33.6)$$

where $-e$ is the charge of the electron. The transition moment has the form of the integral in eqn 33.3; so, once we know the symmetry species of the states, we can use group theory to formulate the selection rules for the transitions.

Example 33.5 Deducing a selection rule

Is $p_x \rightarrow p_y$ an allowed transition in a tetrahedral environment?

Method We must decide whether the product $p_y q p_x$, with $q = x, y$, or z, spans A_1 by using the T_d character table.

Answer The procedure works out as follows:

	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$	
$f_3(p_y)$	3	0	−1	1	−1	T_2
$f_2(q)$	3	0	−1	1	−1	T_2
$f_1(p_x)$	3	0	−1	1	−1	T_2
$f_1 f_2 f_3$	27	0	−1	1	−1	

We now use the decomposition procedure summarized by eqn 33.2 to deduce that A_1 occurs (once) in this set of characters, so $p_x \rightarrow p_y$ is allowed. A more detailed analysis (using the matrix representatives rather than the characters) shows that only $q = z$ gives an integral that may be nonzero, so the transition is z-polarized. That is, the electromagnetic radiation involved in the transition has a component of its electric vector in the z-direction.

Self-test 33.6 What are the allowed transitions, and their polarizations, of an electron in a b_1 orbital in a C_{4v} molecule?

Answer: $b_1 \rightarrow b_1(z)$; $b_1 \rightarrow e(x,y)$

Checklist of concepts

☐ 1. For an integral not to be zero, the integrand must have symmetry species A_1 (or its equivalent in the specific molecular point group).

☐ 2. Only orbitals of the same symmetry species may have nonzero overlap ($S \neq 0$).

☐ 3. A **symmetry-adapted linear combination** (SALC) is a linear combination of atomic orbitals constructed from equivalent atoms and having a specified symmetry.

Checklist of equations

Property	Equation	Comment	Equation number
Decomposition of direct product	$n(\Gamma)=(1/h)\sum_R \chi^{(\Gamma)}(R)\chi(R)$	Real characters*	33.2
Overlap integral	$S=\int \psi_2^* \psi_1 d\tau$	Definition	33.4
Projection operator	$P^{(\Gamma)}=(1/h)\sum_R \chi^{(\Gamma)}(R)R$		33.5
Transition dipole moment	$\mu_{z,\mathrm{fi}}=-e\int \psi_\mathrm{f}^* z \psi_\mathrm{i} \mathrm{d}\tau$	z-component	33.6

* In general, characters may have complex values; throughout this text we encounter only real values.

Focus 7 on Molecular symmetry

Topic 31 The analysis of molecular shape

Discussion questions

31.1 Explain how a molecule is assigned to a point group.

31.2 List the symmetry operations and the corresponding symmetry elements of the point groups.

31.3 State and explain the symmetry criteria that allow a molecule to be polar.

31.4 State the symmetry criteria that allow a molecule to be optically active.

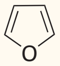
Exercises

31.1(a) The CH_3Cl molecule belongs to the point group C_{3v}. List the symmetry elements of the group and locate them in a drawing of the molecule.
31.1(b) The CCl_4 molecule belongs to the point group T_d. List the symmetry elements of the group and locate them in a drawing of the molecule.

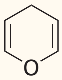
31.2(a) Identify the group to which the naphthalene molecule belongs and locate the symmetry elements in a drawing of the molecule.
31.2(b) Identify the group to which the anthracene molecule belongs and locate the symmetry elements in a drawing of the molecule.

31.3(a) Identify the point groups to which the following objects belong: (a) a sphere, (b) an isosceles triangle, (c) an equilateral triangle, (d) an unsharpened cylindrical pencil.
31.3(b) Identify the point groups to which the following objects belong: (a) a sharpened cylindrical pencil, (b) a three-bladed propeller, (c) a four-legged table, (d) yourself (approximately).

31.4(a) List the symmetry elements of the following molecules and name the point groups to which they belong: (a) NO_2, (b) N_2O, (c) $CHCl_3$, (d) $CH_2=CH_2$.
31.4(b) List the symmetry elements of the following molecules and name the point groups to which they belong: (a) furan (**1**), (b) γ-pyran (**2**), (c) 1,2,5-trichlorobenzene.

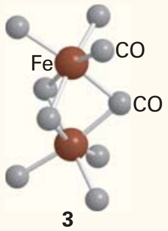


1 Furan



2 γ-Pyran

31.5(a) Assign (a) *cis*-dichloroethene and (b) *trans*-dichloroethene to point groups.
31.5(b) Assign the following molecules to point groups: (a) HF, (b) IF_7 (pentagonal bipyramid), (c) XeO_2F_2 (see-saw), (d) $Fe_2(CO)_9$ (**3**), (e) cubane, C_8H_8, (f) tetrafluorocubane, $C_8H_4F_4$ (**4**).



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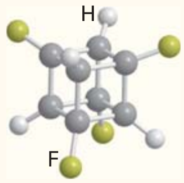

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31.6(a) Which of the following molecules may be polar? (a) pyridine, (b) nitroethane, (c) gas-phase $HgBr_2$, (d) $B_3N_3H_6$.
31.6(b) Which of the following molecules may be polar? (a) CH_3Cl, (b) $HW_2(CO)_{10}$, D_{4h} (c) $SnCl_4$.

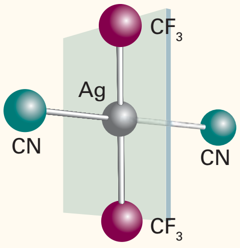
31.7(a) Identify the point groups to which all isomers of dichloronaphthalene belong.
31.7(b) Identify the point groups to which all isomers of dichloroanthracene belong.

31.8(a) Can molecules belonging to the point groups D_{2h} or C_{3h} be chiral? Explain your answer.
31.8(b) Can molecules belonging to the point groups T_h or T_d be chiral? Explain your answer.

Problems

31.1 List the symmetry elements of the following molecules and name the point groups to which they belong: (a) staggered CH_3CH_3, (b) chair and boat cyclohexane, (c) B_2H_6, (d) $[Co(en)_3]^{3+}$, where en is ethylenediamine (1,2-diaminoethane; ignore its detailed structure), (e) crown-shaped S_8. Which of these molecules can be (i) polar, (ii) chiral?

31.2a‡ In the square-planar complex anion [*trans*-$Ag(CF_3)_2(CN)_2]^-$, the Ag–CN groups are collinear. (a) Assume free rotation of the CF_3 groups (that is, disregarding the AgCF and AgCH angles) and name the point group of this complex ion. (b) Now suppose the CF_3 groups cannot rotate freely (because the ion was in a solid, for example). Structure (**5**) shows a plane which bisects the NC–Ag–CN axis and is perpendicular to it. Name the point group of the complex if each CF_3 group has a CF bond in that plane (so the CF_3 groups do not point to either CN group preferentially) and the CF_3 groups are (i) staggered, (ii) eclipsed.



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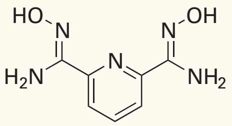
‡ These problems were supplied by Charles Trapp and Carmen Giunta.

31.3‡ B.A. Bovenzi and G.A. Pearse, Jr. (*J. Chem. Soc. Dalton Trans.*, 2763 (1997)) synthesized coordination compounds of the tridentate ligand pyridine-2,6-diamidoxime ($C_7H_9N_5O_2$, **6**). Reaction with $NiSO_4$ produced a complex in which two of the essentially planar ligands are bonded at right angles to a single Ni atom. Name the point group and the symmetry operations of the resulting $[Ni(C_7H_9N_5O_2)_2]^{2+}$ complex cation.



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Topic 32 Group theory

Discussion questions

32.1 Explain what is meant by a 'group'.

32.2 Explain what is meant by (a) a representative and (b) a representation in the context of group theory.

32.3 Explain the construction and content of a character table.

32.4 Explain what is meant by the reduction of a representation to a direct sum of representations.

32.5 Discuss the significance of the letters and subscripts used to denote the symmetry species of a representation.

Exercises

32.1(a) Use as a basis the valence p_z orbitals on each atom in BF_3 to find the representative of the operation σ_h. Take z as perpendicular to the molecular plane.
32.1(b) Use as a basis the valence p_z orbitals on each atom in BF_3 to find the representative of the operation C_3. Take z as perpendicular to the molecular plane.

32.2(a) Use the matrix representatives of the operations σ_h and C_3 in a basis of valence p_z orbitals on each atom in BF_3 to find the operation and its representative resulting from $\sigma_h C_3$. Take z as perpendicular to the molecular plane.
32.2(b) Use the matrix representatives of the operations σ_h and C_3 in a basis of valence p_z orbitals on each atom in BF_3 to find the operation and its representative resulting from $C_3\sigma_h$. Take z as perpendicular to the molecular plane.

32.3(a) Show that all three C_2 operations in the group D_{3h} belong to the same class.
32.3(b) Show that all three σ_v operations in the group D_{3h} belong to the same class.

32.4(a) What is the maximum degeneracy of a particle confined to the interior of an octahedral hole in a crystal?
32.4(b) What is the maximum degeneracy of a particle confined to the interior of an icosahedral nanoparticle?

32.5(a) What is the maximum possible degree of degeneracy of the orbitals in benzene?
32.5(b) What is the maximum possible degree of degeneracy of the orbitals in 1,4-dichlorobenzene?

Problems

32.1 The group C_{2h} consists of the elements E, C_2, σ_h, i. Construct the group multiplication table and find an example of a molecule that belongs to the group.

32.2 The group D_{2h} has a C_2 axis perpendicular to the principal axis and a horizontal mirror plane. Show that the group must therefore have a centre of inversion.

32.3 Consider the H_2O molecule, which belongs to the group C_{2v}. Take as a basis the two H1s orbitals and the four valence orbitals of the O atom and set up the 6×6 matrices that represent the group in this basis. Confirm by explicit matrix multiplication that the group multiplications (a) $C_2\sigma_v = \sigma_v'$ and (b) $\sigma_v\sigma_v' = C_2$. Confirm, by calculating the traces of the matrices, (a) that symmetry elements in the same class have the same character, (b) that the representation is reducible, and (c) that the basis spans $3A_1 + B_1 + 2B_2$.

32.4 Confirm that the z-component of orbital angular momentum is a basis for an irreducible representation of A_2 symmetry in C_{3v}.

32.5 Find the representatives of the operations of the group T_d in a basis of four H1s orbitals, one at each apex of a regular tetrahedron (as in CH_4).

32.6 Confirm that the representatives constructed in Problem 32.5 reproduce the group multiplications $C_3^+C_3^- = E$, $S_4C_3 = S_4'$, and $S_4C_3 = \sigma_d$.

32.7 The (one-dimensional) matrices $\boldsymbol{D}(C_3) = \mathbf{1}$ and $\boldsymbol{D}(C_2) = \mathbf{1}$, and $\boldsymbol{D}(C_3) = \mathbf{1}$ and $\boldsymbol{D}(C_2) = -\mathbf{1}$ both represent the group multiplication $C_3C_2 = C_6$ in the group C_{6v} with $\boldsymbol{D}(C_6) = +1$ and -1, respectively. Use the character table to confirm these remarks. What are the representatives of σ_v and σ_d in each case?

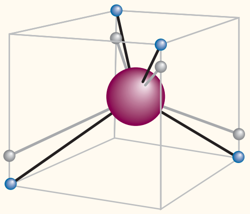
32.8 Construct the multiplication table of the Pauli spin matrices, σ, and the 2×2 unit matrix:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \sigma_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Do the four matrices form a group under multiplication?

32.9 The algebraic forms of the f orbitals are a radial function multiplied by one of the factors (a) $z(5z^2 - 3r^2)$, (b) $y(5y^2 - 3r^2)$, (c) $x(5x^2 - 3r^2)$, (d) $z(x^2 - y^2)$, (e) $y(x^2 - z^2)$, (f) $x(z^2 - y^2)$, (g) xyz. Identify the irreducible representations spanned by these orbitals in (a) C_{2v}, (b) C_{3v}, (c) T_d, (d) O_h. Consider a lanthanoid ion at the centre of (a) a tetrahedral complex, (b) an octahedral complex. What sets of orbitals do the seven f orbitals split into?

32.10‡ A computational study by C.J. Marsden (*Chem. Phys. Lett.* **245**, 475 (1995)) of AM_x compounds, where A is in Group 14 of the periodic table and M is an alkali metal, shows several deviations from the most symmetric structures for each formula. For example, most of the AM_4 structures were not tetrahedral but had two distinct values for MAM bond angles. They could be derived from a tetrahedron by a distortion shown in (**7**). (a) What is the point group of the distorted tetrahedron? (b) What is the symmetry species of the distortion considered as a vibration in the new, less symmetric group? Some AM_6 structures are not octahedral, but could be derived from an octahedron by translating a C–M–C axis as in (**8**). (c) What is the point group of the distorted octahedron? (d) What is the symmetry species of the distortion considered as a vibration in the new, less symmetric group?



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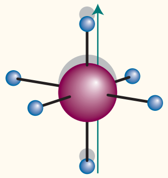

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32.11‡ The H_3^+ molecular ion, which plays an important role in chemical reactions occurring in interstellar clouds, is known to be equilateral triangular. (a) Identify the symmetry elements and determine the point group of this molecule. (b) Take as a basis for a representation of this molecule the three H1s orbitals and set up the matrices for this basis. (c) Obtain the group multiplication table by explicit multiplication of the matrices. (d) Determine if the representation is reducible and, if so, give the irreducible representations obtained.

Topic 33 Applications of symmetry

Discussion question

33.1 Identify and list four applications of character tables.

Exercises

33.1(a) Use symmetry properties to determine whether or not the integral $\int p_x z p_z d\tau$ is necessarily zero in a molecule with symmetry C_{2v}.
33.1(b) Use symmetry properties to determine whether or not the integral $\int p_x z p_z d\tau$ is necessarily zero in a molecule with symmetry D_{3h}.

33.2(a) Is the transition $A_1 \rightarrow A_2$ forbidden for electric dipole transitions in a C_{3v} molecule?
33.2(b) Is the transition $A_{1g} \rightarrow E_{2u}$ forbidden for electric dipole transitions in a D_{6h} molecule?

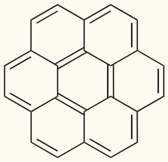
33.3(a) Show that the function xy has symmetry species B_2 in the group C_{4v}.
33.3(b) Show that the function xyz has symmetry species A_1 in the group D_2.

33.4(a) Consider the C_{2v} molecule NO_2. The combination $p_x(A) - p_x(B)$ of the two O atoms (with x perpendicular to the plane) spans A_2. Is there any orbital of the central N atom that can have a nonzero overlap with that combination of O orbitals? What would be the case in SO_2, where 3d orbitals might be available?
33.4(b) Consider the D_{3h} ion NO_3^-. Is there any orbital of the central N atom that can have a nonzero overlap with the combination $2p_z(A) - p_z(B) - p_z(C)$ of the three O atoms (with z perpendicular to the plane)? What would be the case in SO_3, where 3d orbitals might be available?

33.5(a) The ground state of NO_2 is A_1 in the group C_{2v}. To what excited states may it be excited by electric dipole transitions, and what polarization of light is it necessary to use?
33.5(b) The ClO_2 molecule (which belongs to the group C_{2v}) was trapped in a solid. Its ground state is known to be B_1. Light polarized parallel to the y-axis (parallel to the OO separation) excited the molecule to an upper state. What is the symmetry species of that state?

33.6(a) A set of basis functions is found to span a reducible representation of the group C_{4v} with characters 4,1,1,3,1 (in the order of operations in the character table in the *Resource section*). What irreducible representations does it span?
33.6(b) A set of basis functions is found to span a reducible representation of the group D_2 with characters 6,–2,0,0 (in the order of operations in the character table in the *Resource section*). What irreducible representations does it span?

33.7(a) What states of (a) benzene, (b) naphthalene may be reached by electric dipole transitions from their (totally symmetrical) ground states?
33.7(b) What states of (a) anthracene, (b) coronene (**9**) may be reached by electric dipole transitions from their (totally symmetrical) ground states?



9 Coronene

33.8(a) Write $f_1 = \sin\theta$ and $f_2 = \cos\theta$, and show by symmetry arguments using the group C_s that the integral of their product over a symmetrical range around $\theta = 0$ is zero.
33.8(b) Write $f_1 = x$ and $f_2 = 3x^2 - 1$, and show by symmetry arguments using the group C_s that the integral of their product over a symmetrical range around $x = 0$ is zero.

Problems

33.1 What irreducible representations do the four H1s orbitals of CH_4 span? Are there s and p orbitals of the central C atom that may form molecular orbitals with them? Could d orbitals, even if they were present on the C atom, play a role in orbital formation in CH_4?

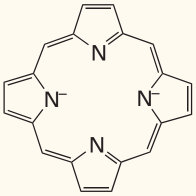
33.2 Suppose that a methane molecule became distorted to (a) C_{3v} symmetry by the lengthening of one bond, (b) C_{2v} symmetry by a kind of scissors action in which one bond angle opened and another closed slightly. Would more d orbitals become available for bonding?

33.3 Does the product $3x^2 - 1$ necessarily vanish when integrated over (a) a cube, (b) a tetrahedron, (c) a hexagonal prism, each centred on the origin?

33.4‡ In a spectroscopic study of C_{60}, Negri, et al. (*J. Phys. Chem.* **100**, 10849 (1996)) assigned peaks in the fluorescence spectrum. The molecule has icosahedral symmetry (I_h). The ground electronic state is A_{1g}, and the lowest-lying excited states are T_{1g} and G_g. (a) Are photon-induced transitions allowed from the ground state to either of these excited states? Explain your answer. (b) What if the molecule is distorted slightly so as to remove its centre of inversion?

33.5 In the square planar XeF_4 molecule, consider the symmetry-adapted linear combination $p_1 = p_A - p_B + p_C - p_D$ where p_A, p_B, p_C, and p_D are $2p_z$ atomic orbitals on the fluorine atoms (clockwise labelling of the F atoms). Using the reduced point group D_4 rather than the full symmetry point group of the molecule, determine which of the various s, p, and d atomic orbitals on the central Xe atom can form molecular orbitals with p_1.

33.6 The chlorophylls that participate in photosynthesis and the haem groups of cytochromes are derived from the porphine dianion group (**10**), which belongs to the D_{4h} point group. The ground electronic state is A_{1g} and the lowest-lying excited state is E_u. Is a photon-induced transition allowed from the ground state to the excited state? Explain your answer.



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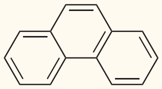
33.7 The NO_2 molecule belongs to the group C_{2v}, with the C_2 axis bisecting the ONO angle. Taking as a basis the N2s, N2p, and O2p orbitals, identify the irreducible representations they span, and construct the symmetry-adapted linear combinations.

33.8 Construct the symmetry-adapted linear combinations of $C2p_z$ orbitals for benzene, and use them to calculate the Hückel secular determinant. This procedure leads to equations that are much easier to solve than using the original orbitals, and show that the Hückel orbitals are those specified in Topic 26.

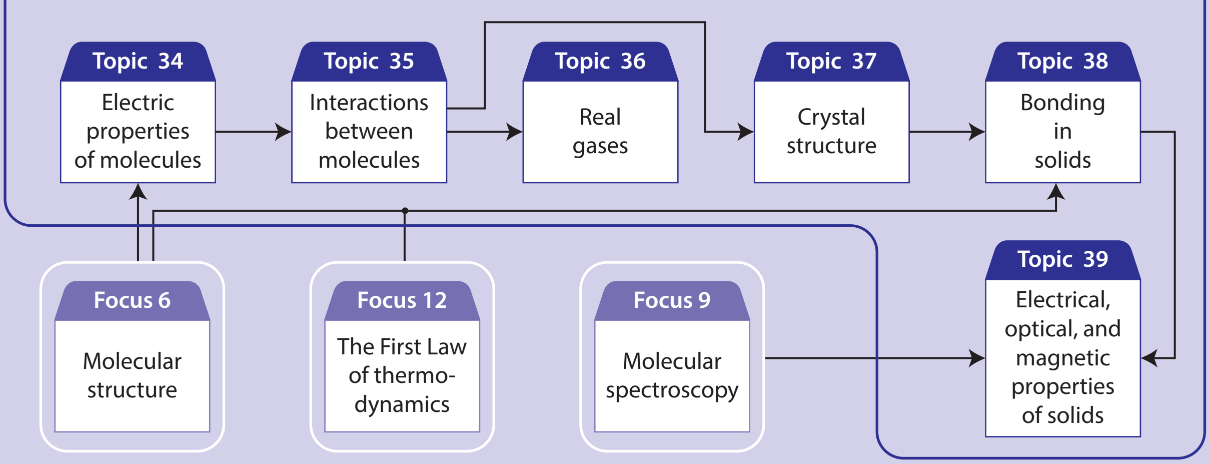
33.9 The phenanthrene molecule (**11**) belongs to the group C_{2v} with the C_2 axis in the plane of the molecule. (a) Classify the irreducible representations spanned by the carbon $2p_z$ orbitals and find their symmetry-adapted linear combinations. (b) Use your results from part (a) to calculate the Hückel secular determinant. (c) What states of phenanthrene may be reached by electric dipole transitions from its (totally symmetrical) ground state?



11 Phenanthrene

33.10 Some linear polyenes, of which β-carotene is an example, are important biological cofactors that participate in processes as diverse as the absorption of solar energy in photosynthesis and protection against harmful biological oxidations. Use as a model of β-carotene a linear polyene containing 22 conjugated C atoms. (a) To what point group does this model of β-carotene belong? (b) Classify the irreducible representations spanned by the carbon $2p_z$ orbitals and find their symmetry-adapted linear combinations. (c) Use your results from part (b) to calculate the Hückel secular determinant. (d) What states of this model of β-carotene may be reached by electric dipole transitions from its (totally symmetrical) ground state?

FOCUS 8 ON Interactions



From a knowledge of electrostatics (*Foundations*, Topic 2) and *Molecular structure* it is possible to construct models for the interactions between atoms or molecules. The result is a better understanding of the factors that govern the properties of gases at high pressure and the structures and properties of liquids and solids.

We begin with an account of the electric properties of molecules, such as 'electric dipole moments' and 'polarizabilities' (**Topic 34**). All these properties reflect the degree to which the nuclei of atoms exert control over the electrons in a molecule. The description of the basic theory of interactions then focuses on 'van der Waals interactions' between closed-shell molecules and 'hydrogen bonding' (**Topic 35**). All liquids and solids are bound together by one or more of these cohesive interactions. Deviations from perfect gas behaviour and the thermodynamic properties of 'real gases' are also explained in terms of these interactions (**Topic 36**).

The solid state includes most of the materials that make modern technology possible. To understand solids, it is necessary to understand the regular arrangement of atoms in crystals and the symmetry of their arrangement. The basic principles of 'X-ray diffraction' are central to the determination of structures and we explain how the diffraction pattern obtained in this technique is interpreted in terms of the distribution of electron density in a 'unit cell' (**Topic 37**). X-ray diffraction studies lead to important information about the structures of metallic, ionic, and molecular solids (**Topic 38**). The energetics of ionic solids can be understood using concepts introduced in *The First Law of thermodynamics*. Equipped with a knowledge of structural features, and aided by the principles of *Molecular spectroscopy*, we show how the electrical, optical, and magnetic properties of solids stem from the arrangement and properties of the constituent atoms (**Topic 39**).

What is the impact of this material?

Interactions between atoms or molecules play important roles in biochemistry, biomedicine, and technology. Biological polymers can be studied by X-ray diffraction (*Impact* 8.1), which reveals the importance of molecular interactions in establishing the three-dimensional structures and biochemical functions of proteins and nucleic acids (*Impact* 8.2), and the ways in which drugs bind to receptor sites in biopolymers, leading to the inhibition of the progress of disease (*Impact* 8.3). The manipulation of molecular interactions could have significant technological consequences. One example is the design of assemblies that can store and deliver hydrogen gas efficiently, thereby making it a viable fuel for commercial development of a host of devices (*Impact* 8.4). Another is the synthesis of 'nanowires', nanometre-sized atomic assemblies that conduct electricity, which is a major step in the fabrication of a new generation of electronic devices (*Impact* 8.5).

To read more about the impact of this material, scan the QR code or go to http://bcs.whfreeman.com/webpub/chemistry/qmc2e/impact/qchem_impact8.html.

TOPIC 34

Electric properties of molecules

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➤ Why do you need to know this material?

Because the molecular interactions responsible for the formation of condensed phases and large molecular assemblies (and which are treated in Topic 35) arise from the electric properties of molecules, you need to know how the electronic structures of molecules lead to these properties.

➤ What is the key idea?

The nuclei of atoms exert control over the electrons in a molecule and can cause electrons to accumulate in particular regions, or permit them to respond more or less strongly to the effects of external fields.

➤ What do you need to know already?

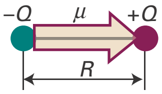
You need to be familiar with the Coulomb law (*Foundations*, Topic 2), molecular geometry (from introductory chemistry), and molecular orbital theory, especially the relevance of the energy gap between a HOMO and LUMO (Topic 26).

The electric properties of molecules are responsible for many of the properties of bulk matter. The small imbalances of charge distributions in molecules allow them to interact with one another and with externally applied fields. One result of this interaction is the weak cohesion of molecules to form the bulk phases of matter. Molecular interactions are also responsible for the shapes adopted by biological and synthetic macromolecules.

34.1 Electric dipole moments

An **electric dipole** consists of two electric charges $+Q$ and $-Q$ with a separation R. A **point electric dipole** is an electric dipole in which R is very small compared with its distance from the observer. The **electric dipole moment** is a vector $\boldsymbol{\mu}$ (**1**) that points from the negative charge to the positive charge and has a magnitude given by

$$\mu = QR \quad \textit{Definition} \quad \text{Magnitude of the electric dipole moment} \qquad (34.1)$$



1 Electric dipole

Although the SI unit of dipole moment is coulomb metre (C m), it is still commonly reported in the non-SI unit debye, D, named after Peter Debye, a pioneer in the study of dipole moments of molecules:

$$1\,\text{D} = 3.335\,64 \times 10^{-30}\,\text{C m} \qquad (34.2)$$

The magnitude of the dipole moment of a pair of charges $+e$ and $-e$ separated by 100 pm is 1.6×10^{-29} C m, corresponding to 4.8 D. The magnitudes of dipole moments of small molecules are typically about 1 D.[1]

A **polar molecule** is a molecule with a permanent electric dipole moment. The permanent dipole moment stems from

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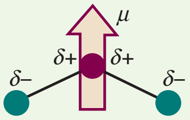
[1] The conversion factor in eqn 34.2 stems from the original definition of the debye in terms of c.g.s. units: 1 D is the dipole moment of two equal and opposite charges of magnitude 1 e.s.u. separated by 1 Å.

the partial charges on the atoms in the molecule that arise from differences in electronegativity or other features of bonding (Topics 25 and 26). Nonpolar molecules acquire an induced dipole moment in an electric field on account of the distortion the field causes in their electronic distributions and nuclear positions; however, this induced moment is only temporary, and disappears as soon as the perturbing field is removed. Polar molecules also have their existing dipole moments temporarily modified by an applied field.

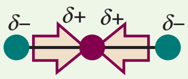
All heteronuclear diatomic molecules are polar, and typical values of μ include 1.08 D for HCl and 0.42 D for HI (Table 34.1). Molecular symmetry is of the greatest importance in deciding whether a polyatomic molecule is polar or not (see also Topics 31 and 32). Indeed, molecular symmetry is more important than the question of whether or not the atoms in the molecule belong to the same element. For this reason, and as we see in *Brief illustration* 34.1, homonuclear polyatomic molecules may be polar if they have low symmetry and the atoms are in non-equivalent positions.

Brief illustration 34.1 Symmetry and the polarity of molecules

The angular molecule ozone (**2**) is homonuclear. However, it is polar because the central O atom is different from the outer two (it is bonded to two atoms, which are each bonded only to one). Moreover, the dipole moments associated with each bond make an angle to each other and do not cancel. The heteronuclear linear triatomic molecule CO_2 (**3**) is nonpolar because, although there are partial charges on all three atoms, the dipole moment associated with the OC bond points in the opposite direction to the dipole moment associated with the CO bond, and the two cancel.



2 Ozone, O_3



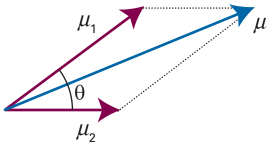
3 Carbon dioxide, CO_2

Self-test 34.1 Is SO_2 polar?

Answer: Yes

To a good first approximation, the dipole moment of a polyatomic molecule can be resolved into contributions from various groups of atoms in the molecule and their relative locations (Fig. 34.1). Thus, 1,4-dichlorobenzene is nonpolar by symmetry on account of the cancellation of two equal but opposing C–Cl moments (exactly as in carbon dioxide). 1,2-Dichlorobenzene, however, has a dipole moment which is approximately the resultant of two chlorobenzene dipole moments arranged at 60° to each other. This technique of 'vector addition' can be applied with fair success to other series of related molecules, and the magnitude of the resultant, $\boldsymbol{\mu}_{\text{res}}$, of two dipole moments, $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$, that make an angle θ to each other (**4**) is approximately (see *Mathematical background* 4)

$$\mu_{\text{res}} \approx (\mu_1^2+\mu_2^2+2\mu_1\mu_2\cos\theta)^{1/2} \tag{34.3a}$$



4 Addition of dipole moments

When the two dipole moments have the same magnitude (as in the dichlorobenzenes), this equation simplifies to

$$\mu_{\text{res}} \approx \{2\mu_1^2(1+\cos\theta)\}^{1/2} \overset{1+\cos\theta=2\cos^2\frac{1}{2}\theta}{\widehat{=}} 2\mu_1\cos\tfrac{1}{2}\theta \tag{34.3b}$$

Brief illustration 34.2 Molecular dipole moments

Consider *ortho* (1,2-) and *meta* (1,3-) disubstituted benzenes, for which $\theta_{ortho}=60°$ and $\theta_{meta}=120°$. It follows from eqn 34.3 that the ratio of the magnitudes of the electric dipole moments is

$$\frac{\mu_{\text{res},ortho}}{\mu_{\text{res},meta}}=\frac{\cos\frac{1}{2}\theta_{ortho}}{\cos\frac{1}{2}\theta_{meta}}=\frac{\cos\left(\frac{1}{2}\times60°\right)}{\cos\left(\frac{1}{2}\times120°\right)}=\frac{(3)^{1/2}/2}{1/2}=(3)^{1/2}\approx1.7$$

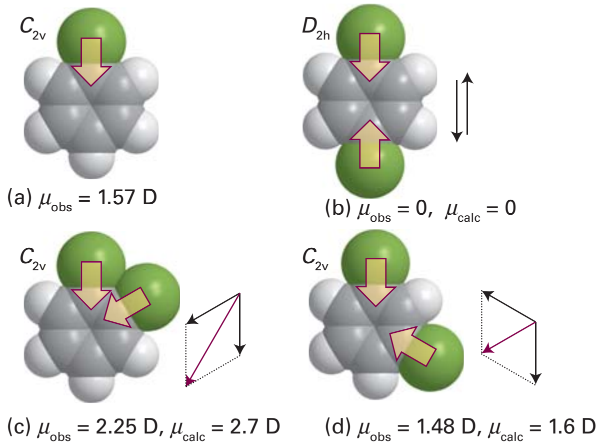
Self-test 34.2 Calculate the resultant magnitude of two dipole moments of magnitude 1.5 D and 0.80 D that make an angle of 109.5° to each other.

Answer: 1.4 D

A more reliable approach to the calculation of dipole moments is to take into account the locations and magnitudes of the partial charges on all the atoms. These partial charges are included in the output of many molecular structure software packages. To calculate the x-component, for instance, we need to know the partial charge on each atom and the atom's x-coordinate relative to a point in the molecule and form the sum

$$\mu_x=\sum_{\text{J}}Q_{\text{J}}x_{\text{J}} \tag{34.4a}$$

Here Q_{J} is the partial charge of atom J, x_{J} is the x-coordinate of atom J, and the sum is over all the atoms in the molecule. Analogous expressions are used for the y- and z-components.



(a) $\mu_{obs} = 1.57$ D

(b) $\mu_{obs} = 0$, $\mu_{calc} = 0$

(c) $\mu_{obs} = 2.25$ D, $\mu_{calc} = 2.7$ D

(d) $\mu_{obs} = 1.48$ D, $\mu_{calc} = 1.6$ D

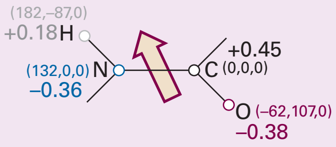
Figure 34.1 The resultant dipole moments (red) of the dichlorobenzene isomers (b to d) can be obtained approximately by vectorial addition of two chlorobenzene dipole moments (with magnitude 1.57 D). (The point groups of the molecules are also indicated.)

For an electrically neutral molecule, the origin of the coordinates is arbitrary, so it is best chosen to simplify the measurements. In common with all vectors, the magnitude of $\boldsymbol{\mu}$ is related to the three components μ_x, μ_y, and μ_z by

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \tag{34.4b}$$

Example 34.1 Calculating a molecular dipole moment

Estimate the electric dipole moment of the amide group shown in (5) by using the partial charges (as multiples of e) and the locations of the atoms shown, with distances in picometres.



5 Amide (peptide) link

Method We use eqn 34.4a to calculate each of the components of the dipole moment and then eqn 34.4b to assemble the three components into the magnitude of the dipole moment. Note that the partial charges are multiples of the fundamental charge, $e = 1.609 \times 10^{-19}$ C.

Answer The expression for μ_x is

$$\begin{aligned}\mu_x &= (-0.36e)\times(132\,\text{pm}) + (0.45e)\times(0\,\text{pm}) + (0.18e)\times(182\,\text{pm}) \\ &\quad + (-0.38e)\times(-62.0\,\text{pm}) \\ &= 8.8e\,\text{pm} \\ &= 8.8\times(1.602\times10^{-19}\,\text{C})\times(10^{-12}\,\text{m}) = 1.4\times10^{-30}\,\text{C m}\end{aligned}$$

corresponding to $\mu_x = +0.42$ D. The expression for μ_y is

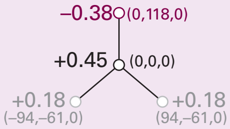
$$\begin{aligned}\mu_y &= (-0.36e)\times(0\,\text{pm}) + (0.45e)\times(0\,\text{pm}) + (0.18e)\times(-87\,\text{pm}) \\ &\quad + (-0.38e)\times(107\,\text{pm}) \\ &= -56e\,\text{pm} \\ &= -19.0\times10^{-30}\,\text{C m}\end{aligned}$$

It follows that $\mu_y = -2.7$ D. The amide group is planar, so $\mu_z = 0$ and

$$\mu = \{(0.42\,\text{D})^2 + (-2.7\,\text{D})^2\}^{1/2} = 2.7\,\text{D}$$

We can find the orientation of the dipole moment by arranging an arrow of length 2.7 units of length to have x, y, and z components of 0.42, –2.7, and 0 units, respectively; the orientation is superimposed on **5**.

Self-test 34.3 Calculate the electric dipole moment of formaldehyde by using the information in **6**.



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Answer: 2.3 D

Molecules may have higher **multipoles**, or arrays of point charges (Fig. 34.2). Specifically, an ***n*-pole** is an array of point charges with an n-pole moment but no lower moment. Thus, a **monopole** ($n=1$) is a point charge, and the monopole moment is what we normally call the overall charge. A dipole ($n=2$), as we have seen, is an array of charges that has no monopole moment (no net charge). A **quadrupole** ($n=3$) consists of an array of point charges that has neither net charge nor dipole moment (as for CO_2 molecules, **3**). An **octupole** ($n=4$) consists

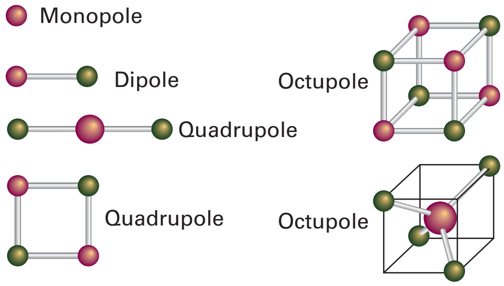
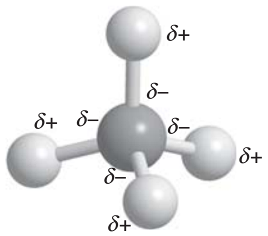


Figure 34.2 Typical charge arrays corresponding to electric multipoles. The field arising from an arbitrary finite charge distribution can be expressed as the superposition of the fields arising from a superposition of multipoles.

of an array of point charges that sum to zero and which has neither a dipole moment nor a quadrupole moment (as for CH_4 molecules, 7).



7 Methane, CH_4

34.2 Polarizabilities

The failure of nuclear charges to control the surrounding electrons totally means that those electrons can respond to external fields. Therefore, an applied electric field can distort a molecule as well as align its permanent electric dipole moment. When the applied field is weak, the magnitude of the **induced dipole moment**, μ^*, is proportional to the field strength, $\mathcal{E}$, and we write

$$\mu^* = \alpha \mathcal{E} \qquad \textit{Definition} \quad \text{Polarizability} \qquad (34.5a)$$

The constant of proportionality α is the **polarizability** of the molecule. The greater the polarizability, the larger is the induced dipole moment for a given applied field. In a formal treatment, we should use vector quantities and allow for the possibility that the induced dipole moment might not lie parallel to the applied field, but for simplicity we discuss polarizabilities in terms of (scalar) magnitudes.

When the applied field is very strong (as in tightly focused laser beams), the induced dipole moment is not strictly linear in the strength of the field, and we write

$$\mu^* = \alpha \mathcal{E} + \tfrac{1}{2}\beta \mathcal{E}^2 + \ldots \qquad \textit{Definition} \quad \text{Hyperpolarizability} \qquad (34.5b)$$

The coefficient β is called the **hyperpolarizability** of the molecule.

Polarizability has the units (coulomb metre)^2 per joule ($C^2\ m^2\ J^{-1}$). That collection of units is awkward, so α is often expressed as a **polarizability volume**, α', by using the relation

$$\alpha' = \frac{\alpha}{4\pi\varepsilon_0} \qquad \textit{Definition} \quad \text{Polarizability volume} \qquad (34.6)$$

where ε_0 is the vacuum permittivity (*Foundations*, Topic 2). Because the units of $4\pi\varepsilon_0$ are coulomb-squared per joule per metre ($C^2\ J^{-1}\ m^{-1}$), it follows that α' has the dimensions of volume (hence its name). Polarizability volumes are similar in magnitude to actual molecular volumes (of the order of 10^{-30} m^3, 10^{-3} nm^3, 1 $Å^3$).

Brief illustration 34.3 The induced dipole moment

The polarizability volume of H_2O is 1.48×10^{-30} m^3. It follows from eqns 34.5a and 34.6 that $\mu^* = 4\pi\varepsilon_0\alpha'\mathcal{E}$ and the dipole moment of the molecule (in addition to the permanent dipole moment) induced by an applied electric field of strength 1.0×10^5 V m^{-1} is

$$\begin{aligned}\mu^* &= 4\pi \times (8.854\times10^{-12}\ J^{-1}\ C^2\ m^{-1}) \times (1.48\times10^{-30}\ m^3) \\ &\quad \times (1.0\times10^5\ J\ C^{-1}\ m^{-1}) \\ &= 31.6\times10^{-35}\ C\ m = 4.9\times10^{-6}\ D = 4.9\ \mu D\end{aligned}$$

where we have used 1 V = 1 J C^{-1}.

Self-test 34.4 What strength of electric field is required to induce an electric dipole moment of magnitude 1.0 μD in a molecule of polarizability volume 2.6×10^{-30} m^3 (like CO_2)?

Answer: 11 kV m^{-1}

The experimental polarizability volumes of some molecules are given in Table 34.1. As shown in the following *Justification*, polarizability volumes correlate with the HOMO–LUMO separations in atoms and molecules (Topic 26). The electron distribution can be distorted readily if the LUMO lies close to the HOMO in energy, so the polarizability is then large. If the LUMO lies high above the HOMO, an applied field cannot perturb the electron distribution significantly, and the polarizability is low. Molecules with small HOMO–LUMO gaps are typically large, with numerous electrons.

Table 34.1* Magnitudes of dipole moments (μ) and polarizability volumes (α')

	μ/D	$\alpha'/(10^{-30}\ m^3)$
CCl_4	0	10.3
H_2	0	0.819
H_2O	1.85	1.48
HCl	1.08	2.63
HI	0.42	5.45

* More values are given in the *Resource section*.

Justification 34.1 Polarizabilities and molecular structures

The energy E of a molecule in an electric field of magnitude $\mathcal{E}$ is related to the molecular dipole moment by

$$E = -\mu\mathcal{E}$$

It follows that when the electric field is increased by dE, the energy changes by $-\mu \mathrm{d}\mathcal{E}$ and, if the molecule is polarizable, we interpret μ as the induced dipole moment μ^* (eqn 34.5). Therefore, the change in energy when the field is increased from 0 to $\mathcal{E}$ is

$$\Delta E = -\int_0^{\mathcal{E}} \mu^* \,\mathrm{d}\mathcal{E} = -\int_0^{\mathcal{E}} \alpha\mathcal{E}\mathrm{d}\mathcal{E} = -\frac{1}{2}\alpha\mathcal{E}^2$$

The contribution to the hamiltonian when a dipole moment is exposed to an electric field $\mathcal{E}$ in the z-direction is

$$\hat{H}^{(1)} = -\hat{\mu}_z\mathcal{E}$$

Comparison of these two expressions suggests that we should use second-order perturbation theory to calculate the energy of the system in the presence of the field, because then we shall obtain an expression proportional to $\mathcal{E}^2$. According to eqn 15.6 of Topic 15, the second-order contribution to the ground-state energy is

$$E^{(2)} = \sum_{n\neq 0} \frac{\left|\int \psi_n^* \hat{H}^{(1)} \psi_0 \mathrm{d}\tau\right|^2}{E_0^{(0)} - E_n^{(0)}} = \mathcal{E}^2 \sum_{n\neq 0} \frac{\left|\int \psi_n^* \hat{\mu}_z \psi_0 \mathrm{d}\tau\right|^2}{E_0^{(0)} - E_n^{(0)}}$$
$$= \mathcal{E}^2 \sum_{n\neq 0} \frac{\left|\mu_{z,0n}\right|^2}{E_0^{(0)} - E_n^{(0)}}$$

where $\mu_{z,0n} = \int \psi_n^* \hat{\mu}_z \psi_0 \mathrm{d}\tau$ is the *transition* electric dipole moment in the z-direction. Transition dipole moments are introduced in Topic 16 and discussed further in Topic 45: for our purposes here they can be interpreted as the electric dipole moment associated with the migration of electron density from the distribution ψ_0 to the distribution ψ_n and ψ_i, and $E_i^{(0)}$ are the wavefunctions and energies, respectively, in the absence of the electric field. By comparing the two expressions for the energy, we conclude that the polarizability of the molecule in the z-direction is

$$\alpha = 2\sum_{n\neq 0} \frac{\left|\mu_{z,0n}\right|^2}{E_n^{(0)} - E_0^{(0)}} \tag{34.7}$$

The content of eqn 34.7 can be appreciated by approximating the excitation energies by a mean value ΔE (an indication of the HOMO–LUMO separation) and supposing that the most important transition dipole moment is approximately equal to the charge of an electron multiplied by the molecular radius, R, of the molecule. then

$$\alpha \approx \frac{2e^2R^2}{\Delta E}$$

This expression shows that α increases with the size of the molecule and with the ease with which it can be excited (the smaller the value of ΔE).

If the excitation energy is approximated by the energy needed to remove an electron to infinity from a distance R from a single positive charge, we can write $\Delta E \approx e^2/(4\pi\varepsilon_0 R)$. When this expression is substituted into the equation above, both sides are divided by $4\pi\varepsilon_0$, and the factor of 2 is ignored in this approximation, we obtain $\alpha' \approx R^3$, which is of the same order of magnitude as the molecular volume.

For most molecules, the polarizability is anisotropic, by which is meant that its value depends on the orientation of the molecule relative to the field. The polarizability volume of benzene when the field is applied perpendicular to the ring is 0.0067 nm^3 and it is 0.0123 nm^3 when the field is applied in the plane of the ring.

Checklist of concepts

☐ 1. An **electric dipole** consists of two electric charges $+Q$ and $-Q$ separated by a distance R.
☐ 2. The **electric dipole moment** $\boldsymbol{\mu}$ is a vector that points from the negative charge to the positive charge of a dipole.
☐ 3. A **polar molecule** is a molecule with a permanent electric dipole moment.
☐ 4. Molecules may have higher electric multipoles: an ***n*-pole** is an array of point charges with an n-pole moment but no lower moment.
☐ 5. The **polarizability** is a measure of the ability of an electric field to induce a dipole moment in a molecule.
☐ 6. **Polarizabilities** (and polarizability volumes) correlate with the HOMO–LUMO separations in atoms and molecules.
☐ 7. For most molecules, the polarizability is anisotropic.

Checklist of equations

Property	Equation	Comment	Equation number
Magnitude of the electric dipole moment	$\mu = QR$	Definition	34.1
Magnitude of the resultant of two dipole moments	$\mu_{\text{res}} \approx (\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta)^{1/2}$		34.3a
Magnitude of the induced dipole moment	$\mu^* = \alpha\mathcal{E}$	Linear approximation; α is the polarizability	34.5a
	$\mu^* = \alpha\mathcal{E} + \frac{1}{2}\beta\mathcal{E}^2$	Quadratic approximation; β is the hyperpolarizability	34.5b
Polarizability volume	$\alpha' = \alpha/4\pi\varepsilon_0$	Definition	34.6

TOPIC 35

Interactions between molecules

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➤ Why do you need to know this material?

You need to understand the many types of molecular interactions responsible for the formation of condensed phases and large molecular assemblies. The molecular interactions described here are of prime importance for solving one of the great problems of molecular biology: how complex molecules, like proteins and nucleic acids, fold into their three-dimensional structures.

➤ What is the key idea?

Attractive interactions result in cohesion but repulsive interactions prevent the complete collapse of matter to nuclear densities.

➤ What do you need to know already?

You need to be familiar with electrostatics, specifically the Coulomb interaction (*Foundations*, Topic 2), and with the relationships between the structure and electric properties of a molecule, specifically its dipole moment and polarizability (Topic 34).

We begin by examining the interactions between the partial charges of polar molecules. Then we discuss **van der Waals interactions**: attractive interactions between closed-shell molecules that depend on the separation of the molecules as the inverse sixth power ($V \propto 1/r^6$), although this precise criterion is often relaxed to include all nonbonding interactions. Finally, we see that repulsive interactions arise from Coulomb forces and, indirectly, from the Pauli principle (Topic 19) and the exclusion of electrons from regions of space where the orbitals of neighbouring species overlap.

35.1 Interactions between partial charges

In general, atoms in molecules have partial charges arising from the spatial variation in electron density in the ground state. If these charges were separated by a vacuum, they would attract or repel each other in accord with Coulomb's law (*Foundations*, Topic 2), and we would write

$$V = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r} \qquad \textit{Vacuum} \quad \text{Coulomb potential energy} \qquad (35.1a)$$

where Q_1 and Q_2 are the partial charges, r is their separation, and ε_0 is the vacuum permittivity. However, we should take into account the possibility that other parts of the molecule, or other molecules, lie between the charges and decrease the strength of the interaction. We therefore write

$$V = \frac{Q_1 Q_2}{4\pi\varepsilon r} \qquad \textit{Any medium} \qquad \text{Coulomb potential energy} \qquad (35.1b)$$

where ε is the permittivity of the medium lying between the charges. The permittivity is usually expressed as a multiple of the vacuum permittivity by writing $\varepsilon = \varepsilon_r \varepsilon_0$, where ε_r is the relative permittivity (formerly known as the *dielectric constant*). The effect of the medium can be very large: for water $\varepsilon_r = 78$, so the potential energy of two charges separated by bulk water is reduced by nearly two orders of magnitude compared to the value it would have if the charges were separated by a vacuum (Fig. 35.1).

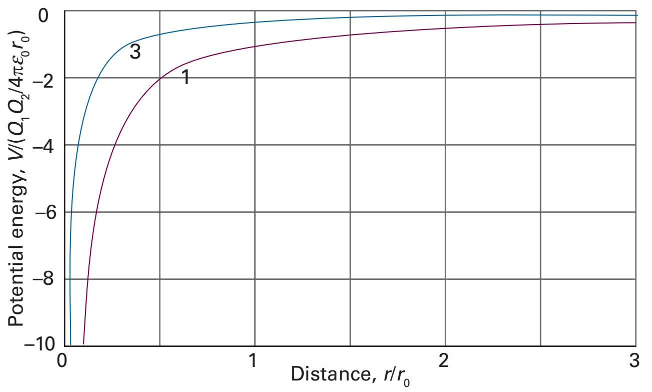


Figure 35.1 The Coulomb potential for two (opposite) charges and its dependence on their separation. The two curves correspond to different relative permittivities ($\varepsilon_r = 1$ for a vacuum, $\varepsilon_r = 3$ for a fluid; r_0 is a scaling factor).

Brief illustration 35.1 The interaction energy of two partial charges

The energy of interaction between a partial charge of −0.36 (that is, $Q_1 = -0.36e$) on the N atom of an amide group and the partial charge of +0.45 ($Q_2 = +0.45e$) on the carbonyl C atom at a distance of 3.0 nm, on the assumption that the medium between them is a vacuum, is

$$\begin{aligned} V &= -\frac{(0.36e)\times(0.45e)}{4\pi\varepsilon_0 \times (3.0\,\text{nm})} \\ &= -\frac{0.36\times 0.45\times(1.602\times 10^{-19}\,\text{C})^2}{4\pi\times(8.854\times 10^{-2}\,\text{J}^{-1}\text{C}^{-2}\text{m}^{-1})\times(3.0\times 10^{-9}\,\text{m})} \\ &= -1.2\times 10^{-20}\,\text{J} \end{aligned}$$

This energy (after multiplication by Avogadro's constant) corresponds to $-7.5\,\text{kJ mol}^{-1}$. However, if the medium has a 'typical' relative permittivity of 3.5, then the interaction energy is reduced by that factor to $-2.1\,\text{kJ mol}^{-1}$.

Self-test 35.1 Repeat the calculation for bulk water as the medium.

Answer: $-0.96\,\text{kJ mol}^{-1}$

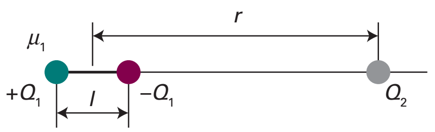
35.2 The interactions of dipoles

Most of the discussion in this and the following sections is based on the Coulombic potential energy of interaction between two charges (eqn 35.1a). This expression can be adapted to find the potential energy of a point charge and a dipole and extend it to the interaction between two dipoles.

(a) Charge–dipole interactions

A **point dipole** is a dipole in which the separation l between the charges is much smaller than the distance r at which the dipole is being observed ($l \ll r$). We show in the following *Justification* that the potential energy of interaction between a point dipole with a dipole moment of magnitude $\mu_1 = Q_1 l$ and the point charge Q_2 in the arrangement shown in **1** is

$$V = -\frac{\mu_1 Q_2}{4\pi\varepsilon_0 r^2} \qquad \text{Energy of interaction between a point dipole and a point charge} \qquad (35.2)$$



1

With μ in coulomb metres, Q_2 in coulombs, and r in metres, V is obtained in joules. The potential energy rises towards zero (the value at infinite separation of the charge and the dipole) more rapidly (as $1/r^2$) than that between two point charges (which varies as $1/r$) because, from the viewpoint of the point charge, the partial charges of the dipole seem to merge and cancel as the distance r increases (Fig. 35.2).

Justification 35.1 The interaction between a point charge and a point dipole

The sum of the potential energies of repulsion between like charges and attraction between opposite charges in the orientation shown in **1** is

$$V=\frac{1}{4\pi\varepsilon_0}\left(-\frac{Q_1Q_2}{r-\frac{1}{2}l}+\frac{Q_1Q_2}{r+\frac{1}{2}l}\right)=\frac{Q_1Q_2}{4\pi\varepsilon_0 r}\left(-\frac{1}{1-x}+\frac{1}{1+x}\right)$$

where $x=l/2r$. Because $l \ll r$ for a point dipole, this expression can be simplified by expanding the terms in x by using (*Mathematical background* 1)

$$\frac{1}{1+x}=1-x+x^2-\cdots \qquad \frac{1}{1-x}=1+x+x^2+\cdots$$

and retaining only the leading surviving term:

$$V=-\frac{2xQ_1Q_2}{4\pi\varepsilon_0 r}=-\frac{2Q_1Q_2 l}{4\pi\varepsilon_0 r^2}$$

With $\mu_1 = Q_1 l$, this expression becomes eqn 35.2. The equation should be multiplied by $\cos\theta$ when the point charge lies at an angle θ to the axis of the dipole.

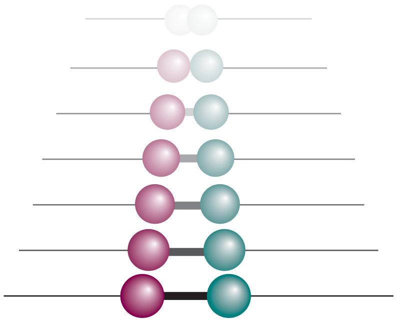


Figure 35.2 There are two contributions to the diminishing field of an electric dipole with distance (here seen from the side). The potentials of the charges decrease (shown here by a fading intensity) and the two charges appear to merge, so their combined effect approaches zero more rapidly than by the distance effect alone.

Brief illustration 35.2 The energy of interaction of a point charge and a point dipole

Consider a Li^+ and a water molecule ($\mu = 1.85$ D) separated by 1.0 nm, with the point charge on the ion and the dipole of the molecule arranged as in **1**. The energy of interaction is given by eqn 35.2 as

$$V=-\frac{\overbrace{(1.602\times10^{-19}\,\mathrm{C})}^{Q_{\mathrm{Li}^+}}\times\overbrace{(1.85\times3.336\times10^{-30}\,\mathrm{C\,m})}^{\mu_{\mathrm{H_2O}}}}{4\pi\times\underbrace{(8.854\times10^{-12}\,\mathrm{J^{-1}C^{-1}m^{-1}})}_{\varepsilon_0}\times\underbrace{(1.0\times10^{-9}\,\mathrm{m})}_{r}{}^{-2}}$$
$$=-8.9\times10^{-21}\,\mathrm{J}$$

This energy corresponds to -5.4 kJ mol^{-1}.

Self-test 35.2 Consider the arrangement in **1** and calculate the molar energy required to reverse the direction of the water molecule when it is at 300 pm from the Li^+ ion.

Answer: 119 kJ mol^{-1}

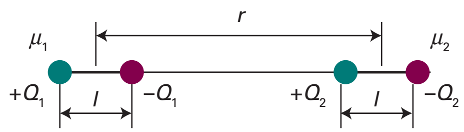
(b) Dipole–dipole interactions

We show in the following *Justification* that the preceding discussion can be extended to the interaction of two dipoles arranged as in **2**. The result is

$$V=-\frac{\mu_1\mu_2}{2\pi\varepsilon_0 r^3} \qquad (35.3)$$

*Arrangement as in **2***

Energy of interaction between two dipoles



2

This interaction energy approaches zero more rapidly (as $1/r^3$) than for the previous case: now both interacting entities appear neutral to each other at large separations.

Justification 35.2 The interaction energy of two dipoles

To calculate the potential energy of interaction of two dipoles separated by r in the arrangement shown in **2** we proceed in exactly the same way as in *Justification* 35.1, but now the total interaction energy is the sum of four pairwise terms, two attractions between opposite charges, which contribute negative terms to the potential energy, and two repulsions between like charges, which contribute positive terms.

The sum of the four contributions is

$$V=\frac{1}{4\pi\varepsilon_0}\left(-\frac{Q_1Q_2}{r+l}+\frac{Q_1Q_2}{r}+\frac{Q_1Q_2}{r}-\frac{Q_1Q_2}{r-l}\right)$$
$$=-\frac{Q_1Q_2}{4\pi\varepsilon_0 r}\left(\frac{1}{1+x}-2+\frac{1}{1-x}\right)$$

with $x=l/r$. As before, provided $l \ll r$ we can expand the two terms in x and retain only the first surviving term, which is equal to $2x^2$. This step results in the expression

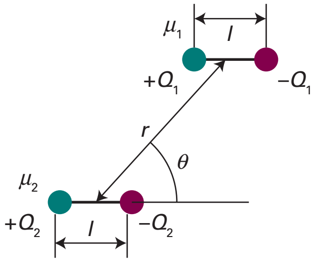
$$V=-\frac{2x^2Q_1Q_2}{4\pi\varepsilon_0 r}$$

Therefore, because $\mu_1=Q_1 l$ and $\mu_2=Q_2 l$, the potential energy of interaction in the alignment shown in **2** is given by eqn 35.3.

Justification 35.2 represents only one possible orientation of two dipoles. More generally, the potential energy of interaction between two polar molecules is a complicated function of their relative orientation. When the two dipoles are parallel and arranged as in **3**, the potential energy is simply

$$V = \frac{\mu_1 \mu_2 f(\theta)}{4\pi\varepsilon_0 r^3} \qquad f(\theta) = 1 - 3\cos^2\theta \qquad (35.4)$$

Energy of interaction between two fixed parallel dipoles



3

Brief illustration 35.3 The dipolar interaction

We can use eqn 35.4 to calculate the molar potential energy of the dipolar interaction between two amide groups. Supposing that the groups are separated by 3.0 nm with $\theta = 180°$ (so that $\cos\theta = -1$ and $1 - 3\cos^2\theta = -2$), we take $\mu_1 = \mu_2 = 2.7$ D, corresponding to 9.1×10^{-30} C m, and find

$$V = \frac{\overbrace{(9.1\times10^{-30}\,\mathrm{C\,m})^2}^{\mu_1\mu_2} \times \overbrace{(-2)}^{1-3\cos^2\theta}}{4\pi \times \underbrace{(8.854\times10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}})}_{\varepsilon_0} \times \underbrace{(3.0\times10^{-9}\,\mathrm{m})^3}_{r^3}}$$
$$= \frac{(9.1\times10^{-30})^2 \times (-2)}{4\pi \times (8.854\times10^{-12}) \times (3.0\times10^{-9})^3} \frac{\mathrm{C^2\,m^2}}{\mathrm{J^{-1}\,C^2\,m^{-1}\,m^3}}$$
$$= -5.5\times10^{-23}\,\mathrm{J}$$

where we have used 1 V C = 1 J. This value corresponds to –33 J mol^{-1}. Note that this energy is considerably less than that between two partial charges at the same separation (see *Brief illustration* 35.1).

Self-test 35.3 Repeat the calculation for an amide group and a water molecule separated by 3.5 nm with $\theta = 90°$, in a medium with relative permittivity of 3.5.

Answer: –2.1 J mol^{-1}

Equation 35.4 applies to polar molecules in a fixed, parallel orientation in a solid. In a fluid of freely rotating molecules, the interaction between dipoles averages to zero because $f(\theta)$ changes sign as the orientation changes, and its average value is zero. Physically, the like partial charges of two freely rotating molecules are as close together as the two opposite charges, and the repulsion of the former is cancelled by the attraction of the latter. Mathematically, this result arises from the fact that, as we show in the following *Justification*, the average (or mean value) of the function $1 - 3\cos^2\theta$ is zero.

Justification 35.3 The dipolar interaction between two freely rotating molecules

Consider the unit sphere shown in Fig. 35.3. The average value (or mean value) of $f(\theta) = 1 - 3\cos^2\theta$ is the sum of its values in each of the infinitesimal regions on the surface of the sphere (that is, the integral of the function over the surface) divided by the surface area of the sphere (which is equal to 4π). With the area element in spherical polar coordinates as $\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$, θ ranging from 0 to π, and ϕ ranging from 0 to 2π, the average value $\langle f(\theta)\rangle$ of $f(\theta)$ is

$$\langle f(\theta)\rangle = \frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi}(1-3\cos^2\theta)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$
$$= \frac{1}{4\pi}\int_0^{2\pi}\mathrm{d}\phi\int_0^{\pi}(1-3\cos^2\theta)\sin\theta\,\mathrm{d}\theta$$
$$= \frac{1}{2}\int_0^{\pi}(1-3\cos^2\theta)\sin\theta\,\mathrm{d}\theta$$

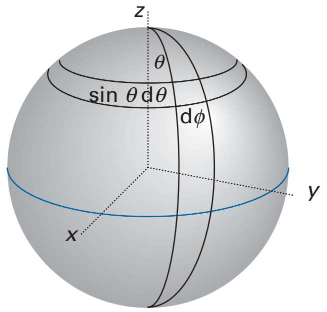


Figure 35.3 A unit sphere showing the area element $\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$.

The integral is calculated as follows:

$$\int_0^{\pi}(1-3\cos^2\theta)\sin\theta\,\mathrm{d}\theta = \int_0^{\pi}\sin\theta\,\mathrm{d}\theta - 3\int_0^{\pi}\cos^2\theta\overbrace{\sin\theta\,\mathrm{d}\theta}^{-\mathrm{d}\cos\theta}$$
$$\overset{\text{Integrals T.1 and T.10}}{=} -\cos\theta\Big|_0^{\pi} - 3\left(-\frac{1}{3}\cos^3\theta\Big|_0^{\pi}\right)$$
$$= \overbrace{-\cos\theta\Big|_0^{\pi}}^{+2} + \overbrace{\cos^3\theta\Big|_0^{\pi}}^{-2} = 0$$

where we have used the standard forms listed in the *Resource section*. It follows that $\langle f(\theta)\rangle = 0$, and, from eqn 35.4, that the dipolar interaction between two freely rotating molecules vanishes.

The interaction energy of two *freely* rotating dipoles is zero. However, because their mutual potential energy depends on their relative orientation, the molecules do not in fact rotate completely freely, even in a gas. In fact, the lower-energy orientations are marginally favoured, so there is a nonzero average interaction between polar molecules. We show in the following *Justification* that the average potential energy of two rotating molecules that are separated by a distance r is

$$\langle V\rangle=-\frac{C}{r^6}\qquad C=\frac{2\mu_1^2\mu_1^2}{3(4\pi\varepsilon_0)^2kT}\tag{35.5}$$

Average potential energy of two rotating polar molecules

This expression describes the **Keesom interaction**, and is the first of the contributions to the van der Waals interaction (when that is taken to be a $1/r^6$ interaction).

Justification 35.4 The Keesom interaction

The detailed calculation of the Keesom interaction energy is quite complicated, but the form of the final answer can be constructed quite simply. First, we note that the average interaction energy of two polar molecules rotating at a fixed separation r is given by

$$\langle V\rangle=\frac{\mu_1\mu_2\langle f(\theta)\rangle}{4\pi\varepsilon_0 r^3}$$

where $\langle f(\theta)\rangle$ now includes a weighting factor in the averaging that is equal to the probability that a particular orientation will be adopted. This probability is given by the Boltzmann distribution, $p\propto \mathrm{e}^{-E/kT}$, with E interpreted as the potential energy of interaction of the two dipoles in that orientation. That is,

$$p\propto \mathrm{e}^{-V/kT}\qquad V=\frac{\mu_1\mu_2 f(\theta)}{4\pi\varepsilon_0 r^3}$$

When the potential energy of interaction of the two dipoles is very small compared with the energy of thermal motion, we can use $V\ll kT$, expand the exponential function in p, and retain only the first two terms:

$$p\propto 1-V/kT+\cdots$$

We now write the weighted average of $f(\theta)$ as

$$\langle f(\theta)\rangle=\frac{\int_0^\pi f(\theta)p\,\mathrm{d}\theta}{\int_0^\pi \mathrm{d}\theta}=\frac{1}{\pi}\int_0^\pi f(\theta)p\,\mathrm{d}\theta=\frac{1}{\pi}\int_0^\pi f(\theta)(1-V/kT)\,\mathrm{d}\theta+\cdots$$

It follows that

$$\begin{aligned}\langle f(\theta)\rangle&=\frac{1}{\pi}\int_0^\pi f(\theta)\mathrm{d}\theta-\frac{1}{\pi}\int_0^\pi f(\theta)\big(V/kT\big)\mathrm{d}\theta+\cdots\\&=\frac{1}{\pi}\int_0^\pi f(\theta)\mathrm{d}\theta-\frac{1}{\pi}\int_0^\pi\frac{\mu_1\mu_2}{4\pi\varepsilon_0 kTr^3}f(\theta)^2\mathrm{d}\theta+\cdots\\&=\overbrace{\frac{1}{\pi}\int_0^\pi f(\theta)\mathrm{d}\theta}^{\langle f(\theta)_0\rangle}-\frac{\mu_1\mu_2}{4\pi\varepsilon_0 kTr^3}\overbrace{\left(\int_0^\pi\frac{1}{\pi}f(\theta)^2\mathrm{d}\theta\right)}^{\langle f(\theta)^2\rangle_0}+\cdots\\&=\langle f(\theta)\rangle_0-\frac{\mu_1\mu_2}{4\pi\varepsilon_0 kTr^3}\langle f(\theta)^2\rangle_0+\cdots\end{aligned}$$

where $\langle\cdots\rangle_0$ denotes an unweighted spherical average. The spherical average of $f(\theta)$ is zero (as in *Justification* 35.3), so the first term in the expression for $\langle f(\theta)\rangle$ vanishes. However, the average value of $f(\theta)^2$ is nonzero because $f(\theta)^2$ is positive at all orientations, so we can write

$$\langle V\rangle=-\frac{\mu_1^2\mu_1^2\langle f(\theta)^2\rangle_0}{\left(4\pi\varepsilon_0\right)^2 kTr^6}$$

The average value $\langle f(\theta)^2\rangle_0$ turns out to be 2/3 when the calculation is carried through in detail. The final result is that quoted in eqn 35.5.

The important features of eqn 35.5 are:

- The negative sign shows that the average interaction is attractive.
- The dependence of the average interaction energy on the inverse sixth power of the separation identifies it as a van der Waals interaction.
- The inverse dependence on the temperature reflects the way that the greater thermal motion overcomes the mutual orientating effects of the dipoles at higher temperatures.
- The inverse sixth power arises from the inverse third power of the interaction potential energy that is weighted by the energy in the Boltzmann term, which is also proportional to the inverse third power of the separation.

Physical interpretation

Brief illustration 35.4 The Keesom interaction

Suppose a water molecule ($\mu_1=1.85\,\mathrm{D}$) can rotate 1.0 nm from an amide group ($\mu_2=2.7\,\mathrm{D}$). The average energy of their interaction at 25 °C (298 K) is

$$\langle V\rangle = -\frac{2\times(\overbrace{1.85\times3.336\times10^{-30}\,\mathrm{C\,m}}^{\mu_1})^2\times(\overbrace{2.7\times3.336\times10^{-30}\,\mathrm{C\,m}}^{\mu_2})^2}{3\times(\underbrace{1.710\times10^{-43}\,\mathrm{J^{-1}\,C^{-2}\,m^{-2}\,K^{-1}}}_{(4\pi\varepsilon_0)^2k})\times(\underbrace{298\,\mathrm{K}}_{T})\times(\underbrace{1.0\times10^{-9}\,\mathrm{m}}_{r})^6}$$

This interaction energy corresponds (after multiplication by Avogadro's constant) to −24 J mol^{-1}, and it is much smaller than the energies involved in the making and breaking of chemical bonds.

> *A note on good practice* Note how the units are included in the calculation and cancel to give the result in joules. It is far better to include the units at each stage of the calculation and treat them as algebraic quantities that can be multiplied and cancelled than to guess the units at the end of the calculation.

Self-test 35.4 Calculate the average interaction energy for pairs of molecules in the gas phase with $\mu = 1$ D when the separation is 0.5 nm at 298 K. Compare this energy with the average molar kinetic energy of the molecules.

Answer: $\langle V\rangle = -0.07\,\mathrm{kJ\,mol^{-1}} \ll \frac{3}{2}RT = 3.7\,\mathrm{kJ\,mol^{-1}}$

Table 35.1 summarizes the various expressions for the interaction of charges and dipoles. It is quite easy to extend the formulas given there to obtain expressions for the energy of interaction of higher multipoles (electric multipoles are described in Topic 34). The feature to remember is that the interaction energy falls off more rapidly the higher the order of the multipole. For the interaction of an n-pole with an m-pole, the potential energy varies with distance as

$$V \propto \frac{1}{r^{n+m+1}} \qquad \text{Energy of interaction between multipoles} \qquad (35.6)$$

Table 35.1 Interaction potential energies

Interaction type	Distance dependence of potential energy	Typical energy (kJ mol^{-1})	Comment
Ion–ion	$1/r$	250	Only between ions
Hydrogen bond		20	Occurs in X–H···Y, where X, Y = N, O, or F
Ion–dipole	$1/r^2$	15	
Dipole–dipole	$1/r^3$	2	Between stationary polar molecules
	$1/r^6$	0.3	Between rotating polar molecules
London (dispersion)	$1/r^6$	2	Between all types of molecules and ions

The reason for the even steeper decrease with distance is the same as before: the array of charges appears to blend together into neutrality more rapidly with distance the higher the number of individual charges that contribute to the multipole. Note that a given molecule may have a charge distribution that corresponds to a superposition of several different multipoles, and in such cases the energy of interaction is the sum of terms given by eqn 35.6.

(c) Dipole–induced dipole interactions

A polar molecule with dipole moment μ_1 can induce a dipole in a neighbouring polarizable molecule (Fig. 35.4). The induced dipole interacts with the permanent dipole of the first molecule, and the two are attracted together. The average interaction energy when the separation of the molecules is r is

$$V = -\frac{C}{r^6} \qquad C = \frac{\mu_1^2\alpha_2'}{4\pi\varepsilon_0} \qquad \text{Potential energy of a polar molecule and a polarizable molecule} \qquad (35.7)$$

where α_2' is the polarizability volume (Topic 34) of molecule 2 and μ_1 is the magnitude of the permanent dipole moment of molecule 1. Note that the C in this expression is different from the C in eqn 35.5 and other expressions below: we are using the same symbol in C/r^6 to emphasize the similarity of form of each expression.

The dipole–induced dipole interaction energy is independent of the temperature because thermal motion has no effect on the averaging process. Moreover, like the dipole–dipole interaction, the potential energy depends on $1/r^6$: this distance dependence stems from the $1/r^3$ dependence of the field (and hence the magnitude of the induced dipole) and the $1/r^3$ dependence of the potential energy of interaction between the permanent and induced dipoles.

Brief illustration 35.5 The dipole–induced dipole interaction

For a molecule with $\mu = 1.0$ D (3.3×10^{-30} C m, such as HCl) separated by 0.30 nm from a molecule of polarizability volume $\alpha' = 10\times10^{-30}\,\mathrm{m^3}$ (such as benzene, Table 34.1), the average interaction energy is

$$V = -\frac{(3.3\times10^{-30}\,\mathrm{C\,m})^2\times(10\times10^{-30}\,\mathrm{m^3})}{4\pi\times(8.854\times10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}})\times(3.0\times10^{-10}\,\mathrm{m})^6}$$
$$= -1.4\times10^{-21}\,\mathrm{J}$$

which, upon multiplication by Avogadro's constant, corresponds to −0.83 kJ mol^{-1}.

Self-test 35.5 Calculate the average interaction energy, in units of joules per mole (J mol^{-1}), between a water molecule and a benzene molecule separated by 1.0 nm.

Answer: −2.1 J mol^{-1}

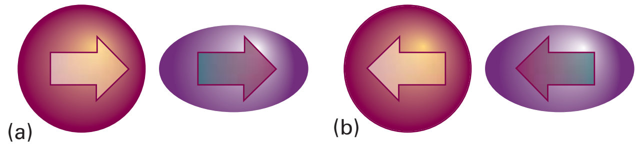


Figure 35.4 (a) A polar molecule (dark arrow) can induce a dipole (light arrow) in a nonpolar molecule, and (b) the orientation of the latter follows that of the former, so the interaction does not average to zero.

(d) Induced dipole–induced dipole interactions

Nonpolar molecules (including closed-shell atoms, such as Ar) attract one another even though neither has a permanent dipole moment. The abundant evidence for the existence of interactions between them is the formation of condensed phases of nonpolar substances, such as the condensation of hydrogen or argon to a liquid at low temperatures and the fact that benzene is a liquid at normal temperatures.

The interaction between nonpolar molecules arises from the transient dipoles that all molecules possess as a result of fluctuations in the instantaneous positions of electrons. To appreciate the origin of the interaction, suppose that the electrons in one molecule flicker into an arrangement that gives the molecule an instantaneous dipole moment of magnitude μ_1^*. This dipole generates an electric field that polarizes the other molecule, and induces in that molecule an instantaneous dipole moment of magnitude μ_2. The two dipoles attract each other and the potential energy of the pair is lowered. Although the first molecule will go on to change the size and direction of its instantaneous dipole, the electron distribution of the second molecule will follow; that is, the two dipoles are correlated in direction (Fig. 35.5). Because of this correlation, the attraction between the two instantaneous dipoles does not average to zero, and gives rise to an induced dipole–induced dipole interaction. This interaction is called either the **dispersion interaction** or the **London interaction** (for Fritz London, who first described it).

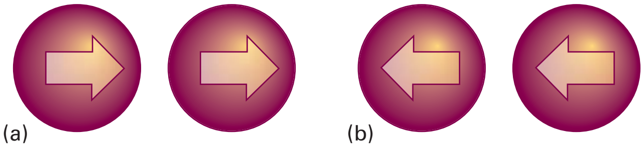


Figure 35.5 (a) In the dispersion interaction, an instantaneous dipole on one molecule induces a dipole on another molecule, and the two dipoles then interact to lower the energy. (b) The two instantaneous dipoles are correlated, and although they occur in different orientations at different instants, the interaction does not average to zero.

The strength of the dispersion interaction depends on the polarizability of the first molecule because the instantaneous dipole moment of magnitude μ_1^* depends on the looseness of the control that the nuclear charge exercises over the outer electrons. The strength of the interaction also depends on the polarizability of the second molecule, for that polarizability determines how readily a dipole can be induced by another molecule. The actual calculation of the dispersion interaction is quite involved, but a reasonable approximation to the interaction energy is given by the **London formula**:

$$V=-\frac{C}{r^6} \qquad C=\frac{3}{2}\alpha_2'\alpha_2'\frac{I_1I_2}{I_1+I_2} \qquad \text{London formula} \qquad (35.8)$$

where I_1 and I_2 are the ionization energies of the two molecules. This interaction energy is also proportional to the inverse sixth power of the separation of the molecules, which identifies it as a third contribution to the van der Waals interaction. The dispersion interaction generally dominates all the interactions between molecules other than hydrogen bonds.

Brief illustration 35.6 The London interaction

For two CH_4 molecules separated by 0.30 nm, we can use eqn 35.8 with $\alpha'=2.6\times10^{-30}\,\text{m}^3$ and $I\approx700\,\text{kJ mol}^{-1}$ and obtain

$$V=-\frac{\frac{3}{2}\times(2.6\times10^{-30}\,\text{m}^3)^2\times\left\{\frac{(7.00\times10^5\,\text{J mol}^{-1})^2}{2\times(7.00\times10^5\,\text{J mol}^{-1})}\right\}}{(0.30\times10^{-9}\,\text{m})^6}$$
$$=-4.9\,\text{kJ mol}^{-1}$$

A very approximate check on this figure is the enthalpy of vaporization of methane, which is 8.2 kJ mol^{-1}. However, this comparison is insecure, partly because the enthalpy of vaporization is a many-body quantity and partly because the long-distance assumption breaks down.

Self-test 35.6 Estimate the energy of the London interaction for two He atoms separated by 1.0 nm.

Answer: $-0.071\,\text{J mol}^{-1}$

35.3 Hydrogen bonding

The interactions described so far are universal in the sense that they are possessed by all molecules independent of their specific identity. However, there is a type of interaction possessed by molecules that have a particular constitution. A **hydrogen bond** is an attractive interaction between two species that arises from a link of the form A–H···B, where A and B are highly electronegative elements and B possesses a lone pair of electrons. Hydrogen bonding is conventionally regarded as being limited to N, O, and F but, if B is an anionic species (such as Cl^-), it may also participate in hydrogen bonding. There is no strict cut-off for an ability to participate in hydrogen bonding, but N, O, and F participate most effectively.

The formation of a hydrogen bond can be regarded either as the approach between a partial positive charge of H and a partial negative charge of B or as a particular example of delocalized molecular orbital formation in which A, H, and B each supply one atomic orbital from which three molecular orbitals are constructed (Fig. 35.6). Experimental evidence and theoretical arguments have been presented in favour of both views and the matter has not yet been resolved. The electrostatic interaction model can be understood readily in terms of the discussion in Section 35.1. Here we develop the molecular orbital model.

Thus, if the A–H bond is regarded as formed from the overlap of an orbital on A, χ_A, and a hydrogen 1s orbital, χ_H, and the lone pair on B occupies an orbital on B, χ_B, then, when the two molecules are close together, we can build three molecular orbitals from the three basis orbitals:

$$\psi = c_1\chi_A + c_2\chi_H + c_3\chi_B$$

One of the molecular orbitals is bonding, one almost nonbonding, and the third antibonding. These three orbitals need to accommodate four electrons (two from the original A–H bond and two from the lone pair of B), so two enter the bonding orbital and two enter the nonbonding orbital. Because the antibonding orbital remains empty, the net effect—depending on the precise energy of the almost nonbonding orbital—may be a lowering of energy.

In practice, the strength of the bond is found to be about 20 kJ mol^{-1}. Because the bonding depends on orbital overlap, it is virtually a contact-like interaction that is turned on when AH touches B and is zero as soon as the contact is broken. If hydrogen bonding is present, it dominates the other intermolecular interactions. The properties of liquid and solid water, for example, are dominated by the hydrogen bonding between H_2O molecules. The structure of DNA and hence the transmission of genetic information is crucially dependent on the strength of hydrogen bonds between base pairs. The structural evidence for hydrogen bonding comes from noting that the internuclear distance between formally nonbonded atoms is less than expected on the basis of their van der Waals radii, which suggests that a dominating attractive interaction is present. For example, the O–O distance in O–H···O is expected to be 280 pm on the basis of van der Waals radii, but is found to be 270 pm in typical compounds. Moreover, the H···O distance is expected to be 260 pm but is found to be only 170 pm.

Hydrogen bonds may be either symmetric or unsymmetric. In a symmetric hydrogen bond, the H atom lies midway between the two other atoms. This arrangement is rare, but occurs in F–H···F$^-$, where both bond lengths are 120 pm. More common is the unsymmetrical arrangement, where the A–H bond is shorter than the H···B bond. Simple electrostatic arguments, treating A–H···B as an array of point charges (partial negative charges on A and B, partial positive on H) suggest that the lowest energy is achieved when the bond is linear, because then the two partial negative charges are furthest apart. The experimental evidence from structural studies supports a linear or near-linear arrangement.

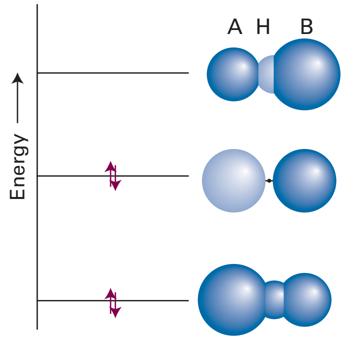
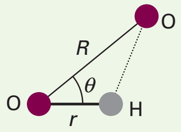


Figure 35.6 The molecular orbital interpretation of the formation of an A–H···B hydrogen bond. From the three A, H, and B orbitals, three molecular orbitals can be formed (their relative contributions are represented by the sizes of the spheres). Only the two lower-energy orbitals are occupied (four electrons total, two from the original A–H bond and two from the B lone pair), and there may therefore be a net lowering of energy compared with the separate AH and B species.

Brief illustration 35.7 The hydrogen bond

A common hydrogen bond is that formed between O—H groups and O atoms, as in liquid water and ice. In Problem 35.4, you are invited to use the electrostatic model to calculate the dependence of the potential energy of interaction on the OOH angle, denoted θ in **4**, and the results are plotted in Fig. 35.7. We see that at $\theta = 0$ when the OHO atoms lie in a straight line; the molar potential energy is −19 kJ mol^{-1}.



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Self-test 35.7 Use Fig. 35.7 to explore the dependence of the interaction energy on angle: at what angle does the interaction energy become negative?

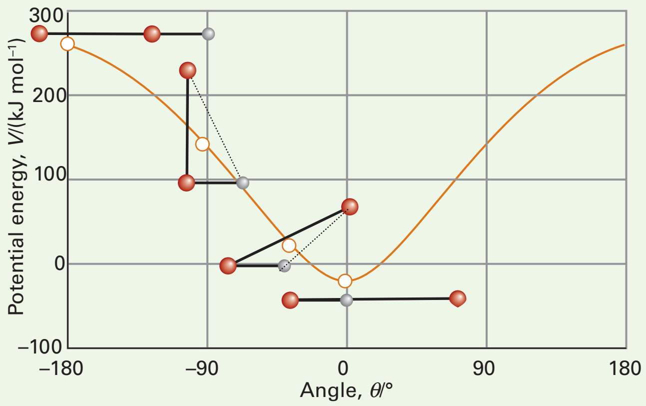


Figure 35.7 The variation of the energy of interaction (according to the electrostatic model) of a hydrogen bond as the angle between the O–H and :O groups is changed.

Answer: Only ±12°, so that the energy is negative (and the interaction is attractive) only when the atoms are close to a linear arrangement.

35.4 The total interaction

Here we consider molecules that are unable to participate in hydrogen bond formation. The total attractive interaction energy between rotating molecules is then the sum of the dipole–dipole, dipole–induced dipole, and dispersion interactions. Only the dispersion interaction contributes if both molecules are nonpolar. In a fluid phase, all three contributions to the potential energy vary as the inverse sixth power of the separation of the molecules, so we may write

$$V = -\frac{C_6}{r^6} \tag{35.9}$$

where C_6 is a coefficient that depends on the identity of the molecules.

Although attractive interactions between molecules are often expressed as in eqn 35.9, we must remember that this equation has only limited validity. First, we have taken into account only dipolar interactions of various kinds, for they have the longest range and are dominant if the average separation of the molecules is large. However, in a complete treatment we should also consider quadrupolar and higher-order multipole interactions, particularly if the molecules do not have permanent dipole moments. Secondly, the expressions have been derived by assuming that the molecules can rotate reasonably freely. That is not the case in most solids, and in rigid media the dipole–dipole interaction is proportional to $1/r^3$ (as in *Justification* 35.2) because the Boltzmann averaging procedure is irrelevant when the molecules are trapped into a fixed orientation.

A different kind of limitation is that eqn 35.9 relates to the interactions of pairs of molecules. There is no reason to suppose that the energy of interaction of three (or more) molecules is the sum of the pairwise interaction energies alone. The total dispersion energy of three closed-shell atoms, for instance, is given approximately by the **Axilrod–Teller formula**:

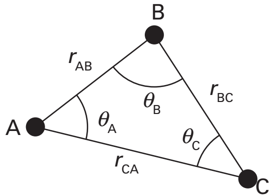
$$V = -\frac{C_6}{r_{AB}{}^6} - \frac{C_6}{r_{BC}{}^6} - \frac{C_6}{r_{CA}{}^6} + \frac{C'}{(r_{AB}r_{BC}r_{CA})^3} \tag{35.10a}$$

Axilrod–Teller formula

where

$$C' = a(3\cos\theta_A \cos\theta_B \cos\theta_C + 1) \tag{35.10b}$$

The parameter a is approximately equal to $\frac{3}{4}\alpha' C_6$; the angles θ are the internal angles of the triangle formed by the three atoms (5). The term in C' (which represents the non-additivity of the pairwise interactions) is negative for a linear arrangement of atoms (so that arrangement is stabilized) and positive for an equilateral triangular cluster (so that arrangement is destabilized). It is found that the three-body term contributes about 10 per cent of the total interaction energy in liquid argon.



5

When molecules are squeezed together, the nuclear and electronic repulsions begin to dominate the attractive forces. The repulsions increase steeply with decreasing separation in a way that can be deduced only by very extensive, complicated molecular structure calculations of the kind described in Topics 28–30 (Fig. 35.8).

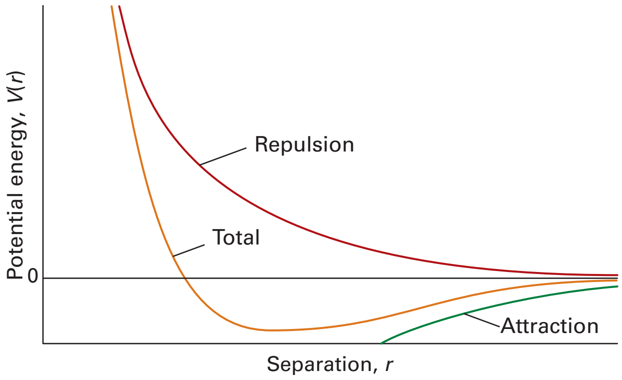


Figure 35.8 The general form of an intermolecular potential energy curve (the graph of the potential energy of two closed-shell species as the distance between them is changed). The attractive (negative) contribution has a long range, but the repulsive (positive) interaction increases more sharply once the molecules come into contact.

In many cases, however, progress can be made by using a greatly simplified representation of the potential energy, where the details are ignored and the general features expressed by a few adjustable parameters. One such approximation is the **hard-sphere potential energy**, in which it is assumed that the potential energy rises abruptly to infinity as soon as the particles come within a separation d:

$$V=\infty \text{ for } r\le d \qquad V=0 \text{ for } r>d \qquad \text{Hard-sphere potential energy} \tag{35.11}$$

This very simple expression for the potential energy is surprisingly useful for assessing a number of properties. Another widely used approximation is the **Mie potential energy**:

$$V=\frac{C_n}{r^n}-\frac{C_m}{r^m} \qquad \text{Mie potential energy} \tag{35.12}$$

with $n>m$. The first term represents repulsions and the second term attractions. The **Lennard-Jones potential energy** is a special case of the Mie potential energy with $n=12$ and $m=6$ (Fig. 35.9); it is often written in the form

$$V=4\varepsilon\left\{\left(\frac{r_0}{r}\right)^{12}-\left(\frac{r_0}{r}\right)^{6}\right\} \qquad \text{Lennard-Jones potential energy} \tag{35.13}$$

The two parameters are ε, the depth of the well (not to be confused with the symbol of the permittivity of a medium), and r_0, the separation at which $V=0$ (Table 35.2).

Table 35.2* Lennard-Jones parameters for the (12,6) potential

	$\varepsilon/(\text{kJ mol}^{-1})$	r_0/pm
Ar	128	362
Br_2	536	427
C_6H_6	454	6177
Cl_2	368	448.5
H_2	34	297
He	11	258
Xe	236	426

* More values are given in the *Resource section*.

Although the Lennard-Jones potential energy has been used in many calculations, there is plenty of evidence to show that $1/r^{12}$ is a very poor representation of the repulsive potential energy, and that an exponential form, e^{-r/r_0}, is greatly superior. An exponential function is more faithful to the exponential decay of atomic wavefunctions at large distances, and hence to the overlap that is responsible for repulsion. The potential energy with an exponential repulsive term and a $1/r^6$ attractive term is known as an **exp-6 potential energy**. These expressions for the potential energy can be used to calculate the virial coefficients of gases, as explained in Topic 36, and through them various properties of real gases, such as the Joule–Thomson coefficient (Topic 56). They are also used to model the structures of condensed fluids.

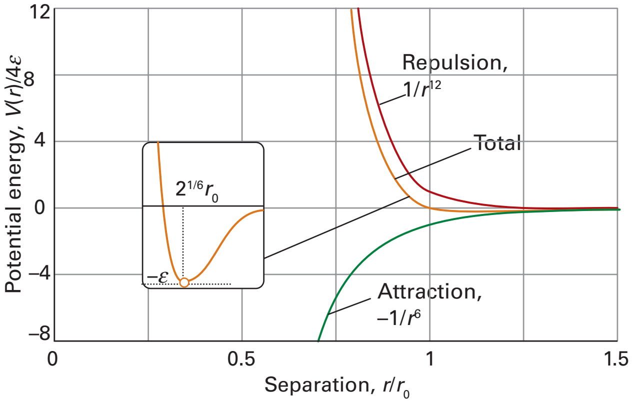


Figure 35.9 The Lennard-Jones potential energy is another approximation to the true intermolecular potential energy curves. It models the attractive component by a contribution that is proportional to $1/r^6$ and the repulsive component by a contribution that is proportional to $1/r^{12}$. Specifically, these choices result in the Lennard-Jones (12,6) potential. Although there are good theoretical reasons for the former, there is plenty of evidence to show that $1/r^{12}$ is only a very poor approximation to the repulsive part of the curve.

With the advent of atomic force microscopy (AFM), in which the force between a molecular sized probe and a surface is monitored (Topic 95), it has become possible to measure directly the forces acting between molecules. The force, F, is the negative slope of the potential energy, so for the Lennard-Jones potential energy between individual molecules we write

$$F=-\frac{\mathrm{d}V}{\mathrm{d}r}=\frac{24\varepsilon}{r_0}\left\{2\left(\frac{r_0}{r}\right)^{13}-\left(\frac{r_0}{r}\right)^{7}\right\} \tag{35.14}$$

Example 35.1 Calculating an intermolecular force from the Lennard-Jones potential energy

Use the expression for the Lennard-Jones potential energy to estimate the greatest net attractive force between two N_2 molecules.

Method The magnitude of the force is greatest at the distance r at which $\mathrm{d}F/\mathrm{d}r=0$. Therefore differentiate eqn 35.14 with respect to r, set the resulting expression to zero, and solve for r. Finally, use the value of r in eqn 35.14 to calculate the corresponding value of F.

Answer Because $\mathrm{d}x^n=nx^{n-1}$, the derivative of F with respect to r is

$$\frac{\mathrm{d}F}{\mathrm{d}r}=\frac{24\varepsilon}{r_0}\left\{2\left(-13r_0^{13}\frac{1}{r^{14}}\right)-\left(-7r_0^{7}\frac{1}{r^{8}}\right)\right\}=24\varepsilon r_0^{6}\left\{\frac{7}{r^{8}}-\frac{26r_0^{6}}{r^{14}}\right\}$$

It follows that $\mathrm{d}F/\mathrm{d}r = 0$ when

$$\frac{7}{r^8} - \frac{26r_0^6}{r^{14}} = 0 \quad \text{or} \quad 7r^6 - 26r_0^6 = 0$$

or

$$r = \left(\frac{26}{7}\right)^{1/6} r_0 = 1.244r_0$$

At this separation the force is

$$F = \frac{24\varepsilon}{r_0}\left\{2\left(\frac{r_0}{1.244r_0}\right)^{13} - \left(\frac{r_0}{1.244r_0}\right)^{7}\right\} = -2.396\varepsilon/r_0$$

From Table 35.2, $\varepsilon = 1.268 \times 10^{-21}$ J and $r_0 = 3.919 \times 10^{-10}$ m. It follows that

$$F = -\frac{2.396 \times (1.268 \times 10^{-21}\,\mathrm{J})}{3.919 \times 10^{-10}\,\mathrm{m}} = -7.752 \times 10^{-12}\,\mathrm{N}$$

where we have used $1\,\mathrm{N} = 1\,\mathrm{J\,m^{-1}}$. That is, the magnitude of the force is about 8 pN.

Self-test 35.8 At what separation r_e does the minimum of the potential energy curve occur for a Lennard-Jones potential?

Answer: $r_e = 2^{1/6} r_0$

Checklist of concepts

☐ 1. A **van der Waals interaction** between closed-shell molecules is inversely proportional to the sixth power of their separation.

☐ 2. The following molecular interactions are important: **charge–charge**, **charge–dipole**, **dipole–dipole**, **dipole–induced dipole**, **dispersion** (**London**), **hydrogen bonding**.

☐ 3. A hydrogen bond is an interaction of the form X–H···Y, where X and Y are typically N, O, or F.

☐ 4. The **Lennard-Jones potential energy** function is a model of the total intermolecular potential energy.

Checklist of equations

Property	Equation	Comment	Equation number
Potential energy of interaction between two point charges in a medium	$V = Q_1Q_2/4\pi\varepsilon r$	The relative permittivity of the medium is $\varepsilon_r = \varepsilon/\varepsilon_0$	35.1b
Energy of interaction between a point dipole and a point charge	$V = -\mu_1 Q_2/4\pi\varepsilon_0 r^2$		35.2
Energy of interaction between two fixed dipoles	$V = \mu_1\mu_2 f(\theta)/4\pi\varepsilon_0 r^3$, $f(\theta) = 1 - 3\cos^2\theta$	Parallel dipoles	35.4
Energy of interaction between two rotating dipoles	$V = -2\mu_1^2\mu_2^2/3(4\pi\varepsilon_0)^2 kTr^6$		35.5
Energy of interaction between a polar molecule and a polarizable molecule	$V = -\mu_1^2\alpha_2'/4\pi\varepsilon_0 r^6$		35.7
London formula	$V = -\frac{3}{2}\alpha_1'\alpha_2'[I_1I_2/(I_1+I_2)]/r^6$		35.8
Axilrod–Teller formula	$V = -C_6/r_{AB}^6 - C_6/r_{BC}^6 - C_6/r_{CA}^6 + C'/(r_{AB}r_{BC}r_{CA})^3$	Applies to closed-shell atoms	35.10
Lennard-Jones potential energy	$V = 4\varepsilon\{(r_0/r)^{12} - (r_0/r)^6\}$		35.13

TOPIC 36

Real gases

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➤ Why do you need to know this material?

To understand the atmospheres of this and other planets, you need to understand gases. Also, many industrial processes involve gases, and both the outcome of the reaction and the design of the reaction vessels depend on a knowledge of their properties.

➤ What is the key idea?

In a real gas weak attractions and repulsions can cause deviations from the perfect gas law.

➤ What do you need to know already?

For the first three sections you need to be familiar with the perfect gas law (*Foundations*, Topic 1) and the origin of the attractive and repulsive molecular interactions, as expressed by the Lennard-Jones potential energy function (Topic 35). You should be familiar with the qualitative features of the kinetic theory of gases (which is treated in depth in Topic 78). For the more advanced final section, you need to be aware of the concept of internal pressure (Topic 58) and the development of thermodynamic equations of state (Topic 66).

The state of a pure gas is specified by giving its volume, amount of substance, pressure, and temperature. However, it has been established experimentally that it is sufficient to specify only three of these variables, for then the fourth variable is fixed. That is, it is an experimental fact that each substance is described by an **equation of state**, an equation that expresses any one of these four variables in terms of the other three. Thus, the general form of an equation of state is

$$p = f(T, V, n) \qquad \text{Equation of state} \qquad (36.1)$$

where p is the pressure, V the volume, n the amount of molecules, and T the (absolute) temperature. This equation tells us that if we know the values of n, T, and V for a particular substance, then the pressure has a fixed value.

Each substance is described by its own equation of state, but the explicit form of the equation is known in only a few special cases. As discussed in Topics 1 and 66, the equation of state of a perfect gas, which is the limiting form of the equation of state for any gas as $p \to 0$, is

$$pV = nRT \qquad \text{Perfect gas law} \qquad (36.2)$$

where R is a universal constant, the same for all gases (*Foundations*, Topic 1). It is established in *Foundations*, Topic 2, that $R = N_A k$, where N_A is Avogadro's constant and k is Boltzmann's constant. Our task is to discover how this equation is modified when intermolecular interactions are important.

At the microscopic level, a perfect gas is characterized by the lack of intermolecular interactions and a completely random distribution of molecules in ceaseless motion (Topic 78). However, in a real gas there are weak attractions and repulsions which have minimal effect on the relative locations of the molecules but which cause deviations from the perfect gas law. Deviations from the law are particularly important at high pressures and low temperatures, especially when a gas is on the point of condensing to liquid at low temperatures. At that point, the molecules of a gas have insufficient kinetic energy to escape from each other's attraction and they stick together. Although molecules attract each other when they are a few diameters apart, they repel each other as soon as they come into contact. This repulsion is responsible for the fact that liquids and solids have a definite bulk and do not collapse to an infinitesimal point.

36.1 Molecular interactions in gases

Repulsive forces between molecules assist expansion and attractive forces assist compression. Repulsive forces are significant only when molecules are almost in contact: they are short-range interactions, even on a scale measured in molecular diameters (Fig. 36.1). Because they are short-range interactions, repulsions can be expected to be important only when the average separation of the molecules is small. This is the case at high pressure, when many molecules occupy a small volume. On the other hand, attractive intermolecular forces have a relatively long range and are effective over several molecular diameters. They are important when the molecules are close together but not necessarily touching (at the intermediate separations in Fig. 36.1, within a few molecular diameters of one another). Attractive forces are ineffective when the molecules are far apart (well to the right in Fig. 36.1). Intermolecular forces are also important when the temperature is so low that the molecules travel with such low mean speeds that they can be captured by one another.

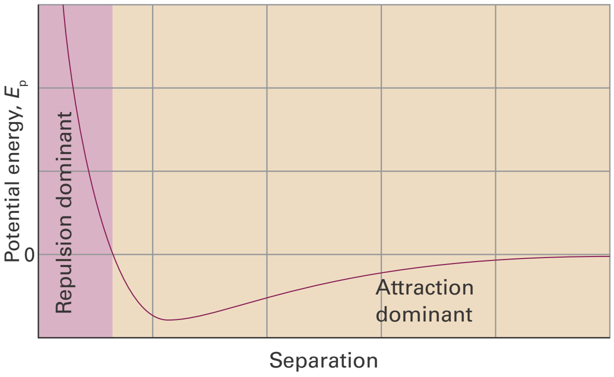


Figure 36.1 The variation of the potential energy of two molecules (at very small separations) indicates that the interactions between them are strongly repulsive at these distances. At intermediate separations, where the potential energy is negative, the attractive interactions dominate. At large separations (on the right) the potential energy is zero and there is no interaction between the molecules.

Brief illustration 36.1 Interactions in gases

To gain some insight into distances that can make interactions between particles in the gas phase important, consider two Ar atoms. A model of the intermolecular potential energy of two atoms is the Lennard-Jones potential energy introduced in Topic 35, $V=4\varepsilon\{(r_0/r)^{12}-(r_0/r)^6\}$, which is a minimum (most negative) at $r=2^{1/6}r_0$ and passes through zero at $r=r_0$. Because $r_0=362$ pm for argon atoms (Table 35.2), the potential energy of interaction between two Ar atoms passes through zero at $r=362$ pm. This is the distance below which repulsions become dominant. Because the diameter of an Ar atom is 142 pm, this distance corresponds to about 2.5 atomic diameters. The potential energy of interaction between two Ar atoms is a minimum (that is, their mutual attraction is greatest) at $r=2^{1/6}\times 362\ \text{pm}=406$ pm, which corresponds to 2.9 atomic diameters.

Self-test 36.1 Estimate the molar energy of the dispersion interaction (use the London formula, eqn 35.8) for two Ar atoms separated by (i) 407 pm (about 3 atomic diameters) and (ii) 1.0 nm (about 7 atomic diameters).

Answer: (i) $-691\ \text{J mol}^{-1}$; (ii) $-3.1\ \text{J mol}^{-1}$

36.2 The virial equation of state

The general form of the equation of state of a real gas can be inferred from measurements of the pressure for various values of the temperature, volume, and amount of molecules in a sample. To do so, it is convenient to begin by defining the **compression factor**, Z, of a gas as the ratio of its measured molar volume, $V_m=V/n$, to the molar volume of a perfect gas, V_m°, at the same pressure and temperature:

$$Z=\frac{V_m}{V_m^\circ} \qquad \text{Compression factor of a gas} \qquad (36.3a)$$

For a perfect gas $V_m=V_m^\circ$, so $Z=1$ under all conditions; therefore, deviation of Z from 1 is a measure of departure from perfect behaviour. Furthermore, because V_m° can be replaced by RT/p, an alternative version of eqn 36.3a is

$$Z=\frac{pV_m}{RT},\ \text{implying}\ pV_m=ZRT\ \text{for all gases} \qquad (36.3b)$$

Some experimental values of Z are plotted in Fig. 36.2. At very low pressures, all the gases shown have $Z\approx 1$ and behave nearly

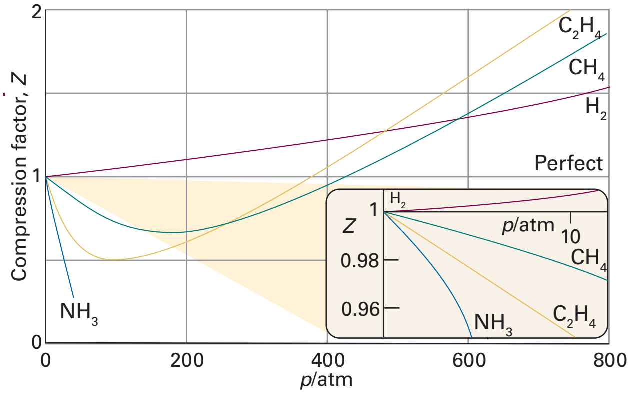


Figure 36.2 The variation of the compression factor, Z, with pressure for several gases at 0 °C. A perfect gas has $Z=1$ at all pressures. Notice that although the curves approach 1 as $p \rightarrow 0$, they do so with different slopes.

perfectly. At high pressures, all the gases have $Z>1$, signifying that they have a larger molar volume than a perfect gas at the same temperature. Repulsive forces are now dominant. At intermediate pressures, most gases have $Z<1$, indicating that the attractive forces are reducing the molar volume relative to that of a perfect gas.

Figure 36.3 shows the experimental **isotherms**, plots of data (in this case pressure and volume data) obtained at constant temperature, for carbon dioxide. At large molar volumes and high temperatures the real-gas isotherms do not differ greatly from perfect-gas isotherms. The small differences suggest that the perfect gas law is in fact the first term in an expression of the form

$$pV_m = RT(1+B'p+C'p^2+\ldots) \qquad \text{Virial equation of state} \qquad (36.4a)$$

This expression is an example of a common procedure in physical chemistry, in which a simple law that is known to be a good first approximation (in this case $pV_m = RT$) is treated as the first term in a series in powers of a variable (in this case p). A more convenient expansion for many applications is

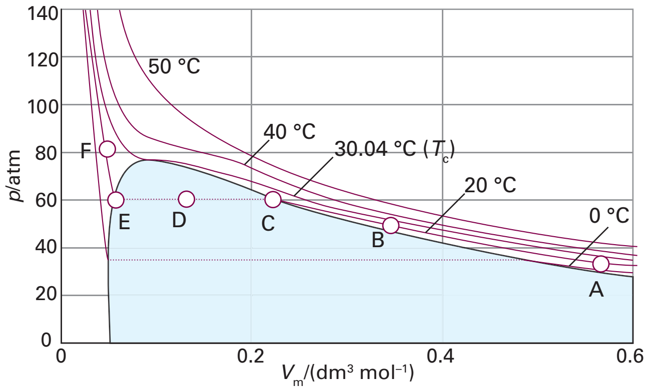


Figure 36.3 Experimental isotherms of carbon dioxide at several temperatures. The 'critical isotherm', the isotherm at the critical temperature, is at 30.04 °C.

Table 36.1* Second virial coefficients, B/(cm^3 mol^{-1})

	Temperature	
	273 K	600 K
Ar	−21.7	11.9
CO_2	−142	−12.4
N_2	−10.5	21.7
Xe	−153.7	−19.6

*More values are given in the *Resource section*.

$$pV_m = RT\left(1+\frac{B}{V_m}+\frac{C}{V_m^2}+\ldots\right) \qquad \text{Virial equation of state} \qquad (36.4b)$$

These two expressions are two versions of the **virial equation of state** (the name *virial* comes from the Latin word for force). By comparing the expression with eqn 36.3 we see that the term in parentheses can be identified with the compression factor, Z:

$$Z = 1+\frac{B}{V_m}+\frac{C}{V_m^2}+\ldots \qquad \text{Compression factor in terms of the virial coefficients} \qquad (36.5)$$

The coefficients B, C, … (which are sometimes denoted B_2, B_3, …) depend on the temperature and are the second, third, … **virial coefficients** (Table 36.1); the first virial coefficient is 1. The third virial coefficient, C, is usually less important than the second coefficient, B, in the sense that at typical molar volumes $C/V_m^2 \ll B/V_m$.

Brief illustration 36.2 The virial equation of state

To use eqn 36.4b (up to the B term), to calculate the pressure exerted at 100 K by 0.104 mol $O_2(g)$ in a vessel of volume 0.225 dm^3, we begin by calculating the molar volume:

$$V_m = \frac{V}{n_{CO_2}} = \frac{0.225\ \text{dm}^3}{0.104\ \text{mol}} = 2.16\ \text{dm}^3\ \text{mol}^{-1} = 2.16\times10^{-3}\,\text{m}^3\,\text{mol}^{-1}$$

Then, by using the value of B found in Table 36.1 of the *Resource section*,

$$\begin{aligned} p &= \frac{RT}{V_m}\left(1+\frac{B}{V_m}\right) \\ &= \frac{(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1})\times(100\,\text{K})}{2.16\times10^{-3}\ \text{m}^3\ \text{mol}^{-1}}\left(1-\frac{1.975\times10^{-4}\,\text{m}^3\ \text{mol}^{-1}}{2.16\times10^{-3}\,\text{m}^3\ \text{mol}^{-1}}\right) \\ &= 3.50\times10^5\ \text{Pa, or } 350\ \text{kPa} \end{aligned}$$

where we have used 1 Pa = 1 J m^{-3}. The perfect gas equation of state, eqn 36.1, would give the calculated pressure as 385 kPa, or 10 per cent higher than the value calculated by using the virial equation of state. The deviation is significant because under these conditions $|B/V_m| \approx 0.1$, which is not negligible relative to 1.

Self-test 36.2 What pressure would 4.56 g of nitrogen gas in a vessel of volume $2.25\,\mathrm{dm^3}$ exert at 273 K if it obeyed the virial equation of state?

Answer: 104 kPa

The virial equation can be used to demonstrate the important point that although the equation of state of a real gas may coincide with the perfect gas law as $p \to 0$, not all its properties necessarily coincide with those of a perfect gas in that limit. Consider, for example, the value of $\mathrm{d}Z/\mathrm{d}p$, the slope of the graph of compression factor against pressure. For a perfect gas $\mathrm{d}Z/\mathrm{d}p = 0$ (because $Z = 1$ at all pressures), but for a real gas from eqn 36.3 and 36.4a we obtain

$$\frac{\mathrm{d}Z}{\mathrm{d}p} = B' + 2pC' + \ldots \to B' \text{ as } p \to 0 \qquad (36.6\mathrm{a})$$

However, B' is not necessarily zero, so the slope of Z with respect to p does not necessarily approach 0 as $p \to 0$, as can be seen in Fig. 36.2. By a similar argument,

$$\frac{\mathrm{d}Z}{\mathrm{d}(1/V_m)} \to B \quad \text{as } V_m \to \infty, \text{ corresponding to } p \to 0 \qquad (36.6\mathrm{b})$$

Because the virial coefficients depend on the temperature, there may be a temperature at which $Z \to 1$ with zero slope at low pressure or high molar volume (Fig. 36.4). At this temperature, which is called the **Boyle temperature**, T_B, the properties of the real gas do coincide with those of a perfect gas as $p \to 0$. According to eqn 36.6b, Z has zero slope as $p \to 0$ if $B = 0$, so we can conclude that $B = 0$ at the Boyle temperature. It then follows from eqn 36.4 that $pV_m \approx RT_B$ over a more extended range of pressures than at other temperatures because the first term after 1 (that is, B/V_m) in the virial equation is zero and C/V_m^2 and higher terms are negligibly small. For helium $T_B = 22.64$ K; for air $T_B = 346.8$ K; more values are given in Table 36.2.

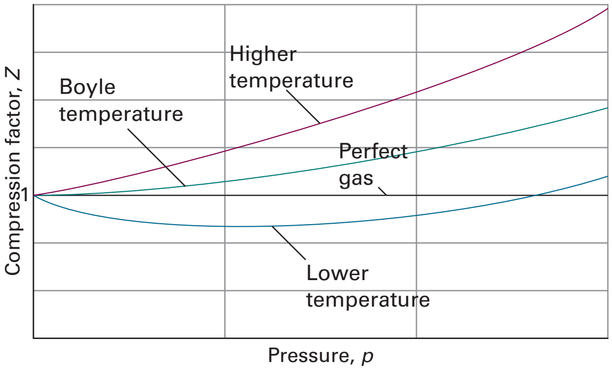


Figure 36.4 The compression factor, Z, approaches 1 at low pressures, but does so with different slopes. For a perfect gas, the slope is zero, but real gases may have either positive or negative slopes, and the slope may vary with temperature. At the Boyle temperature, the slope is zero and the gas behaves perfectly over a wider range of conditions than at other temperatures.

Table 36.2* Boyle temperatures of gases

	T_B/K
Ar	411.5
CO_2	714.8
He	22.64
O_2	405.9

* More values are given in the *Resource section*.

36.3 The van der Waals equation

Conclusions from the virial equations of state can be drawn only by inserting specific values of the coefficients. It is often useful to have a broader, if less precise, view of all gases. Therefore, we introduce the approximate equation of state suggested by J.D. van der Waals in 1873. This equation is an excellent example of an expression that can be obtained by thinking scientifically about a mathematically complicated but physically simple problem; that is, it is a good example of 'model building'.

(a) The development of the equation

The **van der Waals equation** is

$$p = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2 \qquad \text{van der Waals equation} \qquad (36.7\mathrm{a})$$

and a derivation is given in the following *Justification*. The equation is often written in terms of the molar volume $V_m = V/n$ as

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \qquad \textit{Alternative form} \quad \text{van der Waals equation} \qquad (36.7\mathrm{b})$$

The (positive) constants a and b are called the **van der Waals parameters.** They are characteristic of each gas but independent of the temperature (Table 36.3).

Table 36.3* van der Waals parameters

	$a/(\text{atm dm}^6\ \text{mol}^{-2})$	$a/(\text{Pa m}^6\ \text{mol}^{-2})$	$b/(10^{-2}\ \text{dm}^3\ \text{mol}^{-1})$
Ar	1.337	0.1355	3.20
CO_2	3.610	0.3658	4.29
He	0.0341	0.00346	2.38
Xe	4.137	0.4192	5.16

* More values are given in the *Resource section*.

Justification 36.1 The van der Waals equation of state

The repulsive interactions between molecules are taken into account by supposing that they cause the molecules to behave as small but impenetrable spheres. The nonzero volume of the molecules implies that instead of moving in a volume V they are restricted to a smaller volume $V-nb$, where nb is approximately the total volume taken up by the molecules themselves. This argument suggests that the perfect gas law $p=nRT/V$ should be replaced by

$$p=\frac{nRT}{V-nb}$$

when repulsions are significant. The closest distance of two hard-sphere molecules of radius r, and volume $V_{\text{molecule}}=\frac{4}{3}\pi r^3$, is $2r$, so the volume excluded is $\frac{4}{3}\pi(2r)^3$, or $8V_{\text{molecule}}$. The volume excluded per molecule is one-half this volume, or $4V_{\text{molecule}}$, so $b\approx 4V_{\text{molecule}}N_A$.

The pressure depends on both the frequency of collisions with the walls and the force of each collision. Both the frequency of the collisions and their force are reduced by the attractive forces, which act with a strength proportional to the molar concentration, n/V, of molecules in the sample. Therefore, because both the frequency and the force of the collisions are reduced by the attractive forces, the pressure is reduced in proportion to the *square* of this concentration. If the reduction of pressure is written as $-a(n/V)^2$, where a is a positive constant characteristic of each gas, the combined effect of the repulsive and attractive forces is the van der Waals equation of state as expressed in eqn 36.7.

In this *Justification* we have built the van der Waals equation using plausible arguments about the volumes of molecules and the effects of forces. The equation can be derived in other ways, but the present method has the advantage that it shows how to derive the form of an equation out of general ideas. The derivation also has the advantage of keeping imprecise the significance of the parameters a and b: they are much better regarded as empirical parameters than as precisely defined molecular properties (but see eqn 36.11 below and Topic 66 for a precise thermodynamic interpretation of a).

Example 36.1 Using the van der Waals equation to estimate a molar volume

Estimate the molar volume of CO_2 at 500 K and 100 atm by treating it as a van der Waals gas.

Method To express eqn 36.7b as an equation for the molar volume, we multiply both sides by $(V_m-b)V_m^2$, to obtain

$$(V_m-b)V_m^2p=RTV_m^2-(V_m-b)a$$

and, after division by p, collect powers of V_m to obtain

$$V_m^3-\left(b+\frac{RT}{p}\right)V_m^2+\left(\frac{a}{p}\right)V_m-\frac{ab}{p}=0$$

Although closed expressions for the roots of a cubic equation can be given, they are very complicated. Unless analytical solutions are essential, it is usually more expedient to solve such equations by using mathematical software.

Answer According to Table 36.3, $a=3.610\ \text{dm}^6\ \text{atm mol}^{-2}$ and $b=4.29\times10^{-2}\ \text{dm}^3\ \text{mol}^{-1}$. Under the stated conditions, $RT/p=0.410\ \text{dm}^3\ \text{mol}^{-1}$. The coefficients in the equation for V_m are therefore

$$\begin{aligned} b+RT/p&=0.453\ \text{dm}^3\text{mol}^{-1}\\ a/p&=3.61\times10^{-2}(\text{dm}^3\text{mol}^{-1})^2\\ ab/p&=1.55\times10^{-3}(\text{dm}^3\text{mol}^{-1})^3 \end{aligned}$$

Therefore, on writing $x=V_m/(\text{dm}^3\ \text{mol}^{-1})$, the equation to solve is

$$x^3-0.453x^2+(3.61\times10^{-2})x-(1.55\times10^{-3})=0$$

The acceptable root is $x=0.366$, which implies that $V_m=0.366\ \text{dm}^3\ \text{mol}^{-1}$. The molar volume of a perfect gas under these conditions is $0.410\ \text{dm}^3\ \text{mol}^{-1}$.

Self-test 36.3 Calculate the molar volume of argon at 100 °C and 100 atm on the assumption that it is a van der Waals gas.

Answer: $0.298\ \text{dm}^3\ \text{mol}^{-1}$

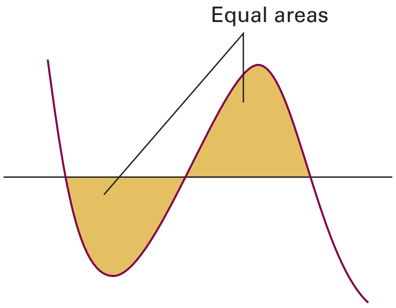
It is too optimistic to expect a single, simple expression to be the true equation of state of all substances, and accurate work on gases must resort to the virial equation, use tabulated values of the coefficients at various temperatures, and analyse the systems numerically. The advantage of the van der Waals equation, however, is that it is analytical (that is, expressed symbolically) and allows us to draw some general conclusions about real gases. When the equation fails we must use one of the other equations of state that have been proposed (some are listed in Table 36.4), invent a new one, or go back to the virial equation.

Table 36.4 Selected equations of state

Equation		Critical constants		
		p_c	V_c	T_c
Perfect gas	$p=\dfrac{RT}{V_m}$			
van der Waals	$p=\dfrac{RT}{V_m-b}-\dfrac{a}{V_m^2}$	$\dfrac{a}{27b^2}$	$3b$	$\dfrac{8a}{27Rb}$
Berthelot	$p=\dfrac{RT}{V_m-b}-\dfrac{a}{TV_m^2}$	$\dfrac{1}{12}\left(\dfrac{2aR}{3b^3}\right)^{1/2}$	$3b$	$\dfrac{2}{3}\left(\dfrac{2a}{3bR}\right)^{1/2}$
Dieterici	$p=\dfrac{RTe^{-a/RTV_m}}{V_m-b}$	$\dfrac{a}{4e^2b^2}$	$2b$	$\dfrac{a}{4bR}$
Virial	$p=\dfrac{RT}{V_m}\left(1+\dfrac{B(T)}{V_m}+\dfrac{C(T)}{V_m^2}+\ldots\right)$			

(b) The reliability of the equation

We can begin to judge reliability of the equation by comparing the isotherms it predicts with the experimental isotherms in Fig. 36.3. Some calculated isotherms are shown in Fig. 36.5 and Fig. 36.6. Apart from the oscillations they do resemble experimental isotherms quite well. The oscillations, the **van der Waals' loops**, are unrealistic because they suggest that under some conditions an increase of pressure results in an increase of volume. Therefore they are replaced by horizontal lines drawn so the loops define equal areas above and below the lines: this procedure is called the **Maxwell construction** (1). The van der Waals parameters, such as those in Table 36.3, are found by fitting the calculated curves to the experimental curves.



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An important feature of the van der Waals equation is that *perfect gas isotherms are obtained at high temperatures and large molar volumes*. When the temperature is high, RT may be so large that the first term in eqn 36.7b greatly exceeds the second. Furthermore, if the molar volume is large, in the sense $V_m \gg b$, then the denominator $V_m - b \approx V_m$. Under these conditions, the equation reduces to $p=RT/V_m$, the perfect gas equation.

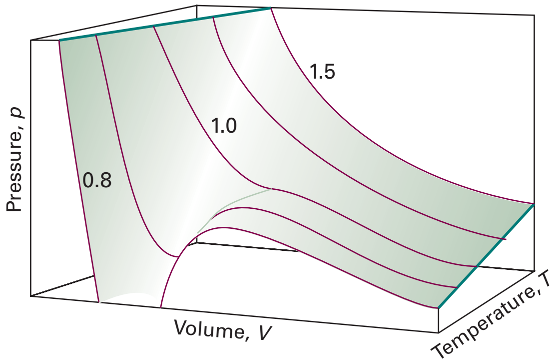


Figure 36.5 The surface of possible states allowed by the van der Waals equation. The curves are labelled with the 'reduced temperature', $T_r=T/T_c$.

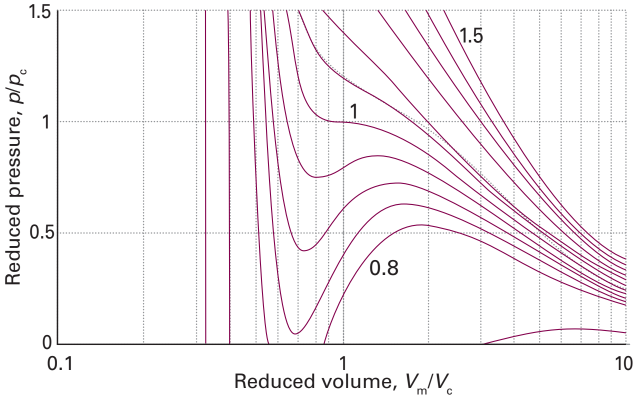


Figure 36.6 Isotherms calculated by using the van der Waals equation of state. The axes are labelled with the 'reduced pressure', p/p_c, and 'reduced volume', V_m/V_c, where $p_c=a/27b^2$ and $V_c=3b$. The individual isotherms are labelled with the 'reduced temperature', T/T_c, where $T_c=8a/27Rb$. The van der Waals' loops are normally replaced by horizontal straight lines.

Brief illustration 36.3 Criteria for perfect gas behaviour

For benzene $a=18.57$ atm dm^6 mol^{-2} (1.882 Pa m^6 mol^{-2}) and $b=0.1193$ dm^3 mol^{-1} (1.193×10^{-4} m^3 mol^{-1}); its normal boiling point is 353 K. Treated as a perfect gas at $T=400$ K and $p=1.0$ atm, benzene vapour has a molar volume of $V_m=RT/p=33$ dm^3 mol^{-1}, so the criterion $V_m \gg b$ for perfect gas behaviour is satisfied. It follows that $a/V_m{}^2\approx0.017$ atm, which is 1.7 per cent of 1.0 atm. Therefore, we can expect benzene vapour to deviate only slightly from perfect gas behaviour at this temperature and pressure.

Self-test 36.4 Can argon gas be treated as a perfect gas at 400 K and 3.0 atm?

Answer: Yes

(c) Critical behaviour

Consider what happens when we compress (reduce the volume of) a sample of gas initially in the state marked A in Fig. 36.3 at constant temperature by pushing in a piston. Near A, the pressure of the gas rises in approximate agreement with the perfect gas law. Serious deviations from that law begin to appear when the volume has been reduced to B.

At C (which corresponds to about 60 atm for carbon dioxide), all similarity to perfect behaviour is lost, for suddenly the piston slides in without any further rise in pressure: this stage is represented by the horizontal line CDE. Examination of the contents of the vessel shows that just to the left of C a liquid appears, and there are two phases separated by a sharply defined surface. As the volume is decreased from C through D to E, the amount of liquid increases. There is no additional resistance to the piston because the gas can respond by condensing. The pressure corresponding to the line CDE, when both liquid and vapour are present in equilibrium, is called the **vapour pressure** of the liquid at the temperature of the experiment.

At E, the sample is entirely liquid and the piston rests on its surface. Any further reduction of volume requires the exertion of considerable pressure, as is indicated by the sharply rising line to the left of E. Even a small reduction of volume from E to F requires a great increase in pressure.

The isotherm at the temperature T_c (304.19 K, or 31.04 °C for CO_2) plays a special role in the theory of the states of matter. An isotherm slightly below T_c behaves as we have already described: at a certain pressure, a liquid condenses from the gas and is distinguishable from it by the presence of a visible surface. If, however, the compression takes place at T_c itself, then a surface separating two phases does not appear and the volumes at each end of the horizontal part of the isotherm have merged to a single point, the **critical point** of the gas. The temperature, pressure, and molar volume at the critical point are called the **critical temperature**, T_c, **critical pressure**, p_c, and **critical molar volume**, V_c, of the substance. Collectively, p_c, V_c, and T_c are the **critical constants** of a substance (Table 36.5).

At and above T_c, the sample has a single phase which occupies the entire volume of the container. Such a phase is, by definition, a gas. Hence, the liquid phase of a substance does not form above the critical temperature. The single phase that fills the entire volume when $T > T_c$ may be much denser that we normally consider typical of gases, and the name **supercritical fluid** is preferred.

Table 36.5* Critical constants of gases

	p_c/atm	V_c/(cm^3 mol^{-1})	T_c/K
Ar	48.0	75.3	150.7
CO_2	72.9	94.0	304.2
He	2.26	57.8	5.2
O_2	50.14	78.0	154.8

* More values are given in the *Resource section*.

Brief illustration 36.4 The critical temperature

The critical temperature of oxygen signifies that it is impossible to produce liquid oxygen by compression alone if its temperature is greater than 155 K. To liquefy oxygen—to obtain a fluid phase that does not occupy the entire volume—the temperature must first be lowered to below 155 K, and then the gas compressed isothermally.

Self-test 36.5 Under which conditions can liquid nitrogen be formed by the application of pressure?

Answer: At $T < 126$ K

We show in the following *Justification* that the critical constants are related to the van der Waals parameters as follows:

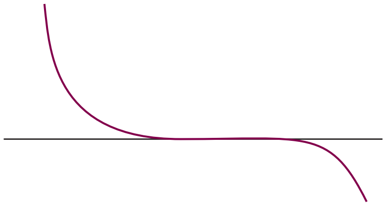
$$V_c = 3b \quad T_c = \frac{8a}{27Rb} \quad p_c = \frac{a}{27b^2} \qquad (36.8)$$

Critical constants in terms of van der Waals parameters

The first of these relations shows that the critical volume is about three times the volume occupied by the molecules themselves. Table 36.4 shows expressions for the critical constants derived from several equations of state.

Justification 36.2 Relating the critical constants to the van der Waals parameters

We see from Fig. 36.6 that, for $T < T_c$, the calculated isotherms oscillate, and each one passes through a minimum followed by a maximum. These extrema converge as $T \to T_c$ and coincide at $T = T_c$; at the critical point the curve has a flat inflexion (2).



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From the properties of curves, we know that an inflexion of this type occurs when both the first and second derivatives are zero. Hence, we can find the critical temperature by calculating these derivatives and setting them equal to zero. It follows from eqn 36.7b that the first and second derivatives of p with respect to V_m are, respectively,

$$\frac{dp}{dV_m} = -\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3}$$

$$\frac{d^2p}{dV_m^2} = \frac{2RT}{(V_m - b)^3} - \frac{6a}{V_m^4}$$

At the critical point $T = T_c$, $V_m = V_c$, and both derivatives are equal to zero:

$$-\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0$$
$$\frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0$$

Solving this pair of equations gives (as you should verify) the expressions for V_c and T_c in eqn 36.8. When they are inserted in the van der Waals equation itself, we find the expression for p_c given there too.

36.4 Thermodynamic considerations

The empirical results discussed above can be understood in terms of the principles of chemical and statistical thermodynamics developed throughout the text, and especially in Topics 58 and 66. The result is deeper insight into the properties of real gases.

(a) The internal pressure

The virial equation and the van der Waals equation are special cases of the thermodynamic equation of state introduced in Topic 66:

$$\pi_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \qquad \text{Thermodynamic equation of state} \tag{36.9}$$

where π_T is the internal pressure, the dependence of the internal energy on the volume at constant temperature:

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T \qquad \text{Internal pressure} \tag{36.10}$$

with $\pi_T = 0$ for a perfect gas, because in the absence of molecular interactions, a change in volume—that is, a change in average intermolecular separation—has no effect on the internal energy of a perfect gas at constant temperature. For a van der Waals gas,

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V - nb}$$

and it follows from eqn 36.9 that

$$\begin{aligned}\pi_T &= \frac{nRT}{V - nb} - \left\{\frac{nRT}{V - nb} - a\frac{n^2}{V^2}\right\} \\ &= a\frac{n^2}{V^2}\end{aligned} \qquad \textit{van der Waals gas} \quad \text{Internal pressure} \tag{36.11}$$

We now have another way of interpreting the role of the van der Waals parameter a: it gives the contribution of molecular interactions to the internal energy of the gas. Moreover, because the internal energy is positive for a van der Waals gas, we can infer that the internal energy increases as the gas expands at constant temperature. That is plausible: the molecules become further apart on average and thus interact favourably less strongly.

Example 36.2 Writing an expression for the internal pressure of a real gas

Write an expression for the internal pressure of a gas that obeys the virial equation of state.

Method Begin by rearranging eqn 36.4b to

$$p = \frac{RT}{V_m}\left(1 + \frac{B}{V_m} + \dots\right)$$

and then use eqn 36.9, noting that the virial coefficients depend on temperature.

Answer Because the virial coefficients depend on temperature, we write

$$\begin{aligned}\left(\frac{\partial p}{\partial T}\right)_V &= \left[\frac{\partial}{\partial T}\overbrace{\frac{RT}{V_m}}^{f}\overbrace{\left(1 + \frac{B}{V_m} + \dots\right)}^{g}\right]_V \\ &\overset{\text{product rule: } d(fg) = fdg + gdf}{=} \frac{RT}{V_m}\left[\frac{\partial}{\partial T}\left(1 + \frac{B}{V_m} + \dots\right)\right]_V + \left(1 + \frac{B}{V_m} + \dots\right)\left[\frac{\partial}{\partial T}\left(\frac{RT}{V_m}\right)\right]_V\end{aligned}$$

After evaluating the derivatives and using eqn 36.4b again to simplify the resulting expression, we obtain

$$\begin{aligned}\left(\frac{\partial p}{\partial T}\right)_V &= \left\{\frac{RT}{V_m^2}\left(\frac{\partial B}{\partial T}\right)_V + \dots\right\} + \underbrace{\frac{R}{V_m}\left(1 + \frac{B}{V_m} + \dots\right)}_{p/T \text{ (eqn 36.4b)}} \\ &= \left\{\frac{RT}{V_m^2}\left(\frac{\partial B}{\partial T}\right)_V + \dots\right\} + \frac{p}{T}\end{aligned}$$

It follows from eqn 36.9 that

$$\begin{aligned}\pi_T &= T\left[\left\{\frac{RT}{V_m^2}\left(\frac{\partial B}{\partial T}\right)_V + \dots\right\} + \frac{p}{T}\right] - p \\ &= \left\{\frac{RT^2}{V_m^2}\left(\frac{\partial B}{\partial T}\right)_V + \dots\right\} + p - p = \frac{RT^2}{V_m^2}\left(\frac{\partial B}{\partial T}\right)_V + \dots\end{aligned}$$

Self-test 36.6 Estimate π_T for argon at 275 K given that $B(250\,\text{K}) = -28.0\,\text{cm}^3\,\text{mol}^{-1}$ and $B(300\,\text{K}) = -15.6\,\text{cm}^3\,\text{mol}^{-1}$ at 1.0 atm. *Hints*: (a) Rewrite the expression for π_T from Example 36.2 in terms of the ratio of differences $\Delta B/\Delta T$, and then take T as the mean value of the two given temperature values; (b) because deviation from perfect gas behaviour is expected to be small, use the perfect gas law to estimate V_m.

Answer: 0.30 kPa

(b) The statistical origins of equations of state

To establish contact between the empirical equations of state and the statistical thermodynamic discussion in Topics 51–54, we need to use the canonical partition function Q to calculate the internal pressure because only that formulation allows us to include the effects of intermolecular interactions. From the expression for U in terms of Q ($\langle E\rangle = -(\partial \ln Q/\partial\beta)_V$ and $U = U(0) + \langle E\rangle$), we can write

$$\pi_T = -\left(\frac{\partial}{\partial V}\left(\frac{\partial \ln Q}{\partial \beta}\right)_V\right)_T \qquad \text{Internal pressure in terms of } Q \qquad (36.12)$$

where $\beta = 1/kT$. To develop this expression, we need to find a way to build an intermolecular potential energy into the expression for Q. The total kinetic energy of a gas is the sum of the kinetic energies of the individual molecules. Therefore, even in a real gas the canonical partition function factorizes into a part arising from the kinetic energy and a factor called the **configuration integral**, $\mathcal{Z}$, which depends on the contributions to the intermolecular potential energy. We write

$$Q = \frac{\mathcal{Z}}{\Lambda^{3N}} \qquad Q \text{ in terms of the configuration integral} \qquad (36.13)$$

where Λ is the thermal wavelength (see eqn 52.7b), $\Lambda = h/(2\pi mkT)^{1/2}$. It then follows that

$$\begin{aligned}
\pi_T &= -\left(\frac{\partial}{\partial V}\left(\frac{\partial \ln(\mathcal{Z}/\Lambda^{3N})}{\partial \beta}\right)_V\right)_T \\
&= -\left(\frac{\partial}{\partial V}\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_V\right)_T - \left(\frac{\partial}{\partial V}\left(\frac{\partial \ln(1/\Lambda^{3N})}{\partial \beta}\right)_V\right)_T \\
&= -\left(\frac{\partial}{\partial V}\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_V\right)_T = -\left(\frac{\partial}{\partial V}\left(\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial \beta}\right)_V\right)_T
\end{aligned} \qquad (36.14)$$

In the second line, although the derivative of Λ with respect to temperature and hence β is nonzero, Λ is independent of volume, so the derivative with respect to volume is zero.

For a real gas of atoms (for which the intermolecular interactions are isotropic), $\mathcal{Z}$ is related to the total potential energy E_p of interaction of all the particles by

$$\mathcal{Z} = \frac{1}{N!}\int e^{-\beta E_p}\,d\tau_1 d\tau_2 \ldots d\tau_N \qquad \textit{Real gas of atoms} \quad \text{Configuration integral} \qquad (36.15)$$

where $d\tau_i$ is the volume element for atom i. The physical origin of this term is that the probability of occurrence of each arrangement of molecules possible in the sample is given by a Boltzmann distribution in which the exponent is given by the potential energy corresponding to that arrangement.

Brief illustration 36.5 The configuration integral

Equation 36.15 is very difficult to manipulate in practice, even for quite simple intermolecular potential energy functions. However, the case of a perfect gas is manageable because when the molecules do not interact with one another, $E_p = 0$ and hence $e^{-\beta E_p} = 1$. Then

$$\mathcal{Z} = \frac{1}{N!}\int \overbrace{e^{-\beta E_p}}^{1}\,d\tau_1 d\tau_2 \ldots d\tau_N = \frac{1}{N!}\overbrace{\underbrace{\int d\tau_1}_{V}\underbrace{\int d\tau_2}_{V}\ldots\underbrace{\int d\tau_N}_{V}}^{V^N} = \frac{V^N}{N!}$$

where $\int d\tau_i = V$, with V as the volume of the container.

Self-test 36.7 Use the result from *Brief illustration* 36.5 and eqn 36.12 to calculate the internal pressure of a perfect gas.

Answer: $\pi_T = 0$; the same result is obtained in Topics 58 and 66

When the potential energy function has the form of a central hard sphere surrounded by a shallow attractive well (Fig. 36.7), then detailed calculation, which is too involved to reproduce here, leads to $\pi_T = an^2/V^2$, where a is a constant that is proportional to the area under the attractive part of

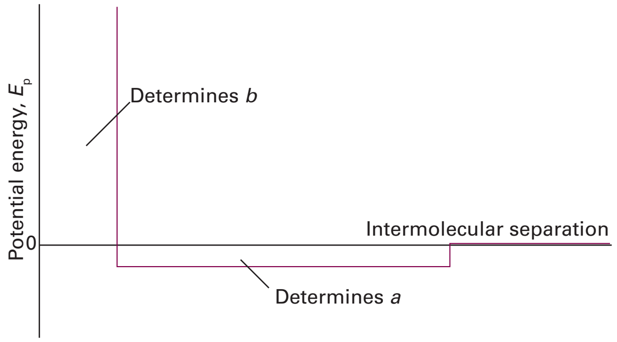

Figure 36.7 The van der Waals equation of state can be derived on the basis that the intermolecular potential energy has a hard core surrounded by a long-range, shallow attractive well.

the potential. Of course, this is also eqn 36.11 for the internal pressure of a van der Waals gas. At this point we can conclude that if there are attractive interactions between molecules in a gas, then its internal energy increases as it expands isothermally (because $\pi_T > 0$, and the slope of U with respect to V is positive). The energy rises because, at greater average separations, the molecules spend less time in regions where they interact favourably.

Checklist of concepts

☐ 1. In **real gases**, molecular interactions affect the equation of state.

☐ 2. The true equation of state of a gas is expressed in terms of **virial coefficients**.

☐ 3. The **van der Waals equation of state** is an approximation to the true equation of state in which attractions are represented by a parameter a and repulsions are represented by a parameter b.

☐ 4. At or above the **critical temperature** a single form of matter, a **supercritical fluid**, fills a container at every value of the pressure, and there is no separation of a liquid from the gas.

☐ 5. The internal pressure of a perfect gas is zero; the internal pressure of a real gas can be written in terms of experimental parameters (such as the virial coefficients or the van der Waals parameters) or the canonical partition function.

Checklist of equations

Property	Equation	Comment	Equation number
Compression factor	$Z = V_m/V_m^\circ$	Definition	36.3a
Virial equation of state	$pV_m = RT(1 + B/V_m + C/V_m^2 + \ldots)$		36.4b
van der Waals equation	$p = RT/(V_m - b) - a/V_m^2$	a: effect of attractions; b: effect of repulsions	36.7b
Critical constants in terms of the van der Waals parameters	$V_c = 3b$ $T_c = 8a/27Rb$ $p_c = a/27b^2$		36.8
Internal pressure	$\pi_T = -an^2/V^2$	van der Waals gas	36.11
	$\pi_T = (\partial(\partial \ln Q/\partial\beta)_V/\partial V)_T$, $Q = \mathcal{Z}/\Lambda^{3N}$	Q is the canonical partition function; $\mathcal{Z}$ is the configuration integral; $\beta = 1/kT$	36.12–36.13

TOPIC 37

Crystal structure

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➤ Why do you need to know this material?

It is necessary to understand the details of the structures of metallic, ionic, and molecular solids if you want to account for their properties. To be prepared for the study of the mechanical, electrical, optical, and magnetic properties of solids that can form the basis of new materials and technologies you need to know how the crystal structures of solids are determined.

➤ What is the key idea?

The details of the regular arrangement of atoms in periodic crystals can be determined by X-ray diffraction techniques.

➤ What do you need to know already?

You need to be familiar with the wave description of electromagnetic radiation (*Foundations*, Topic 3) and the significance of Fourier transforms (*Mathematical background* 6). Light use is made of the de Broglie relation (Topic 4) and the equipartition theorem (*Foundations*, Topic 2).

A crucial aspect of the link between the structure and properties of a solid is the pattern in which the atoms (and molecules) are stacked together, so here we examine how the structures of solids are described and determined. First, we see how to describe the regular arrangement of atoms in solids. Then we consider the basic principles of X-ray diffraction and see how the diffraction pattern can be interpreted in terms of the distribution of electron density in a crystal.

37.1 Periodic crystal lattices

A **periodic crystal** is built up from regularly repeating 'structural motifs', which may be atoms, molecules, or groups of atoms, molecules, or ions. A **space lattice** is the pattern formed by points representing the locations of these motifs (Fig. 37.1). The space lattice is, in effect, an abstract scaffolding for the crystal structure. More formally, a space lattice is a three-dimensional, infinite array of points, each of which is surrounded in an identical way by its neighbours, and which defines the basic structure of the crystal. In some cases there may be a structural motif centred on each lattice point, but that is not necessary. The crystal structure itself is obtained by associating with each lattice point an identical structural motif.

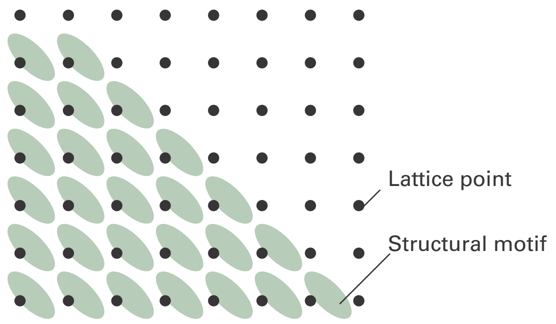


Figure 37.1 Each lattice point specifies the location of a structural motif (for example, a molecule or a group of molecules). The crystal lattice is the array of lattice points; the crystal structure is the collection of structural motifs arranged according to the lattice.

The solids known as **quasicrystals** are 'aperiodic', in the sense that the space lattice, though still filling space, does not have translational symmetry. Our discussion will focus on periodic crystals only and, to simplify the language, we refer to these structures simply as 'crystals'.

The **unit cell** is an imaginary parallelepiped (parallel-sided figure) that contains one unit of the translationally repeating pattern (Fig. 37.2). A unit cell can be thought of as the fundamental region from which the entire crystal may be constructed by purely translational displacements (like bricks in a wall). A unit cell is commonly formed by joining neighbouring lattice points by straight lines (Fig. 37.3). Such unit cells are called **primitive.** It is sometimes more convenient to draw larger **non-primitive unit cells** that also have lattice points at their centres or on pairs of opposite faces. An infinite number of different unit cells can describe the same lattice, but the one with sides that have the shortest lengths and that are most nearly perpendicular to one another is normally chosen. The lengths of the sides of a unit cell are denoted a, b, and c, and the angles between them are denoted α, β, and γ (Fig. 37.4).

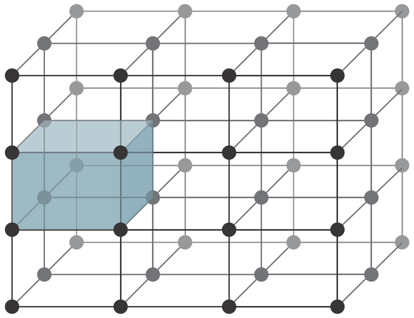


Figure 37.2 A unit cell is a parallel-sided (but not necessarily rectangular) figure from which the entire periodic crystal structure can be constructed by using only translations (not reflections, rotations, or inversions).

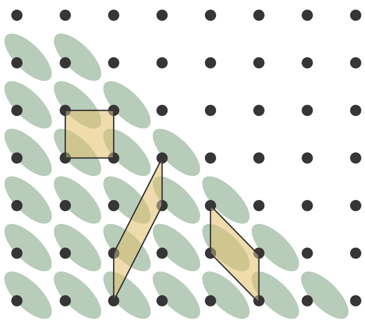


Figure 37.3 A unit cell can be chosen in a variety of ways, as shown here. It is conventional to choose the cell that represents the full symmetry of the lattice. In this rectangular lattice, the rectangular unit cell would normally be adopted.

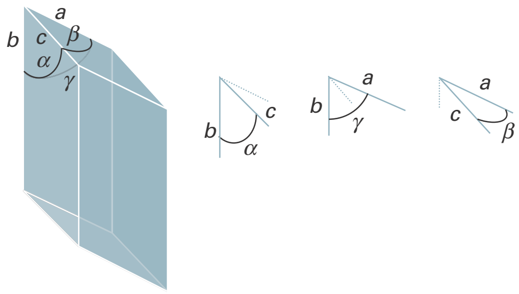


Figure 37.4 The notation for the sides and angles of a unit cell. Note that the angle α lies in the plane (b,c) and perpendicular to the axis a.

Unit cells are classified into seven **crystal systems** by noting the rotational symmetry elements they possess. A **symmetry operation** is an action (such as a rotation, reflection, or inversion) that leaves an object looking the same after it has been carried out. There is a corresponding **symmetry element** for each symmetry operation, which is the point, line, or plane with respect to which the symmetry operation is performed. For instance, an ***n*-fold rotation** (the symmetry operation) about an ***n*-fold axis of symmetry** (the corresponding symmetry element) is a rotation through 360°/n. (See Topics 31–33 for a more detailed discussion of symmetry.)

The following are examples of unit cells:

- A **cubic unit cell** has four threefold axes in a tetrahedral array (Fig. 37.5).
- A **monoclinic unit cell** has one twofold axis; the unique axis is by convention the b axis (Fig. 37.6).
- A **triclinic unit cell** has no rotational symmetry, and typically all three sides and angles are different (Fig. 37.7).

Table 37.1 lists the **essential symmetries**, the elements that must be present for the unit cell to belong to a particular crystal system.

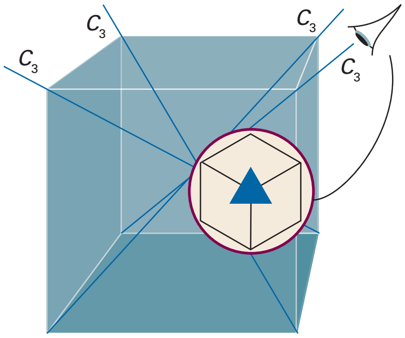


Figure 37.5 A unit cell belonging to the cubic system has four threefold axes, denoted C_3, arranged tetrahedrally. The insert shows the threefold symmetry.

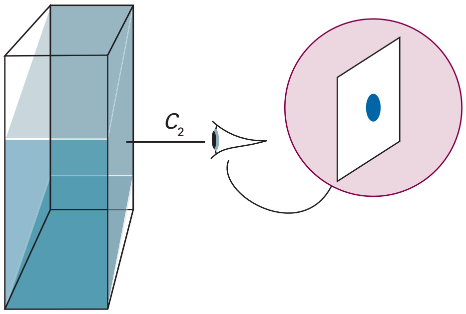


Figure 37.6 A unit cell belonging to the monoclinic system has a twofold axis (denoted C_2 and shown in more detail in the insert).

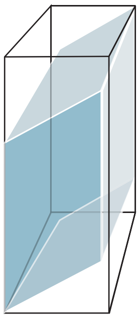


Figure 37.7 A triclinic unit cell has no axes of rotational symmetry.

Table 37.1 The seven crystal systems

System	Essential symmetries
Triclinic	None
Monoclinic	One C_2 axis
Orthorhombic	Three perpendicular C_2 axes
Rhombohedral	One C_3 axis
Tetragonal	One C_4 axis
Hexagonal	One C_6 axis
Cubic	Four C_3 axes in a tetrahedral arrangement

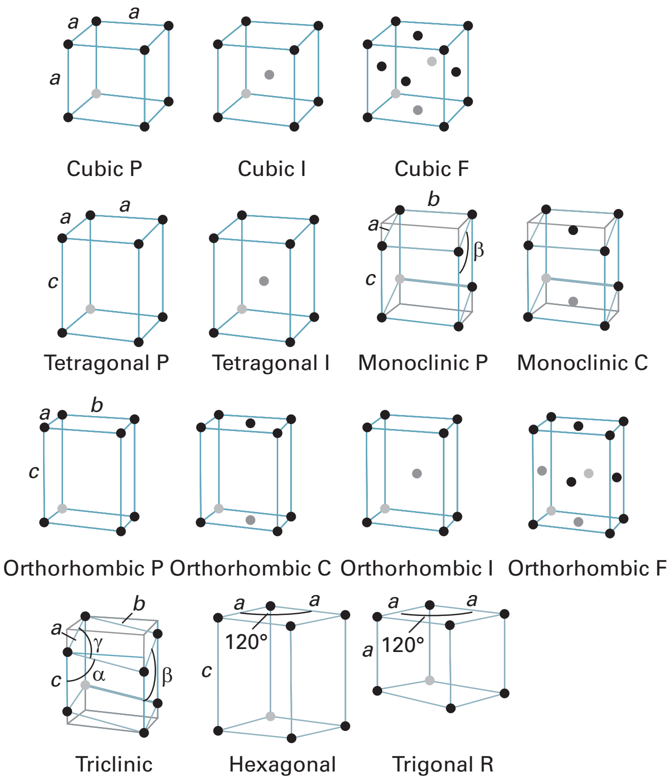


Figure 37.8 The 14 Bravais lattices. The points are lattice points, and are not necessarily occupied by atoms. P denotes a primitive unit cell (R is used for a trigonal lattice), I a body-centred unit cell, F a face-centred unit cell, and C (or A or B) a cell with lattice points on two opposite faces. Trigonal lattices may belong to the rhombohedral or hexagonal systems (Table 37.1).

There are only 14 distinct space lattices in three dimensions. These **Bravais lattices** are illustrated in Fig. 37.8. It is conventional to portray these lattices by primitive unit cells in some cases and by non-primitive unit cells in others. The following notation is used:

- A **primitive unit cell** (with lattice points only at the corners) is denoted P.
- A **body-centred unit cell** (I) also has a lattice point at its centre.
- A **face-centred unit cell** (F) has lattice points at its corners and also at the centres of its six faces.
- A **side-centred unit cell** (A, B, or C) has lattice points at its corners and at the centres of two opposite faces.

For simple structures, it is often convenient to choose an atom belonging to the structural motif, or the centre of a molecule, as the location of a lattice point or the vertex of a unit cell, but that is not a necessary requirement. Equivalent lattice points within the unit cell of a Bravais lattice have identical surroundings.

Brief illustration 37.1 Bravais lattices

Consider a body-centred cubic unit cell of sides a and one of its corners with coordinates $x=0$, $y=0$, $z=0$ (Fig. 37.9). Starting from this corner, the centre of the edge that runs along the y-axis has coordinates $x=0$, $y=\frac{1}{2}a$, $z=0$. It follows that the centres of each edge are equivalent to this point with coordinates $x=0$, $y=\frac{1}{2}a$, $z=0$.

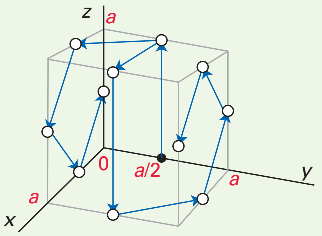


Figure 37.9 The body-centred cubic unit cell used in *Brief illustration* 37.1. The arrows show some of the ways in which the initial (black) point is related by symmetry operations to the remaining points halfway along each edge.

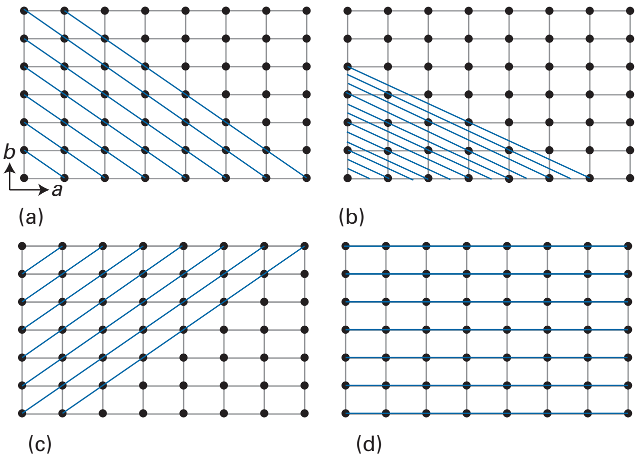
Self-test 37.1 What points within a face-centred cubic unit cell are equivalent to the point $x=\frac{1}{2}a$, $y=0$, $z=\frac{1}{2}a$?

Answer: The centres of each face

37.2 The identification of lattice planes

There are many different sets of lattice planes in a crystal (Fig. 37.10), and we need to be able to identify them. Two-dimensional lattices are easier to visualize than three-dimensional lattices, so we shall introduce the concepts involved by referring to two dimensions initially, and then extend the conclusions by analogy to three dimensions.

(a) The Miller indices



(a) (b) (c) (d)

Figure 37.10 Some of the planes that can be drawn through the points of a rectangular space lattice and their corresponding Miller indices (*hkl*): (a) {110}, (b) {230}, (c) $\{\bar{1}10\}$, and (d) {010}.

Consider a two-dimensional rectangular lattice formed from a unit cell of sides a, b (as in Fig. 37.10). Each plane in the illustration (except the plane passing through the origin) can be distinguished by the distances at which it intersects the a and b axes. One way to label a plane would therefore be to quote the smallest intersection distances. For example, we could denote a representative plane of each type in Fig. 37.10 as (a) $(1a,1b)$, (b) $(\frac{1}{2}a,\frac{1}{3}b)$, (c) $(-1a,1b)$, and (d) $(\infty a,1b)$, where ∞ is used to show that the planes intersect an axis at infinity. However, if we agree to quote distances along the axes as multiples of the lengths of the unit cell, then we can label the planes more simply as (1,1), $(\frac{1}{2},\frac{1}{3})$, $(-1,1)$, and $(\infty,1)$, respectively. If the lattice in Fig. 37.10 is the top view of a three-dimensional orthorhombic lattice in which the unit cell has a length c in the z-direction, all four sets of planes intersect the z-axis at infinity. Therefore, the full labels are $(1,1,\infty)$, $(\frac{1}{2},\frac{1}{3},\infty)$, $(-1,1,\infty)$, and $(\infty,1,\infty)$.

The presence of fractions and infinity in the labels is inconvenient. They can be eliminated by taking the reciprocals of the labels. As we shall see, taking reciprocals turns out to have further advantages. The **Miller indices**, (*hkl*), are the reciprocals of intersection distances. To simplify the notation while providing a great deal of information, the following rules apply:

- Negative indices are written with a bar over the number, as in $(\bar{1}10)$.
- If taking the reciprocal results in a fraction, then the fraction can be cleared by multiplying through by an appropriate factor.

For example, a $(\frac{1}{3},\frac{1}{2},0)$ plane is denoted (2,3,0) after multiplication of all three indices by 6.

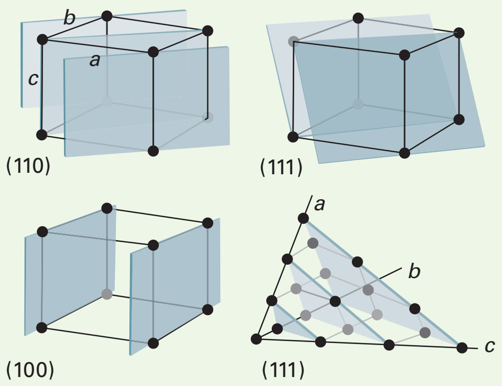
- The notation (*hkl*) denotes an *individual* plane. To specify a *set* of parallel planes we use the notation {*hkl*}.

Thus, we speak of the (110) plane in a lattice, and the set of all {110} planes that lie parallel to the (110) plane.

A helpful feature to remember is that the smaller the absolute value of h in {*hkl*}, the more nearly parallel the set of planes is to the a axis (the {*h*00} planes are an exception). The same is true of k and the b axis and l and the c axis. When $h=0$, the planes intersect the a axis at infinity, so the {0*kl*} planes are parallel to the a axis. Similarly, the {*h*0*l*} planes are parallel to b and the {*hk*0} planes are parallel to c.

Brief illustration 37.2 Miller indices

The $\{1,1,\infty\}$ planes in Fig. 37.10a are the $\{110\}$ planes in the Miller notation. Similarly, the $\{\tfrac{1}{2},\tfrac{1}{3},\infty\}$ planes are denoted $\{230\}$. Figure 37.10c shows the $\{\bar{1}10\}$ planes. The Miller indices for the four types of plane in Fig. 37.10 are therefore $\{110\}$, $\{230\}$, $\{\bar{1}10\}$, and $\{010\}$. Figure 37.11 shows a three-dimensional representation of a selection of planes, including one in a lattice with non-orthogonal axes.



(110) (111)

(100) (111)

Figure 37.11 Some representative planes in three dimensions and their Miller indices. Note that a 0 indicates that a plane is parallel to the corresponding axis, and that the indexing may also be used for unit cells with non-orthogonal axes.

Self-test 37.2 Find the Miller indices of the planes that intersect the crystallographic axes at the distances $(3a, 2b, c)$ and $(2a, \infty b, \infty c)$

Answer: $\{236\}$ and $\{100\}$

(b) The separation of planes

The Miller indices are very useful for expressing the separation of planes. It is shown in the following *Justification* that the separation of the $\{hk0\}$ planes in the square lattice in Fig. 37.12 is given by

$$\frac{1}{d_{hk0}^2}=\frac{h^2+k^2}{a^2} \quad \text{or} \quad d_{hk0}=\frac{a}{(h^2+k^2)^{1/2}} \tag{37.1a}$$

Square lattice Separation of planes

By extension to three dimensions, the separation of the $\{hkl\}$ planes of a cubic lattice is given by

$$\frac{1}{d_{hkl}^2}=\frac{h^2+k^2+l^2}{a^2} \quad \text{or} \quad d_{hkl}=\frac{a}{(h^2+k^2+l^2)^{1/2}} \tag{37.1b}$$

Cubic lattice Separation of planes

Justification 37.1 The separation of lattice planes

Consider the $\{hk0\}$ planes of a square lattice built from a unit cell with sides of length a (Fig. 37.12).

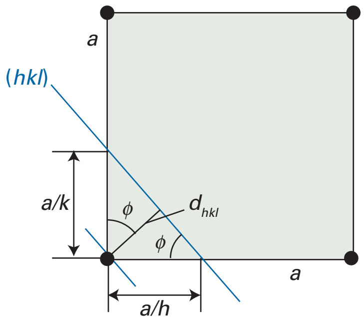


Figure 37.12 The dimensions of a unit cell and their relation to the plane passing through the lattice points.

We can write the following trigonometric expressions for the angle ϕ shown in the illustration:

$$\sin\phi=\frac{d}{(a/h)}=\frac{hd_{hk0}}{a} \qquad \cos\phi=\frac{d}{(a/k)}=\frac{kd_{hk0}}{a}$$

Because the lattice planes intersect the horizontal axis h times and the vertical axis k times, the length of each hypotenuse is calculated by dividing a by h and a by k. Then, because $\sin^2\phi+\cos^2\phi=1$, it follows that

$$\left(\frac{hd_{hk0}}{a}\right)^2+\left(\frac{kd_{hk0}}{a}\right)^2=1$$

which we can rearrange by dividing both sides by d_{hk0}^2 into

$$\frac{1}{d_{hk0}^2}=\frac{h^2}{a^2}+\frac{k^2}{a^2}=\frac{h^2+k^2}{a^2}$$

which is eqn 37.1a.

The corresponding expression for a general orthorhombic lattice (one in which the axes are mutually perpendicular) is the generalization of this expression:

$$\frac{1}{d_{hkl}^2}=\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2} \tag{37.1c}$$

Orthorhombic lattice Separation of planes

Example 37.1 Using the Miller indices

Calculate the separation of (a) the $\{123\}$ planes and (b) the $\{246\}$ planes of an orthorhombic unit cell with $a=0.82$ nm, $b=0.94$ nm, and $c=0.75$ nm.

Method For the first part, simply substitute the information into eqn 37.1c. For the second part, instead of repeating the calculation, note that if all three Miller indices are multiplied by n, then their separation is reduced by that factor (Fig. 37.13):

$$\frac{1}{d^2_{nh,nk,nl}}=\frac{(nh)^2}{a^2}+\frac{(nk)^2}{b^2}+\frac{(nl)^2}{c^2}=n^2\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)=\frac{n^2}{d^2_{hkl}}$$

which implies that

$$d_{nh,nk,nl}=\frac{d_{hkl}}{n}$$

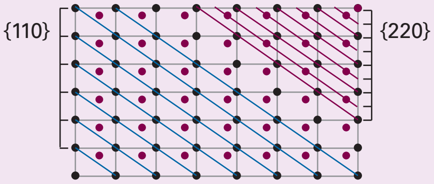


Figure 37.13 The separation of the {220} planes is half that of the {110} planes. In general, the separation of the planes {*nh*,*nk*,*nl*} is *n* times smaller than the separation of the {*hkl*} planes.

Answer Substituting the indices into eqn 37.1c gives

$$\frac{1}{d^2_{123}}=\frac{1^2}{(0.82\ \text{nm})^2}+\frac{2^2}{(0.94\ \text{nm})^2}+\frac{3^2}{(0.75\ \text{nm})^2}=22\ \text{nm}^{-2}$$

Hence, $d_{123}=0.22$ nm. It then follows immediately that d_{246} is one-half this value, or 0.11 nm.

> *A note on good practice* It is always sensible to look for analytical relations between quantities rather than to evaluate expressions numerically each time, for that emphasizes the relations between quantities (and avoids unnecessary work).

Self-test 37.3 Calculate the separation of (a) the {133} planes and (b) the {399} planes in the same lattice.

Answer: (a) 0.19 nm, (b) 0.063 nm

37.3 X-ray crystallography

A characteristic property of waves is that when they are present in the same region of space they interfere with one another, giving a greater displacement where peaks or troughs coincide and a smaller displacement where peaks coincide with troughs (Fig. 37.14). According to classical electromagnetic theory, the intensity of electromagnetic radiation is proportional to the square of the amplitude of the waves. Therefore, the regions of constructive or destructive interference show up as regions of enhanced or diminished intensities. The phenomenon of **diffraction** is the interference caused by an object in the path of waves, and the pattern of varying intensity that results is called the **diffraction pattern**. Diffraction occurs when the dimensions of the diffracting object are comparable to the wavelength of the radiation.

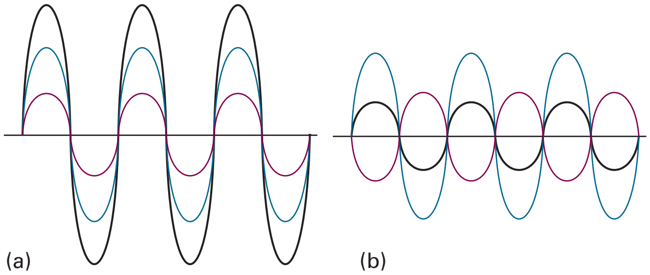


Figure 37.14 When two waves are in the same region of space they interfere. Depending on their relative phase, they may interfere (a) constructively, to give an enhanced amplitude, or (b) destructively, to give a smaller amplitude. The component waves are shown in blue and purple and the resultant in black.

X-rays are electromagnetic radiation with wavelengths of the order of 10^{-10} m, which is comparable to the separation of lattice planes in a crystal. Consequently, X-ray diffraction is the basis of **X-ray crystallography**, a technique of extraordinary power for the determination of crystal structures. The method developed by the Braggs (William and his son Lawrence, who later jointly won the Nobel Prize) is the foundation of almost all modern work in X-ray crystallography. They used a single crystal and a monochromatic beam of X-rays, and rotated the crystal until a reflection was detected. There are many different sets of planes in a crystal, so there are many angles at which a reflection occurs. The raw data consist of the angles at which reflections are observed and their intensities.

Single-crystal diffraction patterns are measured by using a **four-circle diffractometer** (Fig. 37.15). An integrated computer identifies the angular settings of the diffractometer's four circles that are needed to observe any particular intensity peak

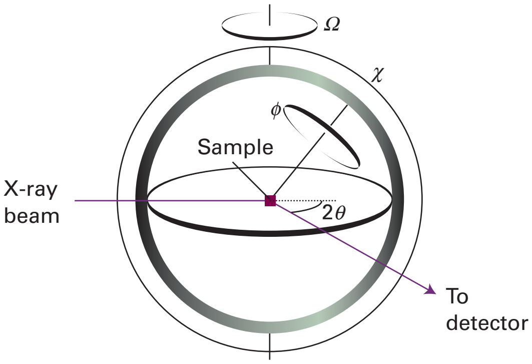


Figure 37.15 A four-circle diffractometer. The settings of the orientations (ϕ, χ, θ, and Ω) of the components are controlled by computer; each (*hkl*) reflection is monitored in turn, and their intensities are recorded.

in the diffraction pattern. At each setting, the diffraction intensity is measured, and background intensities are assessed by making measurements at slightly different settings. Computing techniques are now available that lead not only to automatic indexing but also to the automated determination of the shape, symmetry, and size of the unit cell. Moreover, several techniques are now available for sampling large amounts of data, including area detectors and image plates, which sample whole regions of diffraction patterns simultaneously.

(a) Bragg's law

An early approach to the analysis of diffraction patterns produced by crystals was to regard a lattice plane as a semi-transparent mirror and to model a crystal as a stack of reflecting lattice planes of separation d (Fig. 37.16). The model makes it easy to calculate the angle the crystal must make to the incoming beam of X-rays for constructive interference to occur. It has also given rise to the name **reflection** to denote an intense beam arising from constructive interference.

Consider the reflection of two parallel rays of the same wavelength by two adjacent planes of a lattice, as shown in Fig. 37.16. One ray strikes point D on the upper plane but the other ray must travel an additional distance AB before striking the plane immediately below. Similarly, the reflected rays will differ in path length by a distance BC. The net path-length difference of the two rays is then

$$\mathrm{AB} + \mathrm{BC} = 2d\sin\theta$$

where 2θ is the **glancing angle** (2θ is the angle through which the beam is deflected when it makes an angle θ to the lattice plane). For many glancing angles the path-length difference is not an integer number of wavelengths, and the waves interfere largely destructively. However, when the path-length difference is an integer number of wavelengths ($\mathrm{AB}+\mathrm{BC}=n\lambda$), the reflected waves are in phase and interfere constructively. It follows that a reflection should be observed when the glancing angle satisfies **Bragg's law**:

$$n\lambda = 2d\sin\theta \qquad \text{Bragg's law} \qquad (37.2a)$$

Reflections with $n=2, 3, \ldots$ are called *second-order*, *third-order*, and so on; they correspond to path-length differences of 2, 3, … wavelengths. In modern work it is normal to absorb the n into d, to write Bragg's law as

$$\lambda = 2d\sin\theta \qquad \textit{Alternative form} \quad \text{Bragg's law} \qquad (37.2b)$$

and to regard the nth-order reflection as arising from the $\{nh,nk,nl\}$ planes (see Example 37.1).

The primary use of Bragg's law is in the determination of the spacing between the layers in the lattice, for once the angle θ corresponding to a reflection has been determined, d may readily be calculated.

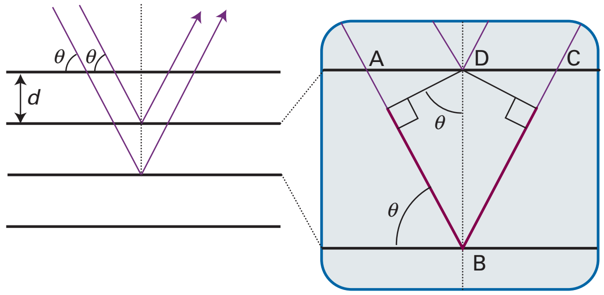


Figure 37.16 The conventional derivation of Bragg's law treats each lattice plane as a plane reflecting the incident radiation. The path lengths differ by AB+BC, which depends on the glancing angle, 2θ. Constructive interference (a 'reflection') occurs when AB+BC is equal to an integer number of wavelengths.

Brief illustration 37.3 Bragg's law 1

A first-order reflection from the {111} planes of a cubic crystal was observed at $\theta=11.2°$ when X-rays of wavelength 154 pm were used. According to eqn 37.2, the {111} planes responsible for the diffraction have separation $d_{111}=\lambda/(2\sin\theta)$. The separation of the {111} planes of a cubic lattice of side a is given by eqn 37.1 as $d_{111}=a/3^{1/2}$. Therefore,

$$a=\frac{3^{1/2}\lambda}{2\sin\theta}=\frac{3^{1/2}\times(154\ \mathrm{pm})}{2\sin 11.2°}=687\ \mathrm{pm}$$

Self-test 37.4 Calculate the angle θ at which the same crystal will give a reflection from the {123} planes.

Answer: 24.8°

Brief illustration 37.4 Bragg's law 2

Some types of unit cell give characteristic and easily recognizable patterns of lines. In a cubic lattice of unit cell dimension a the spacing is given by eqn 37.2, so the angles at which the $\{hkl\}$ planes give first-order reflections are given by

$$\sin\theta=(h^2+k^2+l^2)^{1/2}\frac{\lambda}{2a}$$

The reflections are then predicted by substituting the values of h, k, and l:

$\{hkl\}$	{100}	{110}	{111}	{200}	{210}	{211}	{220}	{300}	{221}	{310}…
$h^2+k^2+l^2$	1	2	3	4	5	6	8	9	9	10…

Notice that 7 (and 15, …) is missing because the sum of the squares of three integers cannot equal 7 (or 15, …). Such absences from the pattern are characteristic of the cubic P lattice.

Self-test 37.5 Normally, experimental procedures measure the glancing angle 2θ rather than θ itself. A diffraction examination of the element polonium gave lines at the following values of 2θ (in degrees) when 71.0 pm X-rays were used: 12.1, 17.1, 21.0, 24.3, 27.2, 29.9, 34.7, 36.9, 38.9, 40.9, 42.8. Identify the unit cell and determine its dimensions.

Answer: cubic P; $a = 337$ pm

(b) The electron density

To prepare the way to discussing methods of structural analysis we need to note that the scattering of X-rays is caused by the oscillations an incoming electromagnetic wave generates in the electrons of atoms. Heavy, electron-rich atoms give rise to stronger scattering than light atoms. This dependence on the number of electrons is expressed in terms of the **scattering factor**, f, of the element. If the scattering factor is large, then the atoms scatter X-rays strongly. An analysis that we do not repeat here concludes that the scattering factor of an atom is related to the electron density distribution in the atom, $\rho(r)$, and the angle 2θ through which the beam is scattered, by

$$f = 4\pi\int_0^\infty \rho(r)\frac{\sin kr}{kr}r^2\mathrm{d}r \quad k = \frac{4\pi}{\lambda}\sin\theta \qquad \text{Scattering factor} \qquad (37.3)$$

The value of f is greatest in the forward direction ($\theta = 0$, Fig. 37.17). The detailed analysis of the intensities of reflections must take this dependence on direction into account. We show in the following *Justification* that, in the forward direction, f is equal to the total number of electrons in the atom.

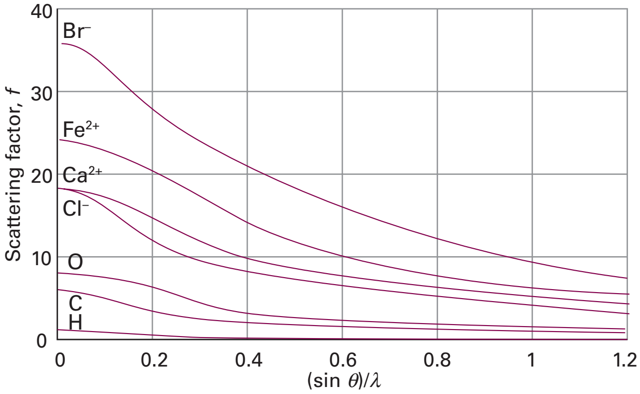


Figure 37.17 The variation of the scattering factor of atoms and ions with atomic number and angle. The scattering factor in the forward direction (at $\theta = 0$, and hence at $(\sin\theta)/\lambda = 0$) is equal to the number of electrons present in the species.

Justification 37.2 The forward scattering factor

As $\theta \to 0$, so $k \propto \sin\theta \to 0$. Because $\sin x = x - \frac{1}{6}x^3 + \cdots$,

$$\lim_{k\to 0}\frac{\sin kr}{kr} = \lim_{k\to 0}\frac{kr - \frac{1}{6}(kr)^3 + \cdots}{kr} = \lim_{k\to 0}(1 - \tfrac{1}{6}(kr)^2 + \cdots) = 1$$

The factor $(\sin kr)/kr$ is therefore equal to 1 for forward scattering. It follows that in the forward direction

$$f = 4\pi\int_0^\infty \rho(r)r^2\mathrm{d}r$$

The integral over the electron density ρ (the number of electrons in an infinitesimal region divided by the volume of the region) multiplied by the volume element $4\pi r^2\mathrm{d}r$, the volume of a spherical shell of radius r and thickness $\mathrm{d}r$, is the total number of electrons, N_e, in the atom. Hence, in the forward direction, $f = N_e$. For example, the scattering factors of Na^+, K^+, and Cl^- are 10, 18, and 18, respectively.

If a unit cell contains several atoms with scattering factors f_j and coordinates $(x_j a, y_j b, z_j c)$, then we show in the following *Justification* that the overall amplitude of a wave diffracted by the $\{hkl\}$ planes is given by

$$F_{hkl} = \sum_j f_j \mathrm{e}^{\mathrm{i}\phi_{hkl}(j)} \qquad \text{Structure factor} \qquad (37.4)$$

where $\phi_{hkl}(j) = 2\pi(hx_j + ky_j + lz_j)$. The sum is over all the atoms in the unit cell. The quantity F_{hkl} is called the **structure factor**.

Justification 37.3 The structure factor

We begin by showing that if in the unit cell there is an A atom at the origin and a B atom at the coordinates (xa,yb,zc), where x, y, and z lie in the range 0 to 1, then the phase difference, ϕ_{hkl}, between the (hkl) reflections of the A and B atoms is equal to $2\pi(hx+ky+lz)$.

Consider the crystal shown schematically in Fig. 37.18. The reflection corresponds to two waves from adjacent A planes; for the wavelength and angle of incidence shown, there is constructive interference and hence a strong reflection when the phase difference of the waves is 2π. If there is a B atom at a fraction x of the distance between the two A planes, then it gives rise to a wave with a phase difference $2\pi x$ relative to an A reflection. To see this conclusion, note that if $x = 0$, there is no phase difference; if $x = \frac{1}{2}$ the phase difference is π; if $x = 1$, the B atom lies where the lower A atom is and the phase difference

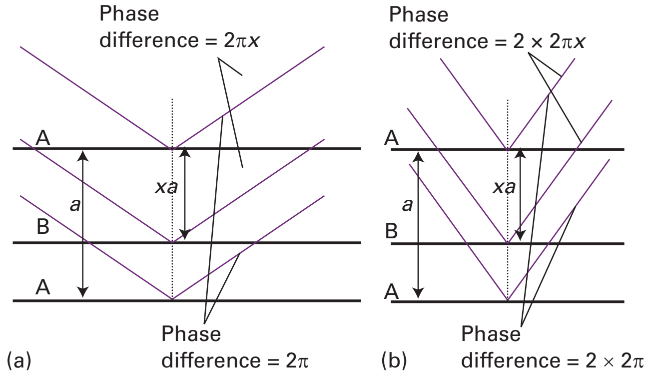


Figure 37.18 Diffraction from a crystal containing two kinds of atoms. (a) For a (100) reflection from the A planes, there is a phase difference of 2π between waves reflected by neighbouring planes. (b) For a (200) reflection, the phase difference is 4π. The reflection from a B plane at a fractional distance *xa* from an A plane has a phase that is *x* times these phase differences.

is 2π. Now consider a (200) reflection. There is now a $2\times 2\pi$ difference between the waves from the two A layers, and if B were to lie at $x=0.5$ it would give rise to a wave that differed in phase by 2π from the wave from the upper A layer.

Thus, for a general fractional position x, the phase difference for a (200) reflection is $2\times 2\pi x$. For a general (h00) reflection, the phase difference is therefore $h\times 2\pi x$. For three dimensions, this result generalizes to eqn 37.4.

Example 37.2 Calculating a structure factor

Calculate the structure factors for the unit cell in Fig. 37.19.

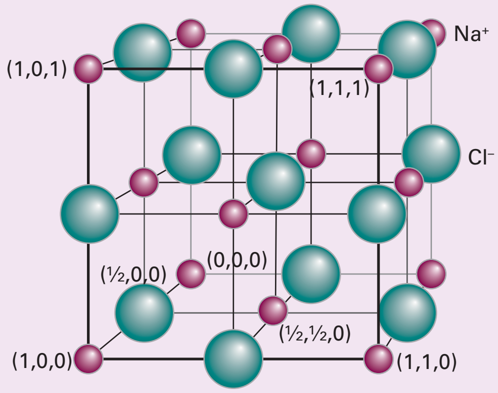


Figure 37.19 The location of the atoms for the structure factor calculation in Example 37.2. The red spheres are Na^+, the green spheres are Cl^-.

Method The structure factor is defined by eqn 37.4. To use this equation, consider the ions at the locations specified in Fig. 37.19. Write f^+ for the Na^+ scattering factor and f^- for the Cl^- scattering factor. Note that ions in the body of the cell contribute to the scattering with a strength f. However, ions on faces are shared between two cells (use $\frac{1}{2}f$), those on edges by four cells (use $\frac{1}{4}f$), and those at corners by eight cells (use $\frac{1}{8}f$). Two useful relations are (*Mathematical background* 3)

$$e^{i\pi}=-1 \qquad \cos\phi=\tfrac{1}{2}(e^{i\phi}+e^{-i\phi})$$

Answer From eqn 37.4, and summing over the coordinates of all 27 atoms in the illustration:

$$\begin{aligned}F_{hkl}&=f^+\left(\tfrac{1}{8}+\tfrac{1}{8}e^{2\pi i l}+\ldots+\tfrac{1}{2}e^{2\pi i(\frac{1}{2}h+\frac{1}{2}k+l)}\right)\\&\quad+f^-\left(e^{2\pi i(\frac{1}{2}h+\frac{1}{2}k+\frac{1}{2}l)}+\tfrac{1}{4}e^{2\pi i(\frac{1}{2}h)}+\ldots+\tfrac{1}{4}e^{2\pi i(\frac{1}{2}h+l)}\right)\end{aligned}$$

To simplify this 27-term expression, we use $e^{2\pi i h}=e^{2\pi i k}=e^{2\pi i l}=1$ because h, k, and l are all integers:

$$\begin{aligned}F_{hkl}&=f^+\{1+\cos(h+k)\pi+\cos(h+l)\pi+\cos(k+l)\pi\}\\&\quad+f^-\{(-1)^{h+k+l}+\cos k\pi+\cos l\pi+\cos h\pi\}\end{aligned}$$

Then, because $\cos h\pi=(-1)^h$,

$$\begin{aligned}F_{hkl}&=f^+\{1+(-1)^{h+k}+(-1)^{h+l}+(-1)^{l+k}\}\\&\quad+f^-\{(-1)^{h+k+l}+(-1)^h+(-1)^k+(-1)^l\}\end{aligned}$$

Now note that:

if h, k, and l are all even, $F_{hkl}=f^+\{1+1+1+1\}$
$+f^-\{1+1+1+1\}=4(f^++f^-)$

if h, k, and l are all odd, $F_{hkl}=4(f^+-f^-)$

if one index is odd and two are even, or vice versa,
$F_{hkl}=0$.

The hkl all-odd reflections are less intense than the hkl all-even. For $f^+=f^-$, which is the case for identical atoms in a cubic P arrangement, the hkl all-odd have zero intensity, corresponding to the absences that are characteristic of cubic P unit cells (see *Brief illustration* 37.4).

Self-test 37.6 Which reflections cannot be observed for a cubic I lattice?

Answer: for $h+k+l$ odd, $F_{hkl}=0$

The intensity of the (hkl) reflection is proportional to $|F_{hkl}|^2$, so in principle we can determine the structure factors experimentally by taking the square root of the corresponding intensities (but see below). Then, once we know all the structure factors F_{hkl}, we can calculate the electron density distribution, $\rho(\boldsymbol{r})$, in the unit cell by using the expression

$$\rho(\boldsymbol{r}) = \frac{1}{V}\sum_{hkl} F_{hkl}\,\mathrm{e}^{-2\pi\mathrm{i}(hx+ky+lz)} \qquad (37.5)$$

Fourier synthesis of the electron density distribution

where V is the volume of the unit cell. Equation 37.5 is called a **Fourier synthesis** of the electron density. Fourier transforms occur throughout chemistry in a variety of guises, and are described in more detail in *Mathematical background* 6.

Example 37.3 Calculating an electron density by Fourier synthesis

Consider the $\{h00\}$ planes of a crystal extending indefinitely in the x-direction. In an X-ray analysis the structure factors were found as follows:

h:	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
F_h	16	−10	2	−1	7	−10	8	−3	2	−3	6	−5	3	−2	2	−3

(and $F_{-h} = F_h$). Construct a plot of the electron density projected on to the x-axis of the unit cell.

Method Because $F_{-h} = F_h$, it follows from eqn 37.5 that

$$V\rho(x) = \sum_{h=-\infty}^{\infty} F_h \mathrm{e}^{-2\pi\mathrm{i}hx} = F_0 + \sum_{h=1}^{\infty}(F_h \mathrm{e}^{-2\pi\mathrm{i}hx} + F_{-h}\mathrm{e}^{2\pi\mathrm{i}hx})$$

$$= F_0 + \sum_{h=1}^{\infty} F_h(\mathrm{e}^{-2\pi\mathrm{i}hx} + \mathrm{e}^{2\pi\mathrm{i}hx}) \overset{\frac{1}{2}(\mathrm{e}^{-2\pi\mathrm{i}hx}+\mathrm{e}^{2\pi\mathrm{i}hx})=\cos 2\pi hx}{\hat{=}} F_0 + 2\sum_{h=1}^{\infty} F_h \cos 2\pi hx$$

and we evaluate the sum (truncated at $h = 15$) for points $0 \leq x \leq 1$ by using mathematical software.

Answer The results are plotted in Fig. 37.20 (green line). The positions of three atoms can be discerned very readily. The more terms there are included, the more accurate the density plot. Terms corresponding to high values of h (short-wavelength cosine terms in the sum) account for the finer details of the electron density; low values of h account for the broad features.

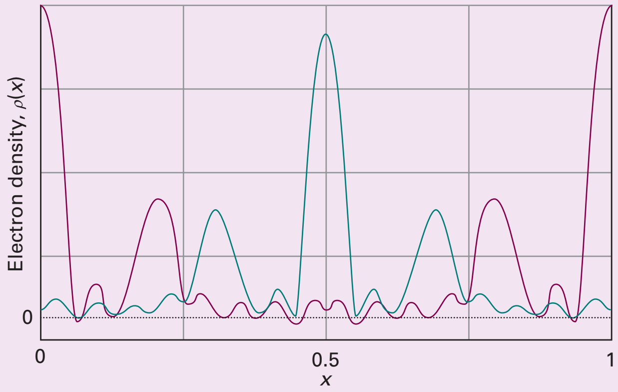


Figure 37.20 The plot of the electron density calculated in Example 37.3 (green) and Self-test 37.7 (purple).

Self-test 37.7 Use mathematical software to experiment with different structure factors (including changing signs as well as amplitudes). For example, use the same values of F_h as above, but with positive signs for $h \geq 6$.

Answer: Fig. 37.20 (purple line)

(c) Determination of the structure

A problem with the procedure outlined above is that the observed intensity I_{hkl} is proportional to the square modulus $|F_{hkl}|^2$, so we do not know whether to use $+|F_{hkl}|$ or $-|F_{hkl}|$ in the sum in eqn 37.5. In fact, the difficulty is more severe for non-centrosymmetric unit cells, because if we write F_{hkl} as the complex number $|F_{hkl}|\mathrm{e}^{\mathrm{i}\alpha}$, where α is the phase of F_{hkl} and $|F_{hkl}|$ is its magnitude, then the intensity lets us determine $|F_{hkl}|$ but tells us nothing of its phase, which may lie anywhere from 0 to 2π. This ambiguity is called the **phase problem**; its consequences are illustrated by comparing the two plots in Fig. 37.20. Some way must be found to assign phases to the structure factors, for otherwise the sum for ρ cannot be evaluated and the method would be useless.

The phase problem can be overcome to some extent by a variety of methods. One procedure that is widely used for inorganic materials with a reasonably small number of atoms in a unit cell and for organic molecules with a small number of heavy atoms is the **Patterson synthesis**. Instead of the structure factors F_{hkl}, the values of $|F_{hkl}|^2$, which can be obtained without ambiguity from the intensities, are used in an expression that resembles eqn 37.5:

$$P(\boldsymbol{r}) = \frac{1}{V}\sum_{hkl} |F_{hkl}|^2 \mathrm{e}^{-2\pi\mathrm{i}(hx+ky+lz)} \qquad (37.6)$$

Patterson synthesis

where the values $\boldsymbol{r}$ correspond to the vector separations between the atoms in the unit cell, that is, the distances and directions between atoms. Whereas the electron density function $\rho(\boldsymbol{r})$ is the probability density of the positions of atoms, the function $P(\boldsymbol{r})$ is a map of the probability density of the separations between atoms: a peak in P at a vector separation $\boldsymbol{r}$ arises from pairs of atoms that are separated by the same separation $\boldsymbol{r}$. Thus, if atom A is at the coordinates (x_A, y_A, z_A) and atom B is at (x_B, y_B, z_B), then there will be a peak at $(x_A - x_B, y_A - y_B, z_A - z_B)$ in the Patterson map. There will also be a peak at the negative of these coordinates, because there is a separation vector from B to A as well as a separation vector from A to B. The height of the peak in the map is proportional to the product of the atomic numbers of the two atoms, Z_AZ_B.

Brief illustration 37.5 The Patterson synthesis

If the unit cell has the structure shown in Fig. 37.21a, the Patterson synthesis would be the map shown in Fig. 37.21b, where the location of each spot relative to the origin gives the separation and relative orientation of each pair of atoms in the original structure.

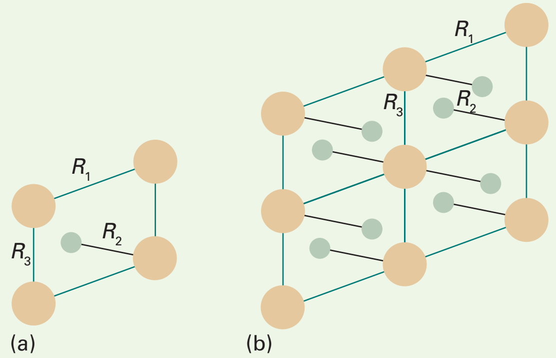


Figure 37.21 The Patterson synthesis corresponding to the pattern in (a) is the pattern in (b). The distance and orientation of each spot from the origin gives the orientation and separation of one atom–atom separation in (a). Some of the typical distances and their contribution to (b) are shown as R_1, etc.

Self-test 37.8 Consider the data in Example 37.3. Show that $VP(x)=|F_0|^2+2\Sigma_{h=1}^{\infty}|F_h|^2\cos 2\pi hx$ and plot the Patterson synthesis.

Answer:

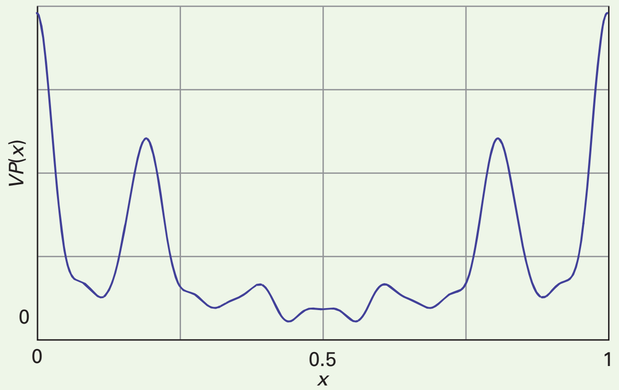


Figure 37.22 Patterson synthesis of the data from Example 37.3.

Heavy atoms dominate the scattering because their scattering factors are large, of the order of their atomic numbers, and their locations may be deduced quite readily. The sign of F_{hkl} can now be calculated from the locations of the heavy atoms in the unit cell, and to a high probability the phase calculated for them will be the same as the phase for the entire unit cell. To see why this is so, we have to note that a structure factor of a centrosymmetric cell has the form

$$F=(\pm)f_{\text{heavy}}+(\pm)f_{\text{light}}+(\pm)f_{\text{light}}+\ldots \tag{37.7}$$

where f_{heavy} is the scattering factor of the heavy atom and f_{light} the scattering factors of the light atoms. The f_{light} are all much smaller than f_{heavy}, and their phases are more or less random if the atoms are distributed throughout the unit cell. Therefore, the net effect of the f_{light} is to change F only slightly from f_{heavy}, and we can be reasonably confident that F will have the same sign as that calculated from the location of the heavy atom. This phase can then be combined with the observed $|F|$ (from the reflection intensity) to perform a Fourier synthesis of the full electron density in the unit cell, and hence to locate the light atoms as well as the heavy atoms.

Modern structural analyses make extensive use of **direct methods**. Direct methods are based on the possibility of treating the atoms in a unit cell as being virtually randomly distributed (from the radiation's point of view), and then to use statistical techniques to compute the probabilities that the phases have a particular value. It is possible to deduce relations between some structure factors and sums (and sums of squares) of others, which have the effect of constraining the phases to particular values (with high probability, so long as the structure factors are large). For example, the **Sayre probability relation** has the form

$$\begin{aligned}&\text{sign of } F_{h+h',k+k',l+l'} \text{ is probably equal}\\&\quad\text{to } (\text{sign of } F_{hkl})\times(\text{sign of } F_{h'k'l'})\end{aligned} \tag{37.8}$$

Sayre probability relation

For example, if F_{122} and F_{232} are both large and negative, then it is highly likely that F_{354}, provided it is large, will be positive.

In the final stages of the determination of a crystal structure, the parameters describing the structure (atom positions, for instance) are adjusted systematically to give the best fit between the observed intensities and those calculated from the model of the structure deduced from the diffraction pattern. This process is called **structure refinement**. Not only does the procedure give accurate positions for all the atoms in the unit cell, but it also gives an estimate of the errors in those positions and in the bond lengths and angles derived from them. The procedure also provides information on the vibrational amplitudes of the atoms.

37.4 Neutron and electron diffraction

According to the de Broglie relation (Topic 4, $\lambda=h/p$), particles have wavelengths and may therefore undergo diffraction.

Neutrons generated in a nuclear reactor and then slowed to thermal velocities have wavelengths similar to those of X-rays and may also be used for diffraction studies. For instance, a neutron generated in a reactor and slowed to thermal velocities by repeated collisions with a moderator (such as graphite) until it is travelling at about 4 km s^{-1} has a wavelength of about 100 pm. In practice, a range of wavelengths occurs in a neutron beam, but a monochromatic beam can be selected by diffraction from a crystal, such as a single crystal of germanium.

Example 37.4 Calculating the typical wavelength of thermal neutrons

Calculate the typical wavelength of neutrons after reaching thermal equilibrium with their surroundings at 373 K. For simplicity, assume that the particles are travelling in one dimension.

Method We need to relate the wavelength to the temperature. There are two linking steps. First, the de Broglie relation expresses the wavelength in terms of the linear momentum. Then the linear momentum can be expressed in terms of the kinetic energy, the mean value of which is given in terms of the temperature by the equipartition theorem (Topic 2).

Answer From the equipartition principle, we know that the mean translational kinetic energy of a neutron at a temperature T travelling in the x-direction is $E_k = \frac{1}{2}kT$. The kinetic energy is also equal to $p^2/2m$, where p is the momentum of the neutron and m is its mass. Hence, $p=(mkT)^{1/2}$. It follows from the de Broglie relation $\lambda=h/p$ that the neutron's wavelength is

$$\lambda=\frac{h}{(mkT)^{1/2}}$$

Therefore, at 373 K,

$$\begin{aligned}\lambda&=\frac{6.626\times10^{-34}\,\text{J s}}{\{(1.675\times10^{-27}\,\text{kg})\times(1.381\times10^{-23}\,\text{J K}^{-1})\times(373\,\text{K})\}^{1/2}}\\&=\frac{6.626\times10^{-34}}{(1.675\times10^{-27}\times1.381\times10^{-23}\times373)^{1/2}}\,\frac{\text{kg m}^2\,\text{s}^{-1}}{(\text{kg}^2\,\text{m}^2\,\text{s}^{-2})^{1/2}}\\&=2.26\times10^{-10}\,\text{m}=226\,\text{pm}\end{aligned}$$

where we have used 1 J = 1 kg m^2 s^{-2}.

Self-test 37.9 Calculate the temperature needed for the average wavelength of the neutrons to be 100 pm.

Answer: 1.90×10^3 K

Neutron diffraction differs from X-ray diffraction in two main respects. First, the scattering of neutrons is a nuclear phenomenon. Neutrons pass through the extra-nuclear electrons of atoms and interact with the nuclei through the 'strong force' that is responsible for binding nucleons together. As a result, the intensity with which neutrons are scattered is independent of the number of electrons and neighbouring elements in the periodic table may scatter neutrons with markedly different intensities. Neutron diffraction can be used to distinguish atoms of elements such as Ni and Co that are present in the same compound and to study order–disorder phase transitions in FeCo. A second difference is that neutrons possess a magnetic moment due to their spin. This magnetic moment can couple to the magnetic fields of atoms or ions in a crystal (if the ions have unpaired electrons) and modify the diffraction pattern. One consequence is that neutron diffraction is well suited to the investigation of magnetically ordered lattices in which neighbouring atoms may be of the same element but have different orientations of their electronic spin (Fig. 37.23).

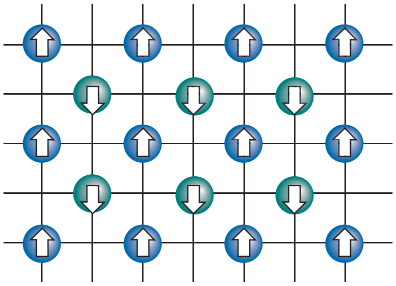


Figure 37.23 If the spins of atoms at lattice points are orderly, as in this material, where the spins of one set of atoms are aligned antiparallel to those of the other set, neutron diffraction detects two interpenetrating simple cubic lattices on account of the magnetic interaction of the neutron with the atoms, but X-ray diffraction would see only a single bcc lattice.

Electrons accelerated through a potential difference of 40 kV have wavelengths of about 6 pm, and so are also suitable for diffraction studies of molecules. Consider the scattering of electrons (or neutrons) from a pair of nuclei separated by a distance R_{ij} and orientated at a definite angle to an incident beam of electrons (or neutrons). When the molecule consists of a number of atoms, the scattering intensity can be calculated by summing over the contribution from all pairs. The total intensity I of the beam scattered through an angle 2θ to the incident direction is given by the **Wierl equation:**

$$I=\sum_{i,j}f_if_j\frac{\sin sR_{ij}}{sR_{ij}}\qquad s=\frac{4\pi}{\lambda}\sin\theta\qquad\text{Wierl equation}\qquad(37.9)$$

where λ is the wavelength of the electrons in the beam, and f is the **electron scattering factor**, a measure of the electron scattering power of the atom. The main application of electron diffraction techniques is to the study of surfaces (Topic 95), and you are invited to explore the Wierl equation in Problem 37.17.

Checklist of concepts

☐ 1. A **space lattice** is the pattern formed by points representing the locations of structural motifs (atoms, molecules, or groups of atoms, molecules, or ions).

☐ 2. The **Bravais lattices** are the 14 distinct space lattices in three dimensions (Fig. 37.8).

☐ 3. A **unit cell** is an imaginary parallelepiped that contains one unit of a translationally repeating pattern.

☐ 4. Unit cells are classified into **seven crystal systems** according to their rotational symmetries.

☐ 5. Crystal planes are specified by a set of **Miller indices** (*hkl*).

☐ 6. The **scattering factor** is a measure of the ability of an atom to diffract radiation.

☐ 7. The **structure factor** is the overall amplitude of a wave diffracted by the {*hkl*} planes.

☐ 8. **Fourier synthesis** is the construction of the electron density distribution from structure factors.

☐ 9. A **Patterson synthesis** is a map of interatomic vectors obtained by Fourier analysis of diffraction intensities.

☐ 10. **Structure refinement** is the adjustment of structural parameters to give the best fit between the observed intensities and those calculated from the model of the structure deduced from the diffraction pattern.

Checklist of equations

Property	Equation	Comment	Equation number
Separation of planes in an orthorhombic lattice	$1/d_{hkl}^2 = h^2/a^2 + k^2/b^2 + l^2/c^2$	*h*, *k*, and *l* are Miller indices	37.1c
Bragg's law	$\lambda = 2d \sin \theta$	*d* is the lattice spacing	37.2b
Scattering factor	$f = 4\pi\int_0^\infty [\{\rho(r)\sin kr\}/kr]r^2\mathrm{d}r,\ k = (4\pi/\lambda)\sin\theta$	Spherically symmetrical atom	37.3
Structure factor	$F_{hkl} = \sum_j f_j \mathrm{e}^{\mathrm{i}\phi_{hkl}(j)},\quad \phi_{hkl}(j) = 2\pi(hx_j + ky_j + lz_j)$	Definition	37.4
Fourier synthesis	$\rho(\boldsymbol{r}) = (1/V)\sum_{hkl} F_{hkl}\mathrm{e}^{-2\pi\mathrm{i}(hx+ky+lz)}$	*V* is the volume of the unit cell	37.5
Patterson synthesis	$P(\boldsymbol{r}) = (1/V)\sum_{hkl} \lvert F_{hkl}\rvert^2\,\mathrm{e}^{-2\pi\mathrm{i}(hx+ky+lz)}$		37.6
Wierl equation	$I(\theta) = \sum_{i,j} f_i f_j(\sin sR_{ij}/sR_{ij}),\quad s = (4\pi/\lambda)\sin\theta$		37.9

TOPIC 38

Bonding in solids

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➤ Why do you need to know this material?

To be prepared for the study of the mechanical, electrical, optical, and magnetic properties of materials that can form the basis of new technologies, you need to know how atoms and molecules interact to form metallic, ionic, and molecular solids.

➤ What is the key idea?

Four characteristic types of bonding in solids are found in metals, ionic solids, covalent solids, and molecular solids.

➤ What do you need to know already?

You need to be familiar with molecular interactions (Topic 35), the features of crystal structure (Topic 37), the principles of Hückel molecular orbital theory (Topic 26), and the calculation of reaction enthalpies (Topic 57).

The bonding within a solid may be of various kinds. Simplest of all are **metals**, where electrons are delocalized over arrays of identical cations and bind the whole together into a rigid but ductile and malleable structure. **Ionic solids** consist of cations and anions packed together in a crystal by electrostatic interactions (*Foundations*, Topic 2). In **covalent solids**, covalent bonds in a definite spatial orientation link the atoms in a network extending through a crystal. **Molecular solids** are bonded together by van der Waals interactions (Topic 35).

38.1 Metallic solids

The crystalline forms of metallic elements can be discussed by representing their atoms as identical hard spheres. Most metallic elements crystallize in one of three simple forms, two of which can be explained in terms of the hard spheres packing together in the closest possible arrangement. In this section we consider not only the geometrical arrangement of the atoms in the crystal, but also the distribution of electrons over the atoms.

(a) Close packing

Figure 38.1 shows a **close-packed** layer of identical spheres, one with maximum utilization of space. A close-packed three-dimensional structure is obtained by stacking such close-packed layers on top of one another. However, this stacking can be done in different ways, which result in close-packed **polytypes**, or structures that are identical in two dimensions (the close-packed layers) but differ in the third dimension.

In all polytypes, the spheres of the second close-packed layer lie in the depressions of the first layer (Fig. 38.2). The third layer may be added in either of two ways. In one, the spheres are placed so that they reproduce the first layer (Fig. 38.3a), to give an ABA pattern of layers. Alternatively, the spheres may be placed over the gaps in the first layer (Fig. 38.3b), so giving an ABC pattern. Two polytypes are formed if the two stacking patterns are repeated in the vertical direction. If the ABA pattern is

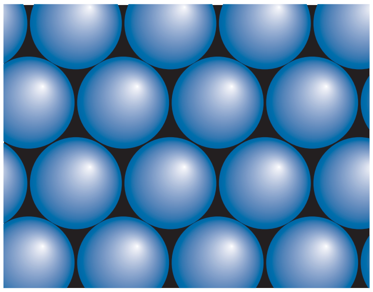

Figure 38.1 The first layer of close-packed spheres used to build a three-dimensional close-packed structure.

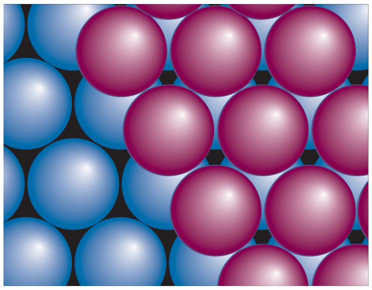

Figure 38.2 The second layer of close-packed spheres occupies the dips of the first layer. The two layers are the AB component of the close-packed structure.

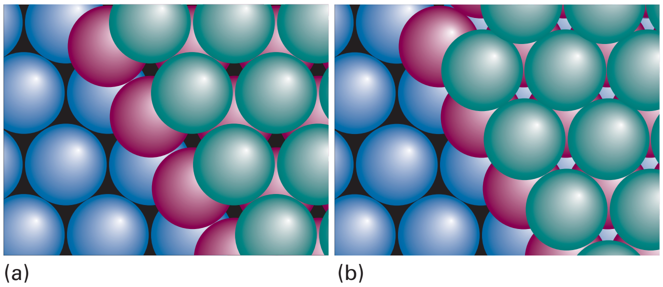

Figure 38.3 (a) The third layer of close-packed spheres might occupy the dips lying directly above the spheres in the first layer, resulting in an ABA structure, which corresponds to hexagonal close-packing. (b) Alternatively, the third layer might lie in the dips that are not above the spheres in the first layer, resulting in an ABC structure, which corresponds to cubic close-packing.

repeated, to give the sequence of layers ABABAB…, the spheres are **hexagonally close-packed** (hcp). Alternatively, if the ABC pattern is repeated, to give the sequence ABCABC…, the spheres are **cubic close-packed** (ccp). We can see the origins of these names by referring to Fig. 38.4. The ccp structure gives rise to a face-centred unit cell, so may also be denoted cubic F (or fcc, for face-centred cubic). It is also possible to have random sequences of layers; however, the hcp and ccp polytypes are the most important. Table 38.1 lists some elements possessing these structures.

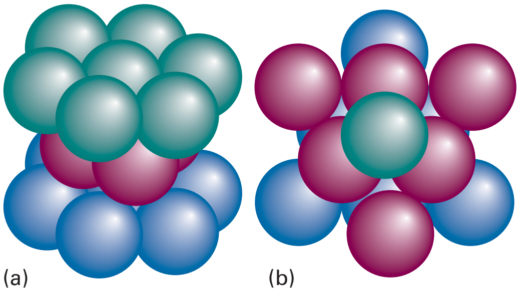

Figure 38.4 A fragment of the structure shown in Fig. 38.3 revealing the (a) hexagonal, (b) cubic symmetry. The tints on the spheres are the same as for the layers in Fig. 38.3.

Table 38.1 The crystal structures of some elements*

Structure	Element
hcp‡	Be, Cd, Co, He, Mg, Sc, Ti, Zn
fcc‡ (ccp, cubic F)	Ag, Al, Ar, Au, Ca, Cu, Kr, Ne, Ni, Pd, Pb, Pt, Rh, Rn, Sr, Xe
bcc (cubic I)	Ba, Cs, Cr, Fe, K, Li, Mn, Mo, Rb, Na, Ta, W, V
cubic P	Po

*The notation used to describe primitive unit cells is introduced in Topic 37.

‡ Close-packed structures.

The compactness of close-packed structures is indicated by their **coordination number,** the number of spheres immediately surrounding any selected sphere, which is 12 in all cases. Another measure of their compactness is the **packing fraction**, the fraction of space occupied by the spheres, which is 0.740 (see Example 38.1). That is, in a close-packed solid of identical hard spheres, only 26.0 per cent of the volume is empty space. The fact that many metals are close-packed accounts for their high mass densities.

Example 38.1 Calculating a packing fraction

Calculate the packing fraction of a ccp structure with spheres of radius R.

Method Refer to Fig. 38.5. First calculate the volume of a unit cell, and then calculate the total volume of the spheres that occupy it fully or partially. The first part of the calculation is an exercise in geometry. The second part involves counting the fraction of spheres that occupy the cell.

Answer We see in Fig. 38.5 that a diagonal of any face passes completely through one sphere and halfway through two other spheres. Therefore, the length of a diagonal is $4R$. The length of a side is therefore $8^{1/2}R$ and the volume of the unit cell is $8^{3/2}R^3$. As Fig 38.5 shows, each of the eight vertices of the cube contains the equivalent of $\frac{1}{8}$ of a sphere. Also, each of the six remaining

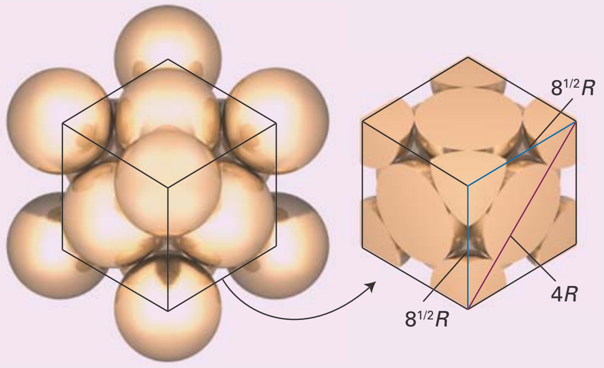

Figure 38.5 The calculation of the packing fraction of a ccp unit cell.

spheres contributes $\frac{1}{2}$ of its volume to the cell. Therefore, each cell contains the equivalent of $6\times\frac{1}{2}+8\times\frac{1}{8}=4$ spheres. Because the volume of each sphere is $\frac{4}{3}\pi R^3$, the total occupied volume is $\frac{16}{3}\pi R^3$. The fraction of space occupied is therefore

$$\frac{\frac{16}{3}\pi R^3}{8^{3/2}R^3}=\frac{16\pi}{3\times 8^{3/2}}=0.740$$

Because an hcp structure has the same coordination number, its packing fraction is the same.

Self-test 38.1 The packing fractions of structures that are not close-packed are calculated similarly. Calculate the packing fraction of a structure with one sphere at the centre of a cube formed by eight others: this is a cubic I (bcc) structure.

Answer: 0.68

As shown in Table 38.1, a number of common metals adopt structures that are less than close-packed. The departure from close packing suggests that factors such as specific covalent bonding between neighbouring atoms are beginning to influence the structure and impose a specific geometrical arrangement. One such arrangement results in a cubic I (bcc, for body-centred cubic) structure, with one sphere at the centre of a cube formed by eight others. The coordination number of a bcc structure is only 8, but there are six more atoms not much further away than the eight nearest neighbours. The packing fraction of 0.68 (Self-test 38.1) is not much smaller than the value for a close-packed structure (0.74), and shows that about two-thirds of the available space is actually occupied.

(b) Electronic structure of metals

The central aspect of solids that determines their electrical properties (Topic 39) is the distribution of their electrons. There are two models of this distribution. In one, the **nearly free-electron approximation**, the valence electrons are assumed to be trapped in a box with a periodic potential, with low energy at the locations of cations. In the **tight-binding approximation**, the valence electrons are assumed to occupy molecular orbitals delocalized throughout the solid. The latter model is more in accord with our discussion of electrical properties of solids (Topic 39), so we confine our attention to it.

Consider a one-dimensional solid, which consists of a single, infinitely long line of atoms. At first sight, this model may seem too restrictive and unrealistic. However, not only does it give us the concepts we need to understand the structure and electrical properties of three-dimensional, macroscopic samples of metals and semiconductors, it is also the starting point for the description of long and thin structures, such as carbon nanotubes.

Suppose that each atom has one s orbital available for forming molecular orbitals. We can construct the LCAO-MOs of the solid by adding N atoms in succession to a line, and then infer the electronic structure by using the building-up principle. One atom contributes one s orbital at a certain energy (Fig. 38.6). When a second atom is brought up it overlaps the first and forms bonding and antibonding orbitals. The third atom overlaps its nearest neighbour (and only slightly the next-nearest), and from these three atomic orbitals, three molecular orbitals are formed: one is fully bonding, one fully antibonding, and the intermediate orbital is nonbonding between neighbours. The fourth atom leads to the formation of a fourth molecular orbital. At this stage, we can begin to see that the general effect of bringing up successive atoms is to spread the range of energies covered by the molecular orbitals, and also to fill in the range of energies with more and more orbitals (one more for each atom). When N atoms have been added to the line, there are N molecular orbitals covering a band of energies of finite width, and the Hückel secular determinant (Topic 26) is

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 & 0 & \cdots & 0 \\ \beta & \alpha-E & \beta & 0 & 0 & \cdots & 0 \\ 0 & \beta & \alpha-E & \beta & 0 & \cdots & 0 \\ 0 & 0 & \beta & \alpha-E & \beta & \cdots & 0 \\ 0 & 0 & 0 & \beta & \alpha-E & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & 0 & \cdots & \alpha-E \end{vmatrix}=0$$

where α is the Coulomb integral and β is the (s,s) resonance integral. The theory of determinants applied to such a symmetrical example as this (technically a 'tridiagonal determinant') leads to the following expression for the roots:

$$E_k=\alpha+2\beta\cos\frac{k\pi}{N+1}\qquad k=1,2,\ldots,N \qquad (38.1)$$

Linear array of s orbitals Energy levels

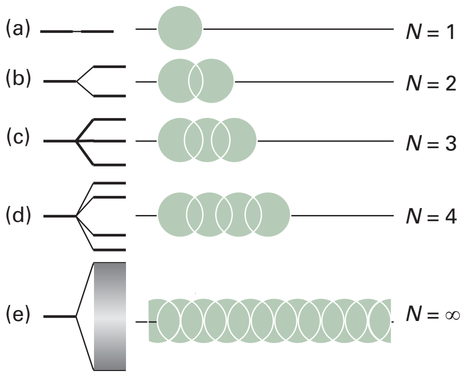

Figure 38.6 The formation of a band of *N* molecular orbitals by successive addition of *N* atoms to a line. Note that the band remains of finite width as *N* becomes infinite and, although it looks continuous, it consists of *N* different orbitals.

We show in the following *Justification* that when *N* is infinitely large, $E_{k+1}-E_k$ is infinitely small, but the band still has finite width overall (Fig. 38.6):

$$E_N - E_1 \to -4\beta \quad \text{as } N\to\infty \qquad \textit{Linear array of s orbitals} \quad \text{Band width} \tag{38.2}$$

(Note that because $\beta<0, -4\beta>0$.) We can think of this band as consisting of *N* different molecular orbitals, the lowest energy orbital ($k=1$) being fully bonding, and the highest energy orbital ($k=N$) being fully antibonding between adjacent atoms (Fig. 38.7). The molecular orbitals of intermediate energy have $k-1$ nodes distributed along the chain of atoms. Similar bands form in three-dimensional solids.

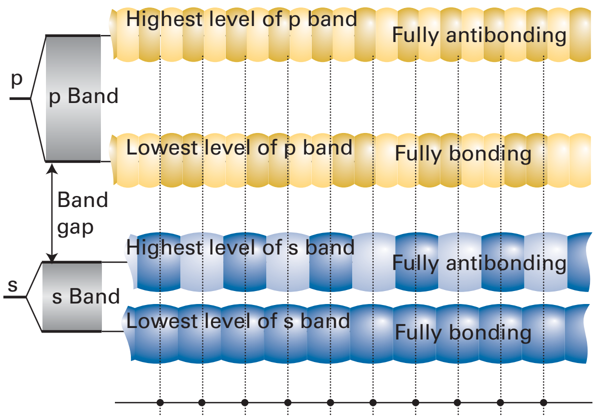

Figure 38.7 The overlap of s orbitals gives rise to an s band and the overlap of p orbitals gives rise to a p band. In this case, the s and p orbitals of the atoms are so widely spaced in energy that there is a band gap. In many cases the separation is less and the bands overlap.

Justification 38.1 The properties of a band

From eqn 38.1 we see that the energy separation between neighbouring energy levels *k* and $k+1$ is

$$\begin{aligned}E_{k+1}-E_k &= \left(\alpha+2\beta\cos\frac{(k+1)\pi}{N+1}\right)-\left(\alpha+2\beta\cos\frac{k\pi}{N+1}\right)\\ &=2\beta\left(\cos\frac{(k+1)\pi}{N+1}-\cos\frac{k\pi}{N+1}\right)\end{aligned} \tag{38.3}$$

By using the trigonometric identity $\cos(A+B)=\cos A\cos B-\sin A\sin B$, the first term in parentheses is

$$\cos\frac{(k+1)\pi}{N+1}=\cos\frac{k\pi}{N+1}\overbrace{\cos\frac{\pi}{N+1}}^{\to 1 \text{ as } N\to\infty}-\sin\frac{k\pi}{N+1}\overbrace{\sin\frac{\pi}{N+1}}^{\to 0 \text{ as } N\to\infty}$$

Therefore, as $N\to\infty$,

$$E_{k+1}-E_k \to 2\beta\left(\cos\frac{k\pi}{N+1}-\cos\frac{k\pi}{N+1}\right)=0$$

It follows that when *N* is infinitely large, the difference between neighbouring energy levels is infinitely small.

To assess the effect of *N* on the width E_N-E_1 of a band, we proceed as follows. The energy of the level with $k=1$ is

$$E_1=\alpha+2\beta\cos\frac{\pi}{N+1}$$

We already saw that as $N\to\infty$, $\cos 0\to 1$. Therefore, in this limit

$$E_1=\alpha+2\beta$$

When *k* has its maximum value of *N*,

$$E_N=\alpha+2\beta\cos\frac{N\pi}{N+1}$$

As *N* approaches infinity, we can ignore the 1 in the denominator, and the cosine term becomes $\cos\pi=-1$. Therefore, in this limit $E_N=\alpha-2\beta$, and $E_N-E_1\to-4\beta$, as in eqn 38.2.

Brief illustration 38.1 Energy levels in a band

To illustrate the dependence of $E_{k+1}-E_k$ on *N*, we use eqn 38.3 to calculate

$$N=3:\quad E_2-E_1=2\beta\left(\cos\frac{2\pi}{4}-\cos\frac{\pi}{4}\right)\approx-1.414\beta$$

$$N=300:\quad E_2-E_1=2\beta\left(\cos\frac{2\pi}{301}-\cos\frac{\pi}{301}\right)\approx-3.628\times10^{-4}\beta$$

We see that the energy difference decreases with increasing *N*.

Self-test 38.2 For $N=300$, at which value of *k* would $E_{k+1}-E_k$ have its maximum value? *Hint*: Use mathematical software.

Answer: $k=150$

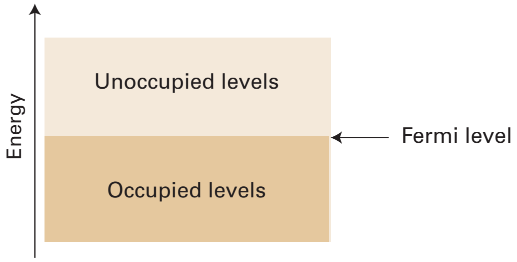

Figure 38.8 When N electrons occupy a band of N orbitals, it is only half full at $T = 0$ and the electrons near the Fermi level (the top of the filled levels) are mobile.

The band formed from overlap of s orbitals is called the **s band**. If the atoms have p orbitals available, the same procedure leads to a **p band** (as shown in the upper half of Fig. 38.7). If the atomic p orbitals lie higher in energy than the s orbitals, then the p band lies higher than the s band, and there may be a **band gap**, a range of energies to which no orbital corresponds. However, the s and p bands may also be contiguous or even overlap (as is the case for the 3s and 3p bands in magnesium).

Now consider the electronic structure of a solid formed from atoms each able to contribute one electron (for example, the alkali metals). There are N atomic orbitals and therefore N molecular orbitals packed into an apparently continuous band. There are N electrons to accommodate. At $T = 0$, only the lowest $\frac{1}{2}N$ molecular orbitals are occupied (Fig. 38.8), and the HOMO is called the **Fermi level**. However, unlike in molecules, there are empty orbitals very close in energy to the Fermi level, so it requires hardly any energy to excite the uppermost electrons. Some of the electrons are therefore very mobile and give rise to electrical conductivity (Topic 39).

38.2 Ionic solids

Two questions arise when we consider ionic solids: the relative locations adopted by the ions and the energetics of the resulting structure.

(a) Structure

When crystals of compounds of monatomic ions (such as NaCl and MgO) are modelled by stacks of hard spheres it is necessary to allow for the different ionic radii (typically with the cations smaller than the anions) and different electrical charges. The coordination number of an ion is the number of nearest neighbours of opposite charge; the structure itself is characterized as having **(N_+,N_-) coordination**, where N_+ is the coordination number of the cation and N_- that of the anion.

Even if, by chance, the ions have the same size, the problems of ensuring that the unit cells are electrically neutral make it impossible to achieve 12-coordinate close-packed ionic structures. As a result, ionic solids are generally less dense than metals. The best packing that can be achieved is the (8,8)-coordinate **caesium chloride structure** in which each cation is surrounded by eight anions and each anion is surrounded by eight cations (Fig. 38.9). In this structure, an ion of one charge occupies the centre of a cubic unit cell with eight counter-ions at its corners. The structure is adopted by CsCl itself and also by CaS.

When the radii of the ions differ more than in CsCl, even eight-coordinate packing cannot be achieved. One common structure adopted is the (6,6)-coordinate **rock salt structure** typified by NaCl (Fig. 38.10). In this structure, each cation is surrounded by six anions and each anion is surrounded by six cations. The rock salt structure can be pictured as consisting of two interpenetrating, slightly expanded cubic F (fcc) arrays, one composed of cations and the other of anions. This structure is adopted by NaCl itself and also by several other MX compounds, including KBr, AgCl, MgO, and ScN.

The switch from the caesium chloride structure to the rock salt structure is related to the value of the **radius ratio**, γ:

$$\gamma = \frac{r_{\text{smaller}}}{r_{\text{larger}}} \qquad \textit{Definition} \quad \text{Radius ratio} \qquad (38.4)$$

The two radii are those of the larger and smaller ions in the crystal. The **radius-ratio rule**, which is derived by considering

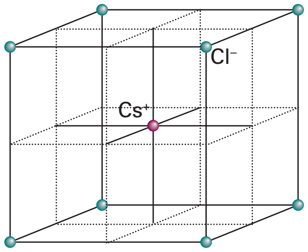

Figure 38.9 The caesium chloride structure consists of two interpenetrating simple cubic arrays of ions, one of cations and the other of anions, so that each cube of ions of one kind has a counter-ion at its centre.

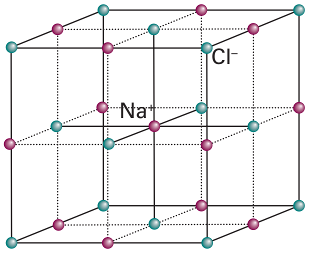

Figure 38.10 The rock salt (NaCl) structure consists of two mutually interpenetrating, slightly expanded face-centred cubic arrays of ions. The entire assembly shown here is the unit cell.

the geometrical problem of packing the maximum number of hard spheres of one radius around a hard sphere of a different radius, can be summarized as follows:

Radius ratio	Structural type
$\gamma < 2^{1/2} - 1 = 0.414$	Sphalerite (or zinc blende, Fig. 38.11)
$2^{1/2} - 1 = 0.414 < \gamma < 0.732$	Rock salt
$\gamma > 3^{1/2} - 1 = 0.732$	Caesium chloride

The deviation of a structure from that expected on the basis of this rule is often taken to be an indication of a shift from ionic towards covalent bonding. A major source of unreliability, though, is the arbitrariness of ionic radii and their variation with coordination number.

Ionic radii are derived from the distance between centres of adjacent ions in a crystal. However, we need to apportion the total distance between the two ions by defining the radius of one ion and then inferring the radius of the other ion. One scale that is widely used is based on the value 140 pm for the radius of the O^{2-} ion (Table 38.2). Other scales are also available (such as one based on F^- for discussing halides), and it is essential not to mix values from different scales. Because ionic radii are so arbitrary, predictions based on them must be viewed cautiously.

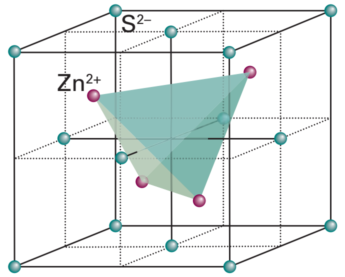

Figure 38.11 The structure of the sphalerite form of ZnS showing the location of the Zn atoms in the tetrahedral holes formed by the array of S atoms. (There is an S atom at the centre of the cube inside the tetrahedron of Zn atoms.)

Table 38.2* Ionic radii, *r*/pm

Na^+	102 (6‡), 116 (8)
K^+	138 (6), 151 (8)
F^-	128 (2), 131 (4)
Cl^-	181 (close packing)

* More values are given in the *Resource section*. This scale is based on a value 140 pm for the radius of the O^{2-} ion.

‡ Coordination number.

Brief illustration 38.2 The radius ratio

Using values of ionic radii from the Table 38.2, the radius ratio for MgO is

$$\gamma = \frac{\overbrace{72\,\text{pm}}^{\text{radius of Mg}^{2+}}}{\underbrace{140\,\text{pm}}_{\text{radius of O}^{2-}}} = 0.51$$

which is consistent with the observed rock salt structure of MgO crystals.

Self-test 38.3 Predict the crystal structure of TlCl.

Answer: $\gamma = 0.88$; caesium chloride structure

(b) Energetics

The **lattice energy** of a solid is the difference in Coulombic potential energy of the ions packed together in a solid and widely separated as a gas. The lattice energy is always positive; a high lattice energy indicates that the ions interact strongly with one another to give a tightly bonded solid. The **lattice enthalpy**, ΔH_L, is the change in standard molar enthalpy for the process

$$MX(s) \rightarrow M^+(g) + X^-(g)$$

and its equivalent for other charge types and stoichiometries. The lattice enthalpy is equal to the lattice energy at $T = 0$; at normal temperatures they differ by only a few kilojoules per mole, and the difference is normally neglected.

Each ion in a solid experiences electrostatic attractions from all the other oppositely charged ions and repulsions from all the other like-charged ions. The total Coulombic potential energy is the sum of all the electrostatic contributions. Each cation is surrounded by anions, and there is a large negative contribution from the attraction of the opposite charges. Beyond those nearest neighbours, there are cations that contribute a positive term to the total potential energy of the central cation. There is also a negative contribution from the anions beyond those cations, a positive contribution from the cations beyond them, and so on to the edge of the solid. These repulsions and attractions become progressively weaker as the distance from the central ion increases, but the net outcome of all these contributions is a lowering of energy.

First, consider a simple one-dimensional model of a solid consisting of a long line of uniformly spaced alternating cations and anions, with d the distance between their centres, the sum of the ionic radii (Fig. 38.12). If the charge numbers of the ions have the same absolute value (+1 and −1, or +2 and −2, for instance), then $z_1 = +z$, $z_2 = -z$, and $z_1 z_2 = -z^2$. The potential

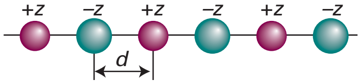

Figure 38.12 A line of alternating cations and ions used in the calculation of the Madelung constant in one dimension.

energy of the central ion is calculated by summing all the terms, with negative terms representing attractions to the other oppositely charged ions and positive terms representing repulsions from like-charged ions. For the interaction with ions extending in a line to the right of the central ion, the lattice energy is

$$\begin{aligned}E_\mathrm{p} &= \frac{1}{4\pi\varepsilon_0}\times\left(-\frac{z^2e^2}{d}+\frac{z^2e^2}{2d}-\frac{z^2e^2}{3d}+\frac{z^2e^2}{4d}-\ldots\right)\\ &= \frac{z^2e^2}{4\pi\varepsilon_0 d}\times\left(-1+\frac{1}{2}-\frac{1}{3}+\frac{1}{4}-\ldots\right)\\ &= -\frac{z^2e^2}{4\pi\varepsilon_0 d}\times\ln 2\end{aligned}$$

We have used the relation $1-\frac{1}{2}+\frac{1}{3}-\frac{1}{4}+\ldots=\ln 2$. Finally, we multiply E_p by 2 to obtain the total energy arising from interactions on each side of the ion and then multiply by Avogadro's constant, N_A, to obtain an expression for the lattice energy per mole of ions. The outcome is

$$E_\mathrm{p} = -2\ln 2\times\frac{z^2N_\mathrm{A}e^2}{4\pi\varepsilon_0 d}$$

with $d=r_\text{cation}+r_\text{anion}$. This energy is negative, corresponding to a net attraction. This calculation can be extended to three-dimensional arrays of ions with different charges:

$$E_\mathrm{p} = -A\times\frac{|z_\mathrm{A}z_\mathrm{B}|N_\mathrm{A}e^2}{4\pi\varepsilon_0 d} \tag{38.5}$$

The factor A is a positive numerical constant called the **Madelung constant**; its value depends on how the ions are arranged about one another. For ions arranged in the same way as in sodium chloride, $A=1.748$. Table 38.3 lists Madelung constants for other common structures.

Table 38.3 Madelung constants

Structural type	A
Caesium chloride	1.763
Fluorite	2.519
Rock salt	1.748
Rutile	2.408
Sphalerite	1.638
Wurtzite	1.641

There are also repulsions arising from the overlap of the filled atomic orbitals of the ions and, consequently, the role of the Pauli principle. These repulsions are taken into account by supposing that, because wavefunctions decay exponentially with distance at large distances from the nucleus, and repulsive interactions depend on the overlap of orbitals, the repulsive contribution to the potential energy has the form

$$E_\mathrm{p}^{*} = N_\mathrm{A}C'\mathrm{e}^{-d/d^{*}} \tag{38.6}$$

with C' and d^* constants; the value of C' is not needed (it cancels) and that of d^* is commonly taken to be 34.5 pm. The total potential energy is the sum of E_p and E_p^{*}, and passes through a minimum when $\mathrm{d}(E_\mathrm{p}+E_\mathrm{p}^{*})/\mathrm{d}d=0$ (Fig. 38.13). A short calculation leads to the following expression for the minimum total potential energy (see Problem 38.8):

$$E_\text{p,min} = -\frac{N_\mathrm{A}|z_\mathrm{A}z_\mathrm{B}|e^2}{4\pi\varepsilon_0 d}\left(1-\frac{d^{*}}{d}\right)A \quad \text{Born–Mayer equation} \tag{38.7}$$

This expression is called the **Born–Mayer equation**. Provided we ignore zero-point contributions to the energy, the negative of this potential energy can be identified with the lattice energy. The important features of this equation are:

- Because $E_\text{p,min}\propto|z_\mathrm{A}z_\mathrm{B}|$, the potential energy becomes more negative with increasing charge number of the ions.
- Because $E_\text{p,min}\propto 1/d$, the potential energy becomes more negative with decreasing ionic radius.

Physical interpretation

The second conclusion follows from the fact that the smaller the ionic radii, the smaller the value of d. We see that large lattice energies are expected when the ions are highly charged (so $|z_\mathrm{A}z_\mathrm{B}|$ is large) and small (so d is small).

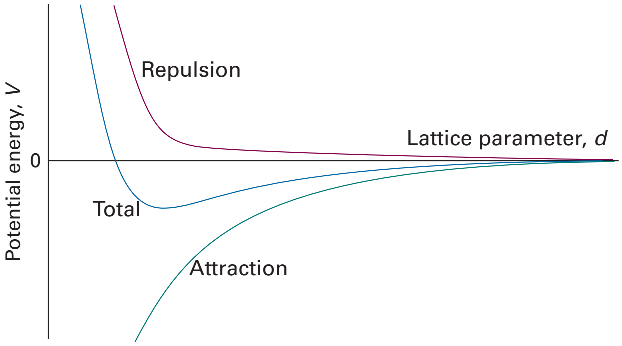

Figure 38.13 The contributions to the total potential energy of an ionic crystal.

Brief illustration 38.3 The Born–Mayer equation

To estimate $E_{\mathrm{p,min}}$ for MgO, which has a rock salt structure ($A=1.748$), we use $d=r(\mathrm{Mg}^{2+})+r(\mathrm{O}^{2-})=72+140\ \mathrm{pm}=212\ \mathrm{pm}$. We also use

$$\frac{N_{\mathrm{A}}e^2}{4\pi\varepsilon_0}=\frac{(6.022\,14\times10^{23}\ \mathrm{mol^{-1}})\times(1.602\,176\times10^{-19}\ \mathrm{C})^2}{4\pi\times(8.854\,19\times10^{-12}\ \mathrm{J^{-1}\,C^2\,m^{-1}})}$$
$$=1.3895\times10^{-4}\ \mathrm{J\,m\,mol^{-1}}$$

and obtain

$$E_{\mathrm{p,min}}=-\frac{\overbrace{4}^{|z_{\mathrm{Mg^{2+}}}z_{\mathrm{O^{2-}}}|}}{\underbrace{2.12\times10^{-10}\ \mathrm{m}}_{d}}\times\overbrace{(\,1.3895\times10^{-4}\ \mathrm{J\,m\,mol^{-1}})}^{N_{\mathrm{A}}e^2/4\pi\varepsilon_0}$$
$$\times\overbrace{\left(1-\frac{34.5\ \mathrm{pm}}{212\ \mathrm{pm}}\right)}^{1-d^*/d}\times\overbrace{1.748}^{A}=-3.84\times10^3\ \mathrm{kJ\,mol^{-1}}$$

Self-test 38.4 Which can be expected to have the greater lattice energy, magnesium oxide or strontium oxide?

Answer: MgO

Experimental values of the lattice enthalpy (the enthalpy, rather than the energy) are obtained by using a **Born–Haber cycle**, a closed path of transformations starting and ending at the same point, one step of which is the formation of the solid compound from a gas of widely separated ions.

Example 38.2 Using the Born–Haber cycle

Use the Born–Haber cycle to calculate the lattice enthalpy of KCl.

Method The Born–Haber cycle for KCl is shown in Fig 38.14. It consists of the following steps (for convenience, starting at the elements):

	$\Delta H/(\mathrm{kJ\,mol^{-1}})$	
1. Sublimation of K(s)	+89	[dissociation enthalpy of K(s)]
2. Dissociation of $\frac{1}{2}\mathrm{Cl_2(g)}$	+122	[$\frac{1}{2}\times$dissociation enthalpy of $\mathrm{Cl_2(g)}$]
3. Ionization of K(g)	+418	[ionization enthalpy of K(g)]
4. Electron attachment to Cl(g)	−349	[electron gain enthalpy of Cl(g)]
5. Formation of solid from gaseous ions	$-\Delta H_{\mathrm{L}}/(\mathrm{kJ\,mol^{-1}})$	
6. Decomposition of compound	+437	[negative of enthalpy of formation of KCl(s)]

Because this is a closed cycle, the sum of these enthalpy changes is equal to zero, and the lattice enthalpy can be inferred from the resulting equation.

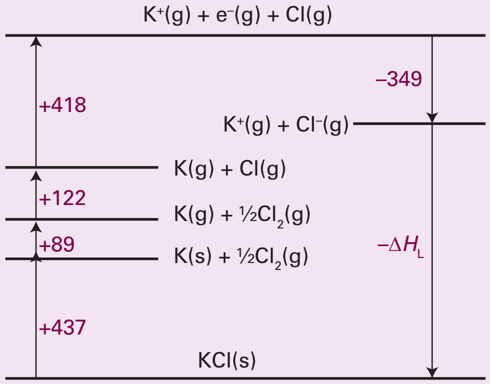

Figure 38.14 The Born–Haber cycle for KCl at 298 K. Enthalpy changes are in kilojoules per mole.

Answer The equation associated with the cycle is

$$89+122+418-349-\Delta H_{\mathrm{L}}/(\mathrm{kJ\,mol^{-1}})+437=0$$

It follows that $\Delta H_{\mathrm{L}}=+717\ \mathrm{kJ\,mol^{-1}}$.

Self-test 38.5 Calculate the lattice enthalpy of CaO from the following data:

	$\Delta H/(\mathrm{kJ\,mol^{-1}})$
Sublimation of Ca(s)	+178
Ionization of Ca(g) to $\mathrm{Ca^{2+}(g)}$	+1735
Dissociation of $\mathrm{O_2(g)}$	+249
Electron attachment to O(g)	−141
Electron attachment to $\mathrm{O^-(g)}$	+844
Formation of CaO(s) from Ca(s) and $\mathrm{O_2(g)}$	−635

Answer: +3500 kJ mol^{-1}

Some lattice enthalpies obtained by the Born–Haber cycle are listed in Table 38.4. As can be seen from the data, the trends in values are in general accord with the predictions of the Born–Mayer equation. Agreement is typically taken to imply that the ionic model of bonding is valid for the substance; disagreement implies that there is a covalent contribution to the bonding. It is important, though, to be cautious, because numerical agreement might be coincidental.

Table 38.4* Lattice enthalpies at 298 K, $\Delta H_{\mathrm{L}}/(\mathrm{kJ\,mol^{-1}})$

NaCl	787
NaBr	752
MgO	3850
MgS	3406

* More values are given in the *Resource section*.

38.3 Molecular solids and covalent networks

X-ray diffraction studies of solids reveal a huge amount of information, including interatomic distances, bond angles, stereochemistry, and vibrational parameters. In this section we can do no more than hint at the diversity of types of solids found when molecules pack together or atoms link together in extended networks.

In **covalent network solids**, covalent bonds in a definite spatial orientation link the atoms in a network extending through the crystal. The demands of directional bonding, which have only a small effect on the structures of many metals, now override the geometrical problem of packing spheres together, and elaborate and extensive structures may be formed.

Brief illustration 38.4 Diamond and graphite

Diamond and graphite are two allotropes of carbon. In diamond each sp^3-hybridized carbon is bonded tetrahedrally to its four neighbours (Fig. 38.15). The network of strong C–C bonds is repeated throughout the crystal and, as a result, diamond is very hard (in fact, the hardest known substance). In graphite, σ bonds between sp^2-hybridized carbon atoms form hexagonal rings which, when repeated throughout a plane, give rise to 'graphene' sheets (Fig. 38.16). Because the sheets can slide against each other when impurities are present, graphite is used widely as a lubricant.

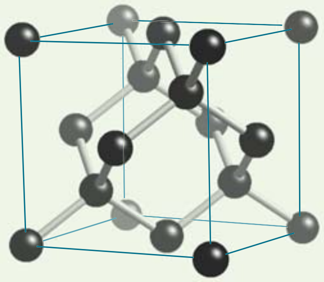

Figure 38.15 A fragment of the structure of diamond. Each C atom is tetrahedrally bonded to four neighbours. This framework-like structure results in a rigid crystal.

Self-test 38.6 Identify the solids that form covalent networks: silicon, boron nitride, red phosphorus, and calcium carbonate.

Answer: Silicon, boron nitride, and red phosphorus are covalent networks; calcium carbonate is an ionic solid

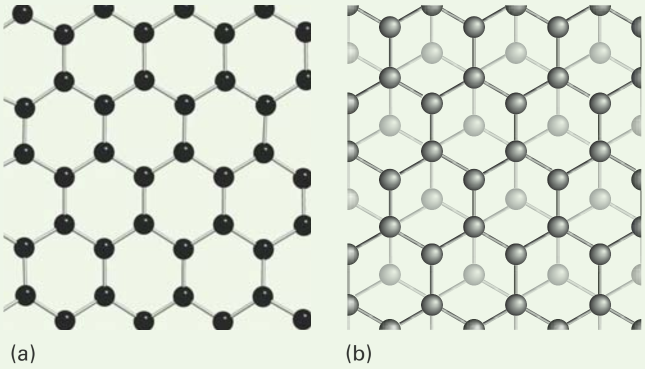

Figure 38.16 Graphite consists of flat planes of hexagons of carbon atoms lying above one another. (a) The arrangement of carbon atoms in a 'graphene' sheet; (b) the relative arrangement of neighbouring sheets. When impurities are present, the planes can slide over one another easily.

Molecular solids, which are the subject of the overwhelming majority of modern structural determinations, are held together by van der Waals interactions (Topic 35). The observed crystal structure is nature's solution to the problem of condensing objects of various shapes into an aggregate of minimum energy (actually, for $T>0$, of minimum Gibbs energy). The prediction of the structure is difficult, but software specifically designed to explore interaction energies can now make reasonably reliable predictions. The problem is made more complicated by the role of hydrogen bonds, which in some cases dominate the crystal structure, as in ice (Fig. 38.17), but in others (for example, in phenol) distort a structure that is determined largely by the van der Waals interactions.

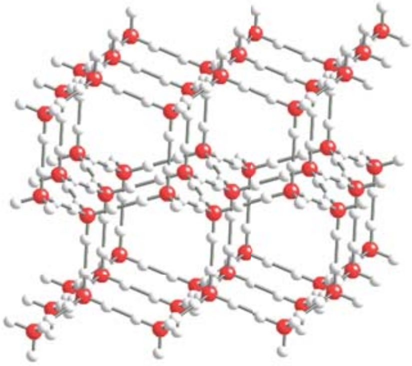

Figure 38.17 A fragment of the crystal structure of ice (ice-I). Each O atom is at the centre of a tetrahedron of four O atoms at a distance of 276 pm. The central O atom is attached by two short O–H bonds to two H atoms and by two long hydrogen bonds to the H atoms of two of the neighbouring molecules. Both alternative H atoms locations are shown for each O–O separation. Overall, the structure consists of planes of hexagonal puckered rings of H_2O molecules (like the chair form of cyclohexane).

Checklist of concepts

☐ 1. The **coordination number** of an atom in a metal is the number of its nearest neighbours.

☐ 2. Many elemental metals have close-packed structures with coordination number 12.

☐ 3. Close-packed structures may be either **cubic** (ccp) or **hexagonal** (hcp).

☐ 4. The **packing fraction** is the fraction of space occupied by spheres in a crystal.

☐ 5. Electrons in metals occupy molecular orbitals formed from the overlap of atomic orbitals.

☐ 6. The **Fermi level** is the highest occupied molecular orbital at $T=0$.

☐ 7. Representative ionic structures include the **caesium chloride**, **rock salt**, and **zinc blende** structures.

☐ 8. The coordination number of an ionic lattice is denoted (N_+,N_-), with N_+ the number of nearest-neighbour anions around a cation and N_- the number of nearest-neighbour cations around an anion.

☐ 9. The **radius ratio** (see below) is a guide to the likely lattice type.

☐ 10. The **lattice enthalpy** is the change in enthalpy (per mole of formula units) accompanying the complete separation of the components of the solid.

☐ 11. A **Born–Haber cycle** is a closed path of transformations starting and ending at the same point, one step of which is the formation of the solid compound from a gas of widely separated ions.

☐ 12. A **covalent network solid** is a solid in which covalent bonds in a definite spatial orientation link the atoms in a network extending through the crystal.

☐ 13. A **molecular solid** is a solid consisting of discrete molecules held together by van der Waals interactions.

Checklist of equations

Property	Equation	Comment	Equation number
Energy levels in a linear array of orbitals	$E_k=\alpha+2\beta\cos(k\pi/(N+1)), k=1,2,\ldots,N$	Linear array of s orbitals	38.1
Radius ratio	$\gamma=r_{\text{smaller}}/r_{\text{larger}}$	For criteria, see Section 38.2	38.4
Born–Mayer equation	$E_{\text{p,min}}=-\left\{N_{\text{A}}\lvert z_{\text{A}}z_{\text{B}}\rvert e^2/4\pi\varepsilon_0 d\right\}(1-d^*/d)A$	A is the Madelung constant	38.7

TOPIC 39

Electrical, optical, and magnetic properties of solids

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➤ Why do you need to know this material?

Careful consideration and manipulation of the electrical, optical, and magnetic properties of solids are needed for the development of modern materials and an understanding of their properties.

➤ What is the key idea?

The electrical, optical, and magnetic properties of solids stem from relative energies and occupation of the available orbitals in the material.

➤ What do you need to know already?

You need to be familiar with electromagnetic fields (Topic 3), atomic structure (Topic 19), bonding arrangements in solids (Topic 38), and the factors that determine the absorption of light by atoms and molecules (Topics 40, 45, and 46). The Topic draws a little on the properties of the Boltzmann distribution (*Foundations*, Topic 2 and Topic 51).

Here we consider how the bulk properties of solids, particularly their electrical, optical, and magnetic properties, stem from the properties of their constituent atoms.

39.1 Electrical properties

We confine our attention to electronic conductivity, but note that some ionic solids display ionic conductivity in which complete ions migrate through the lattice. Two types of solid are distinguished by the temperature dependence of their electrical conductivity (Fig. 39.1):

> A **metallic conductor** is a substance with a conductivity that decreases as the temperature is raised.
> A **semiconductor** is a substance with a conductivity that increases as the temperature is raised.

A semiconductor generally has a lower conductivity than that typical of metals, but the magnitude of the conductivity is not the criterion of the distinction. It is conventional to classify semiconductors with very low electrical conductivities, such as most synthetic polymers, as **insulators**. We shall use this term, but it should be appreciated that it is one of convenience rather than one of fundamental significance. A **superconductor** is a solid that conducts electricity without resistance.

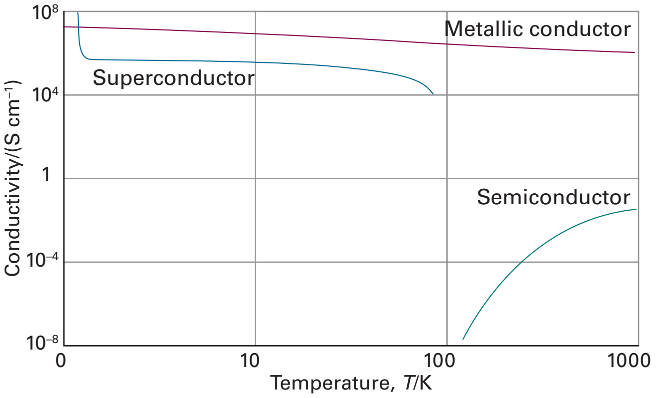

Figure 39.1 The variation of the electrical conductivity of a substance with temperature is the basis of its classification as a metallic conductor, a semiconductor, or a superconductor. Conductivity is expressed in siemens per metre (S m^{-1} or, as here, S cm^{-1}), where 1 S = 1 Ω^{-1} (the resistance is expressed in ohms, Ω).

(a) Conductors

To understand the origins of electronic conductivity in conductors and semiconductors, we need to explore the consequences of the formation of bands in different materials (Topic 38). Our starting point is Fig 38.8, which is repeated here for convenience (Fig. 39.2). It shows the electronic structure of a solid formed from atoms each able to contribute one electron (such as the alkali metals). At $T=0$, only the lowest $\frac{1}{2}N$ molecular orbitals are occupied, up to the Fermi level.

At temperatures above absolute zero, electrons are excited by the thermal motion of the atoms. The electrical conductivity of a metallic conductor decreases with increasing temperature even though more electrons are excited into empty orbitals. This apparent paradox is resolved by noting that the increase in temperature causes more vigorous thermal motion of the atoms, so collisions between the moving electrons and an atom are more likely. That is, the electrons are scattered out of their paths through the solid, and are less efficient at transporting charge.

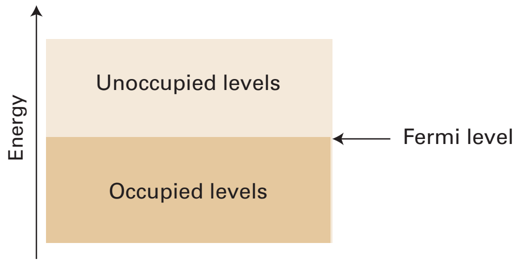

Figure 39.2 When N electrons occupy a band of N orbitals, it is only half full at $T=0$ and the electrons near the Fermi level (the top of the filled levels) are mobile. (This is also Fig. 38.8.)

A more quantitative treatment of conductivity in metals requires an expression for the variation with temperature of the distribution of electrons over the available energy states. We begin by considering the density of states, $\rho(E)$, at the energy E: the number of states between E and $E+\mathrm{d}E$ divided by $\mathrm{d}E$. Note that the 'state' of an electron includes its spin, so each spatial orbital counts as two states. Then it follows that $\rho(E)\mathrm{d}E$ is the number of states between E and $E+\mathrm{d}E$. To obtain the number of electrons $\mathrm{d}N(E)$ that occupy states between E and $E+\mathrm{d}E$, we multiply $\rho(E)\mathrm{d}E$ by the probability $f(E)$ of occupation of the state with energy E. That is,

$$\mathrm{d}N(E)=\overbrace{\rho(E)\mathrm{d}E}^{\text{Number of states between }E\text{ and d}E}\times\overbrace{f(E)}^{\text{Probability of occupation of a state with energy }E}\qquad(39.1)$$

The function $f(E)$ is the **Fermi–Dirac distribution**, a version of the Boltzmann distribution that takes into account the Pauli exclusion principle that each orbital can be occupied by no more than two electrons (Fig. 39.3):

$$f(E)=\frac{1}{\mathrm{e}^{(E-\mu)/kT}+1}\qquad\text{Fermi–Dirac distribution}\qquad(39.2\text{a})$$

where μ is a temperature-dependent parameter known as the 'chemical potential' (it has a subtle relation to the familiar chemical potential of thermodynamics), and provided $T>0$ is the energy of the state for which $f=\frac{1}{2}$. At $T=0$, only states up to a certain energy known as the **Fermi energy**, E_{F}, are occupied (Fig. 39.2). Provided the temperature is not so high that

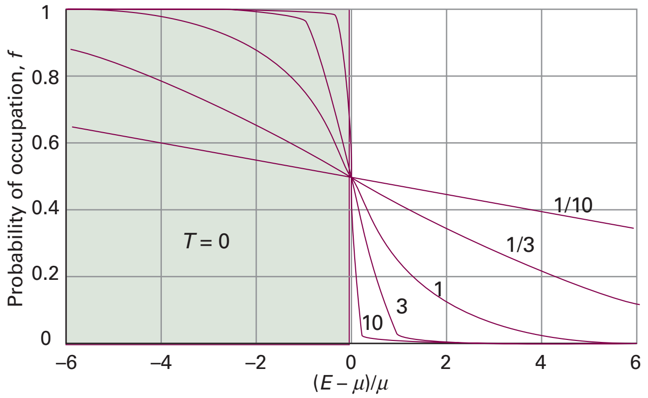

Figure 39.3 The Fermi–Dirac distribution, which gives the probability of occupation of the state at a temperature T. The high-energy tail decays exponentially towards zero. The curves are labelled with the value of μ/kT. The tinted region shows the occupation of levels at $T=0$.

many electrons are excited to states above the Fermi energy, the chemical potential can be identified with E_F, in which case the Fermi–Dirac distribution becomes

$$f(E)=\frac{1}{e^{(E-E_F)/kT}+1} \tag{39.2b}$$

Fermi–Dirac distribution

Moreover, for energies well above E_F, the exponential term in the denominator is so large that the 1 in the denominator can be neglected, and then

$$f(E)\approx e^{-(E-E_F)/kT} \tag{39.2c}$$

Approximate form for $E>E_F$ Fermi–Dirac distribution

The function now resembles a Boltzmann distribution, decaying exponentially with increasing energy; the higher the temperature, the longer the exponential tail.

Brief illustration 39.1 The Fermi–Dirac distribution at $T=0$

Consider cases in which $E<E_F$. Then, as $T\to 0$ we write

$$\lim_{T\to 0}\{E-E_F\}/kT=-\infty$$

because $E_F>0$ and $E-E_F<0$. It follows that

$$\lim_{T\to 0} f(E)=\lim_{T\to 0}\frac{1}{e^{(E-E_F)/kT}+1}=1$$

We conclude that as $T\to 0$, $f(E)\to 1$, and all the energy levels below $E=E_F$ are populated. A similar calculation for $E>E_F$ (Self-test 39.1) shows that $f(E)\to 0$ as $T\to 0$. The Fermi–Dirac distribution function confirms that only the levels below E_F are populated as $T\to 0$.

Self-test 39.1 Repeat the calculation for $E>E_F$.

Answer: $f(E)\to 0$ as $T\to 0$

(b) Insulators and semiconductors

Now consider a one-dimensional solid in which each atom provides two electrons: the $2N$ electrons fill the N orbitals of the band. The Fermi level now lies at the top of the band (at $T=0$), and there is a gap before the next band begins (Fig. 39.4). As the temperature is increased, the tail of the Fermi–Dirac distribution extends across the gap, and electrons leave the lower band, which is called the **valence band**, and populate the empty orbitals of the upper band, which is called the **conduction band**. As a consequence of electron promotion, positively charged 'holes' are left in in the valence band. The holes and promoted electrons are now mobile, and the material is now a conductor. In fact, we call it a semiconductor, because the electrical conductivity depends on the number of electrons that are promoted across the gap, and that number increases as the temperature is raised. If the gap is large, though, very few electrons are promoted at ordinary temperatures and the conductivity remains close to zero, resulting in an insulator. Thus, the conventional distinction between an insulator and a semiconductor is related to the size of the band gap and is not an absolute distinction like that between a metal (incomplete bands at $T=0$) and a semiconductor (full bands at $T=0$).

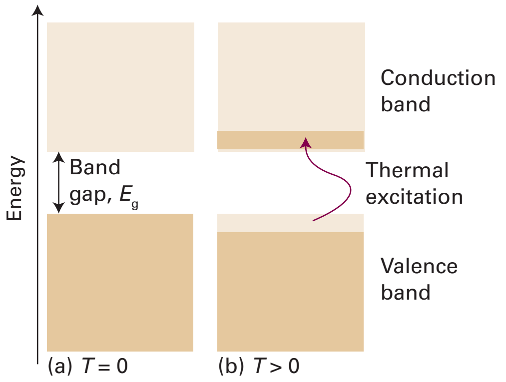

Figure 39.4 (a) When $2N$ electrons are present, the band is full and the material is an insulator at $T=0$. (b) At temperatures above $T=0$, electrons populate the levels of the upper conduction band and the solid is a semiconductor.

Figure 39.4 depicts conduction in an **intrinsic semiconductor**, in which semiconduction is a property of the band structure of the pure material. Examples of intrinsic semiconductors include silicon and germanium. A **compound semiconductor** is an intrinsic semiconductor that is a combination of different elements, such as GaN, CdS, and many d-metal oxides. An **extrinsic semiconductor** is one in which charge carriers are present as a result of the replacement of some atoms (to the extent of about 1 in 10^9) by **dopant** atoms, the atoms of another element. If the dopants can trap electrons, they withdraw electrons from the filled band, leaving holes which allow the remaining electrons to move (Fig. 39.5a). This procedure gives rise to **p-type semiconductivity**, the p indicating that the holes are positive relative to the electrons in the band. An example is silicon doped with indium. We can picture the semiconduction as arising from the transfer of an electron from a Si atom to a neighbouring In atom. The electrons at the top of the silicon valence band are now mobile, and carry current through the solid. Alternatively, a dopant might carry excess electrons (for example, phosphorus atoms introduced into germanium), and these additional electrons occupy otherwise empty bands, giving **n-type semiconductivity**, where n denotes the negative charge of the carriers (Fig. 39.5b).

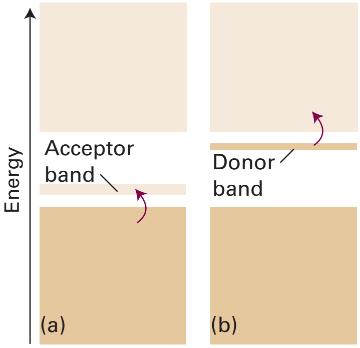

Figure 39.5 (a) A dopant with fewer electrons than its host can form a narrow band that accepts electrons from the valence band. The holes in the band are mobile and the substance is a p-type semiconductor. (b) A dopant with more electrons than its host forms a narrow band that can supply electrons to the conduction band. The electrons it supplies are mobile and the substance is an n-type semiconductor.

Brief illustration 39.2 The effect of doping on semiconductivity

Consider the doping of pure silicon (a Group 14 element) by arsenic (a Group 15 element). Because each Si atom has four valence electrons and each As atom has five valence electrons, the addition of arsenic increases the number of electrons in the solid. These electrons populate the empty conduction band of silicon, and the doped material is an n-type semiconductor.

Self-test 39.2 Is gallium-doped germanium a p-type or n-type semiconductor?

Answer: p-type semiconductor

Now consider the properties of a **p–n junction**, the interface of a p-type and n-type semiconductor. When a 'reverse bias' is applied to the junction, in the sense that a negative electrode is attached to the p-type semiconductor and a positive electrode is attached to the n-type semiconductor, the positively charged holes in the p-type semiconductor are attracted to the negative electrode and the negatively charged electrons in the n-type semiconductor are attracted to the positive electrode (Fig. 39.6a). As a consequence, charge does not flow across the junction. Now consider the application of a 'forward bias' to the junction, in the sense that the positive electrode is attached to the p-type semiconductor and the negative electrode is attached to the n-type semiconductor (Fig. 39.6b). Now charge flows across the junction, with electrons in the n-type semiconductor moving toward the positive electrode and holes moving in the opposite direction.

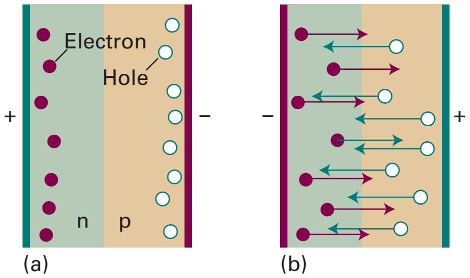

Figure 39.6 A p–n junction under (a) reverse bias, (b) forward bias.

It follows that a p–n junction affords a great deal of control over the magnitude and direction of current through a material. This control is essential for the operation of transistors and diodes, which are key components of modern electronic devices.

As electrons and holes move across a p–n junction under forward bias, they recombine and release energy. However, as long as the forward bias continues to be applied, the flow of charge from the electrodes to the semiconductors replenishes them with electrons and holes, so the junction sustains a current. In some solids, the energy of electron–hole recombination is released as heat and the device becomes warm. The reason lies in the fact that the return of the electron to a hole involves a change in the electron's linear momentum. The atoms of the lattice must absorb the difference, and therefore electron–hole recombination stimulates lattice vibrations. This is the case for silicon semiconductors, and is one reason why computers need efficient cooling systems.

39.2 Optical properties

Consider again Fig. 39.2, which shows bands in an idealized metallic conductor. The absorption of a photon can excite electrons from the occupied levels to the unoccupied levels. There is a near continuum of unoccupied energy levels above the Fermi level, so we expect to observe absorption over a wide range of frequencies. In metals, the bands are sufficiently wide that radiation from radiofrequencies to the middle of the ultraviolet region of the electromagnetic spectrum is absorbed. Metals are transparent to very high-frequency radiation, such as X-rays and γ-rays. Because this range of absorbed frequencies includes the entire visible spectrum, we might therefore expect all metals to appear black. However, we know that metals are lustrous (that is, they reflect light) and some are coloured (that is, they absorb light of only certain wavelengths), so we need to extend our model.

To explain the lustrous appearance of a smooth metal surface, we need to realize that the absorbed energy can be re-emitted very efficiently as light, with only a small fraction of the energy being released to the surroundings as heat. Because the atoms near the surface of the material absorb most of the radiation, emission also occurs primarily from the surface. In essence, if the sample is excited with visible light, then visible light will be reflected from the surface, accounting for the lustre of the material.

The perceived colour of a metal depends on the frequency range of reflected light which, in turn, depends on the frequency range of light that can be absorbed and, by extension, on the band structure. Silver reflects light with nearly equal efficiency across the visible spectrum because its band structure has many unoccupied energy levels that can be populated by absorption of, and depopulated by emission of, visible light. On the other hand, copper has its characteristic colour because it has relatively fewer unoccupied energy levels that can be excited with violet, blue, and green light. The material reflects at all wavelengths, but more light is emitted at lower frequencies (corresponding to yellow, orange, and red). Similar arguments account for the colours of other metals, such as the yellow of gold.

Now consider semiconductors. We have already seen that promotion of electrons from the valence band to the conduction band of a semiconductor can be the result of thermal excitation, if the band gap E_g is comparable to the energy that can be supplied by heating. In some materials, the band gap is very large and electron promotion can occur only by excitation with electromagnetic radiation. However, we see from Fig. 39.4 that there is a frequency $\nu_{\min}=E_g/h$ below which light absorption cannot occur. Above this frequency threshold, a wide range of frequencies can be absorbed by the material, as in a metal.

Brief illustration 39.3 Optical properties of a semiconductor

The semiconductor cadmium sulfide (CdS) has a band gap energy of 2.4 eV (equivalent to 3.8×10^{-19} J). It follows that the minimum electronic absorption frequency is

$$\nu_{\min}=\frac{3.8\times10^{-19}\,\text{J}}{6.626\times10^{-34}\,\text{J s}}=5.8\times10^{14}\,\text{s}^{-1}$$

This frequency, 5.8×10^{14} Hz, corresponds to a wavelength of 520 nm (green light). Lower frequencies, corresponding to yellow, orange, and red, are not absorbed and consequently CdS appears yellow-orange.

Self-test 39.3 Predict the colours of the following materials, given their band-gap energies (in parentheses): GaAs (1.43 eV), HgS (2.1 eV), and ZnS (3.6 eV).

Answer: Black, red, and colourless

39.3 Magnetic properties

The magnetic properties of metallic solids and semiconductors depend strongly on the band structures of the material. Here we confine our attention largely to magnetic properties that stem from collections of individual molecules or ions such as d-metal complexes. Much of the discussion applies to liquid- and gas-phase samples as well as to solids.

(a) Magnetic susceptibility

The magnetic and electric properties of molecules and solids are analogous. For instance, some molecules possess permanent magnetic dipole moments, and an applied magnetic field can induce a magnetic moment, with the result that the entire solid sample becomes magnetized. The **magnetization**, $\mathcal{M}$, is the magnitude of the average molecular magnetic dipole moment multiplied by the number density of molecules in the sample. The magnetization induced by a field of strength $\mathcal{H}$ is proportional to $\mathcal{H}$, and we write

$$\mathcal{M}=\chi\mathcal{H} \qquad \text{Magnetization} \qquad (39.3)$$

where χ is the dimensionless **volume magnetic susceptibility**. A closely related quantity is the **molar magnetic susceptibility**, χ_m:

$$\chi_m=\chi V_m \qquad \text{Molar magnetic susceptibility} \qquad (39.4)$$

where V_m is the molar volume of the substance.

We can think of the magnetization as contributing to the density of lines of force in the material (Fig. 39.7). Materials for which $\chi>0$ are called **paramagnetic**; they tend to move into a magnetic field and the density of lines of force within them is greater than in a vacuum. Those for which $\chi<0$ are called **diamagnetic** and tend to move out of a magnetic field; the density of lines of force within them is lower than in a vacuum.

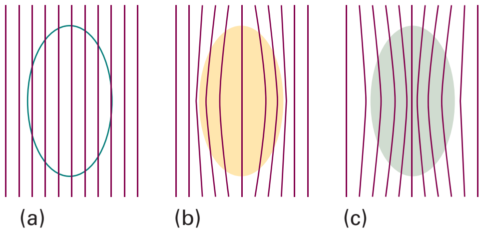

Figure 39.7 (a) In a vacuum, the strength of a magnetic field can be represented by the density of lines of force; (b) in a diamagnetic material, the lines of force are reduced; (c) in a paramagnetic material, the lines of force are increased.

A paramagnetic material consists of ions or molecules with unpaired electrons, such as radicals and many d-metal complexes; a diamagnetic substance (a far more common property) is one with no unpaired electrons.

Brief illustration 39.4 The magnetic character of metallic solids and molecules

Solid magnesium is a metal in which the two valence electrons of each Mg atom are donated to a band of orbitals constructed from 3s orbitals. From *N* atomic orbitals we can construct *N* molecular orbitals spreading through the metal. Each atom supplies two electrons, so there are 2*N* electrons to accommodate. These occupy and fill the *N* molecular orbitals. There are no unpaired electrons, so the metal is diamagnetic. An O_2 molecule has the electronic structure described in Topic 24, where we see that two electrons occupy separate antibonding π orbitals with parallel spins. We conclude that O_2 is a paramagnetic gas.

Self-test 39.4 Repeat the analysis for Zn(s) and NO(g).

Answer: Zn diamagnetic, NO paramagnetic

The magnetic susceptibility is traditionally measured with a **Gouy balance**. This instrument consists of a sensitive balance from which the sample hangs in the form of a narrow cylinder and lies between the poles of a magnet. If the sample is paramagnetic, it is drawn into the field, and its apparent weight is greater than when the field is off. A diamagnetic sample tends to be expelled from the field and appears to weigh less when the field is turned on. The balance is normally calibrated against a sample of known susceptibility. The modern version of the determination makes use of a **superconducting quantum interference device** (SQUID, Fig. 39.8). A SQUID takes advantage of the property of current loops in superconductors that, as part of the circuit, include a weakly conducting link through which electrons must tunnel: the current that flows in the loop in a magnetic field depends on the value of the magnetic flux, and a SQUID can be exploited as a very sensitive magnetometer.

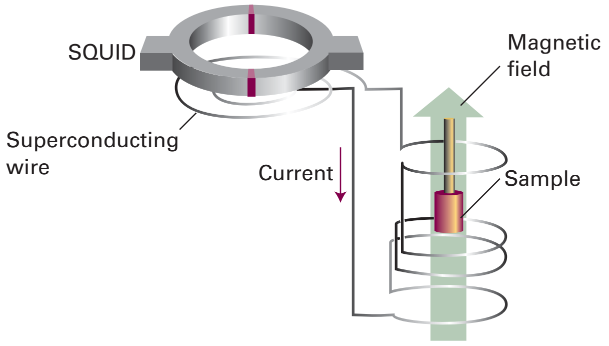

Figure 39.8 The arrangement used to measure magnetic susceptibility with a SQUID. The sample is moved upwards in small increments and the potential difference across the SQUID is measured.

Table 39.1 lists some experimental values. A typical paramagnetic volume susceptibility is about 10^{-3}, and a typical diamagnetic volume susceptibility is about $(-)10^{-5}$.

(b) Permanent and induced magnetic moments

The permanent magnetic moment of a molecule arises from any unpaired electron spins in the molecule. In practice, a contribution to the paramagnetism also arises from the orbital angular momenta of electrons, but here we discuss the spin-only contribution.

The magnitude of the magnetic moment of an electron is proportional to the magnitude of the spin angular momentum, $\{s(s+1)\}^{1/2}\hbar$:

$$m = g_e\{s(s+1)\}^{1/2}\mu_B \qquad \mu_B = \frac{e\hbar}{2m_e} \qquad \textit{Magnitude} \qquad \text{Magnetic moment} \qquad (39.5)$$

where $g_e = 2.0023$ and $\mu_B = 9.274 \times 10^{-24}\ \text{J T}^{-1}$. If there are several electron spins in each molecule, they combine to a total spin *S*, and then $s(s+1)$ should be replaced by $S(S+1)$.

The magnetization and consequently the magnetic susceptibility depend on the temperature because the orientations of the electron spins fluctuate, whether the molecules are in fluid phases or trapped in solids: some orientations have lower energy than others, and the magnetization depends on the randomizing influence of thermal motion. Thermal averaging of the permanent magnetic moments in the presence of an applied magnetic field contributes to the magnetic susceptibility an amount proportional to $m^2/3kT$.[1] It follows that the spin contribution to the molar magnetic susceptibility is

$$\chi_m = \frac{N_A g_e^2 \mu_0 \mu_B^2 S(S+1)}{3kT} \qquad \textit{Spin contribution} \qquad \text{Molar magnetic susceptibility} \qquad (39.6)$$

Table 39.1* Magnetic susceptibilities at 298 K

	$\chi/10^{-6}$	$\chi_m/(10^{-10}\ \text{m}^3\ \text{mol}^{-1})$
$H_2O(l)$	−9.02	−1.63
NaCl(s)	−16	−3.8
Cu(s)	−9.7	−0.69
$CuSO_4{\cdot}5H_2O(s)$	+167	+183

* More values are given in the *Resource section*.

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[1] See our other *Physical chemistry* (2014) for the derivation of this contribution.

This expression shows that the susceptibility is positive, so the spin magnetic moments contribute to the paramagnetic susceptibilities of materials. The contribution decreases with increasing temperature because the thermal motion randomizes the spin orientations.

Example 39.1 Calculating a molar magnetic susceptibility

Consider a complex salt with three unpaired electrons per complex cation at 298 K, and molar volume 61.7 cm³ mol⁻¹. Calculate the molar magnetic susceptibility and the volume magnetic susceptibility of the complex.

Method Use the data and eqn 39.6 to calculate the molar magnetic susceptibility. Then use the values of χ_m and V_m, and eqn 39.4, to calculate the volume magnetic susceptibility.

Answer First note that the constants can be collected into the term

$$\frac{N_\mathrm{A} g_\mathrm{e}^2 \mu_0 \mu_\mathrm{B}^2}{3k} = 6.3001\times10^{-6}\,\mathrm{m^3\,K^{-1}\,mol^{-1}}$$

Consequently eqn 39.6 becomes

$$\chi_\mathrm{m} = 6.3001\times10^{-6}\times\frac{S(S+1)}{T/\mathrm{K}}\,\mathrm{m^3\,mol^{-1}}$$

Substitution of the data with $S=\frac{3}{2}$ gives

$$\chi_\mathrm{m} = 6.3001\times10^{-6}\times\frac{\frac{3}{2}(\frac{3}{2}+1)}{298}\,\mathrm{m^3\,mol^{-1}} = 7.93\times10^{-8}\,\mathrm{m^3\,mol^{-1}}$$

It follows from eqn 39.4 that, to obtain the volume magnetic susceptibility, the molar susceptibility is divided by the molar volume $V_\mathrm{m} = 61.7\,\mathrm{cm^3\,mol^{-1}} = 6.17\times10^{-5}\,\mathrm{m^3\,mol^{-1}}$ and

$$\chi = \frac{\chi_\mathrm{m}}{V_\mathrm{m}} = \frac{7.93\times10^{-8}\,\mathrm{m^3\,mol^{-1}}}{6.17\times10^{-5}\,\mathrm{m^3\,mol^{-1}}} = 1.29\times10^{-3}$$

Self-test 39.5 Repeat the calculation for a complex with five unpaired electrons, molar mass 322.4 g mol⁻¹, and a mass density of 2.87 g cm⁻³ at 273 K.

Answer: $\chi_\mathrm{m} = 2.02\times10^{-7}\,\mathrm{m^3\,mol^{-1}}$; $\chi = 1.79\times10^{-3}$

At low temperatures, some paramagnetic solids make a phase transition to a state in which large domains of spins align with parallel orientations. This cooperative alignment gives rise to a very strong magnetization and is called **ferromagnetism** (Fig. 39.9). In other cases, exchange interactions lead to alternating spin orientations: the spins are locked into a low-magnetization arrangement to give an **antiferromagnetic phase**. The ferromagnetic phase has a nonzero magnetization in the absence of an applied field, but the antiferromagnetic phase has a zero magnetization because the spin magnetic moments cancel. The ferromagnetic transition occurs at the **Curie temperature**, and the antiferromagnetic transition occurs at the **Néel temperature**. Which type of cooperative behaviour occurs depends on the details of the band structure of the solid.

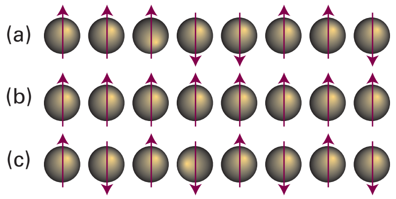


Figure 39.9 (a) In a paramagnetic material, the electron spins are aligned at random in the absence of an applied magnetic field. (b) In a ferromagnetic material, the electron spins are locked into a parallel alignment over large domains. (c) In an antiferromagnetic material, the electron spins are locked into an antiparallel arrangement. The latter two arrangements survive even in the absence of an applied field.

Magnetic moments can also be induced in molecules. To see how this effect arises, we need to note that the circulation of electronic currents induced by an applied field gives rise to a magnetic field which usually opposes the applied field, so the substance is diamagnetic. In a few cases the induced field augments the applied field, and the substance is then paramagnetic.

The great majority of molecules with no unpaired electron spins are diamagnetic. In these cases, the induced electron currents occur within the orbitals of the molecule that are occupied in its ground state. In the few cases in which molecules are paramagnetic despite having no unpaired electrons, the induced electron currents flow in the opposite direction because they can make use of unoccupied orbitals that lie close to the HOMO in energy. This orbital paramagnetism can be distinguished from spin paramagnetism by the fact that it is temperature-independent: this is why it is called **temperature-independent paramagnetism** (TIP).

We can summarize these remarks as follows. All molecules have a diamagnetic component to their susceptibility, but it is dominated by spin paramagnetism if the molecules have unpaired electrons. In a few cases (where there are low-lying excited states) TIP is strong enough to make the molecules paramagnetic even though their electrons are paired.

39.4 Superconductivity

The resistance to flow of electrical current of a normal metallic conductor decreases smoothly with temperature but never vanishes. However, certain solids known as **superconductors** conduct electricity without resistance below a critical temperature, T_c. Following the discovery in 1911 that mercury is a superconductor below 4.2 K, the normal boiling point of liquid helium, physicists and chemists made slow but steady progress in the discovery of superconductors with higher values of T_c. Metals, such as tungsten, mercury, and lead, tend to have T_c values below about 10 K. Intermetallic compounds, such as Nb_3X (X = Sn, Al, or Ge), and alloys, such as Nb/Ti and Nb/Zr, have intermediate T_c values ranging between 10 K and 23 K. In 1986, **high-temperature superconductors** (HTSC) were discovered. Several *ceramics*, inorganic powders that have been fused and hardened by heating to a high temperature, containing oxocuprate motifs, Cu_mO_n, are now known with T_c values well above 77 K, the boiling point of the inexpensive refrigerant liquid nitrogen. For example, $HgBa_2Ca_2Cu_2O_8$ has $T_c = 153$ K.

Superconductors have unique magnetic properties. Some superconductors, classed as *Type I*, show abrupt loss of superconductivity when an applied magnetic field exceeds a critical value $\mathcal{H}_c$ characteristic of the material. It is observed that the value of $\mathcal{H}_c$ depends on temperature and T_c as

$$\mathcal{H}_c(T) = \mathcal{H}_c(0)\left(1 - \frac{T^2}{T_c^2}\right) \qquad \text{Dependence of } \mathcal{H}_c \text{ on } T_c \qquad (39.7)$$

where $\mathcal{H}_c(0)$ is the value of $\mathcal{H}_c$ as $T \to 0$.

Example 39.2 Calculating the temperature at which a material becomes superconducting

Lead has $T_c = 7.19$ K and $\mathcal{H}_c(0) = 63.9\,\text{kA m}^{-1}$. At what temperature does lead become superconducting in a magnetic field of $20\,\text{kA m}^{-1}$?

Method Rearrange eqn 39.7 and use the data to calculate the temperature at which the substance becomes superconducting.

Answer Rearrangement of eqn 39.7 gives

$$T = T_c\left(1 - \frac{\mathcal{H}_c(T)}{\mathcal{H}_c(0)}\right)^{1/2}$$

and substitution of the data gives

$$T = (7.19\,\text{K}) \times \left(1 - \frac{20\,\text{kA m}^{-1}}{63.9\,\text{kA m}^{-1}}\right)^{1/2} = 6.0\,\text{K}$$

That is, lead becomes superconducting at temperatures below 6.0 K.

Self-test 39.6 Tin has $T_c = 3.72$ K and $\mathcal{H}_c(0) = 25\,\text{kA m}^{-1}$. At what temperature does tin become superconducting in a magnetic field of $15\,\text{kA m}^{-1}$?

Answer: 2.4 K

Type I superconductors are also completely diamagnetic below $\mathcal{H}_c$, meaning that the magnetic field does not penetrate into the material. This complete exclusion of a magnetic field from a material is known as the **Meissner effect**, which can be demonstrated by the levitation of a superconductor above a magnet. *Type II* superconductors, which include the HTSCs, show a gradual loss of superconductivity and diamagnetism with increasing magnetic field.

There is a degree of periodicity in the elements that exhibit superconductivity. The metals iron, cobalt, nickel, copper, silver, and gold do not display superconductivity, nor do the alkali metals. It is observed that, for simple metals, ferromagnetism and superconductivity never coexist, but in some of the oxocuprate superconductors ferromagnetism and superconductivity can coexist. One of the most widely studied oxocuprate superconductors, $YBa_2Cu_3O_7$ (informally known as '123' on account of the proportions of the metal atoms in the compound), has the structure shown in Fig. 39.10. The square pyramidal CuO_5 units arranged as two-dimensional layers and the square planar CuO_4 units arranged in sheets are common structural features of oxocuprate HTSCs.

The mechanism of superconduction is well understood for low-temperature materials, and is based on the existence of a **Cooper pair**, a pair of electrons that exists on account of the indirect electron–electron interactions fostered by the nuclei of the atoms in the lattice. Thus, if one electron is in a particular region of a solid, the nuclei there move toward it to give a distorted local structure (Fig. 39.11). Because that local distortion is rich in positive charge, it is favourable for a second electron to join the first. Hence, there is a virtual attraction between the two electrons, and they move together as a pair. The local distortion can be easily disrupted by thermal motion of the ions in the solid, so the virtual attraction occurs only at very low temperatures. A Cooper pair undergoes less

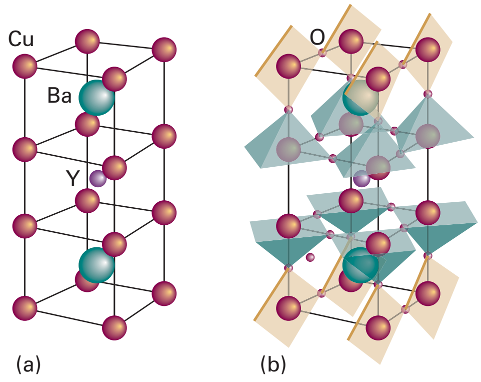


Figure 39.10 Structure of the $YBa_2Cu_3O_7$ superconductor. (a) Metal atom positions. (b) The polyhedra show the positions of oxygen atoms and indicate that the metal ions are in square-planar and square pyramidal coordination environments.

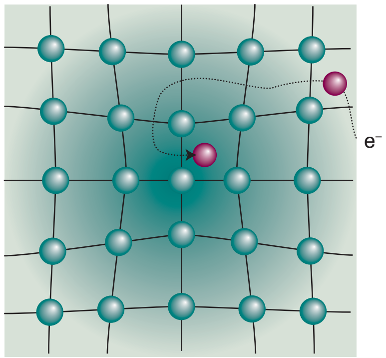


Figure 39.11 The formation of a Cooper pair. One electron distorts the crystal lattice and the second electron has a lower energy if it goes to that region. These electron–lattice interactions effectively bind the two electrons into a pair.

scattering than an individual electron as it travels through the solid because the distortion caused by one electron can attract back the other electron should it be scattered out of its path in a collision. Because the Cooper pair is stable against scattering, it can carry charge freely through the solid, and hence give rise to superconduction.

The Cooper pairs responsible for low-temperature superconductivity are likely to be important in HTSCs, but the mechanism for pairing is hotly debated. There is evidence implicating the arrangement of CuO_5 layers and CuO_4 sheets in the mechanism of high-temperature superconduction. It is believed that movement of electrons along the linked CuO_4 units accounts for superconductivity, whereas the linked CuO_5 units act as 'charge reservoirs' that maintain an appropriate number of electrons in the superconducting layers.

Checklist of concepts

☐ 1. Electronic conductors are classified as **metallic conductors** or **semiconductors** according to the temperature dependence of their conductivities.
☐ 2. An **insulator** is a semiconductor with a very low electrical conductivity.
☐ 3. The spectroscopic properties of metallic conductors and semiconductors can be understood in terms of the photon-induced promotion of electrons from **valence bands** to **conduction bands**.
☐ 4. A material is **diamagnetic** and moves out of a magnetic field; it has a negative **volume magnetic susceptibility**.
☐ 5. A material is **paramagnetic** and moves into a magnetic field; it has a positive volume magnetic susceptibility.
☐ 6. **Ferromagnetism** is the cooperative alignment of electron spins in a material and gives rise to strong **magnetization**.
☐ 7. **Antiferromagnetism** results from alternating spin orientations in a material and leads to weak magnetization.
☐ 8. **Temperature-independent paramagnetism** arises from induced electron currents within the orbitals of a molecule that are occupied in its ground state.
☐ 9. **Superconductors** conduct electricity without resistance below a critical temperature T_c.

Checklist of equations

Property	Equation	Comment	Equation number
Fermi–Dirac distribution	$f(E)=1/(e^{(E-\mu)/kT}+1)$	μ is the chemical potential	39.2a
Magnetization	$\mathcal{M}=\chi\mathcal{H}$		39.3
Molar magnetic susceptibility	$\chi_m=\chi V_m$	Definition	39.4
Magnitude of the magnetic moment	$m=g_e\{s(s+1)\}^{1/2}\mu_B$	$\mu_B=e\hbar/2m_e$	39.5
Molar magnetic susceptibility	$\chi_m=N_A g_e^2\mu_0\mu_B^2 S(S+1)/3kT$	Spin contribution	39.6
Dependence of $\mathcal{H}_c$ on T_c	$\mathcal{H}_c(T)=\mathcal{H}_c(0)(1-T^2/T_c^2)$		39.7

Focus 8 on Interactions

Topic 34 Electric properties of molecules

Discussion questions

34.1 Explain how the permanent dipole moment and the polarizability of a molecule arise.

34.2 Distinguish between an electric monopole, dipole, quadrupole, and octupole. Explain the distance dependence of the fields to which they give rise.

Exercises

34.1(a) Which of the following molecules may be polar: ClF_3, O_3, H_2O_2?
34.1(b) Which of the following molecules may be polar: SO_3, XeF_4, SF_4?

34.2(a) Calculate the resultant of two dipole moments of magnitude 1.0 D and 2.0 D that make an angle of 45° to each other.
34.2(b) Calculate the resultant of two dipole moments of magnitude 2.5 D and 0.50 D that make an angle of 120° to each other.

34.3(a) Calculate the magnitude and direction of the dipole moment of the following arrangement of charges in the xy-plane: (i) $3e$ at (0,0), (ii) $-e$ at (0.32 nm, 0), and (iii) $-2e$ at an angle of 20° from the x-axis and a distance of 0.23 nm from the origin.

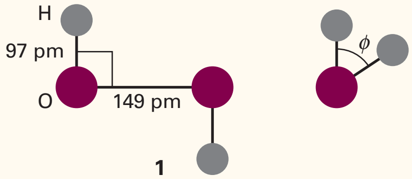
34.3(b) Calculate the magnitude and direction of the dipole moment of the following arrangement of charges in the xy-plane: (i) $4e$ at (0, 0), (ii) $-2e$ at (162 pm, 0), and (iii) $-2e$ at an angle of 300° from the x-axis and a distance of 143 pm from the origin.

34.4(a) The polarizability volume of HCl is $2.63\times10^{-30}\,\text{m}^3$; calculate the magnitude of the dipole moment of the molecule (in addition to the permanent dipole moment) induced by an applied electric field of strength $7.5\,\text{kV m}^{-1}$.
34.4(b) The polarizability volume of NH_3 is $2.22\times10^{-30}\,\text{m}^3$; calculate the magnitude of the dipole moment of the molecule (in addition to the permanent dipole moment) induced by an applied electric field of strength $15.0\,\text{kV m}^{-1}$.

Problems

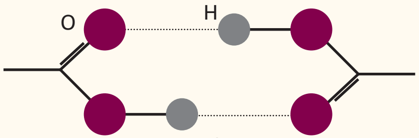
34.1 The electric dipole moment of toluene (methylbenzene) has a magnitude of 0.4 D. Estimate the magnitudes of the dipole moment of the three xylenes (dimethylbenzene). Which answer can you be sure about?

34.2 Plot the magnitude of the electric dipole moment of hydrogen peroxide as the H–O–O–H (azimuthal) angle ϕ changes from 0 to 2π. Use the dimensions shown in **1**.



1

34.3 Acetic acid vapour contains a proportion of planar, hydrogen-bonded dimers (**2**). The apparent dipole moment of molecules in pure gaseous acetic acid has a magnitude that increases with increasing temperature. Suggest an interpretation of this observation.



2

34.4 The magnitude of the electric field at a distance r from a point charge Q is equal to $Q/4\pi\varepsilon_0 r^2$. How close to a water molecule (of polarizability volume $1.48\times10^{-30}\,\text{m}^3$) must a proton approach before the dipole moment it induces has a magnitude equal to that of the permanent dipole moment of the molecule (1.85 D)?

34.5‡ Nelson, et al. (*Science* **238**, 1670 (1987)) examined several weakly bound gas-phase complexes of ammonia in search of examples in which the H atoms in NH_3 formed hydrogen bonds, but found none. For example, they found that the complex of NH_3 and CO_2 has the carbon atom nearest the nitrogen (299 pm away): the CO_2 molecule is at right angles to the C–N 'bond', and the H atoms of NH_3 are pointing away from the CO_2. The magnitude of the permanent dipole moment of this complex is reported as 1.77 D. If the N and C atoms are the centres of the negative and positive charge distributions, respectively, what is the magnitude of those partial charges (as multiples of e)?

34.6 An H_2O molecule is aligned by an external electric field of strength $1.0\,\text{kV m}^{-1}$ and an Ar atom ($\alpha'=1.66\times10^{-30}\,\text{m}^3$) is brought up slowly from one side. At what separation is it energetically favourable for the H_2O molecule to flip over and point towards the approaching Ar atom?

34.7 The relative permittivity of a substance is large if its molecules are polar or highly polarizable. The quantitative relation between the relative permittivity, the polarizability, and the permanent dipole moment of the molecule is expressed by the *Debye equation*,

$$\frac{\varepsilon_r-1}{\varepsilon_r+2}=\frac{\rho N_A}{3M\varepsilon_0}\left(\alpha+\frac{\mu^2}{3kT}\right)$$

where ρ is the mass density of the sample and M is the molar mass of the molecules. The relative permittivity of camphor (**3**) was measured at a series of temperatures with the results given below. Determine the magnitude of the dipole moment and the polarizability volume of the molecule. *Hint*: Plot the data in such a way that a fit to a straight line yields the magnitude of the permanent dipole moment and polarizability from the slope and y-intercept, respectively.

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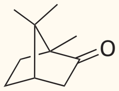
‡ These problems were supplied by Charles Trapp and Carmen Giunta.



3 Camphor

$\theta/°\mathrm{C}$	0	20	40	60	80	100	120	140	160	200
$\rho/(\mathrm{g\,cm^{-3}})$	0.99	0.99	0.99	0.99	0.99	0.99	0.97	0.96	0.95	0.91
ε_r	12.5	11.4	10.8	10.0	9.50	8.90	8.10	7.60	7.11	6.21

Topic 35 Interactions between molecules

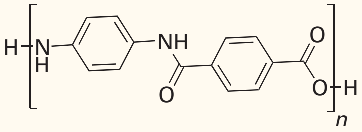
Discussion questions

35.1 Identify the terms in and limit the generality of the following expressions: (a) $V = -Q_2\mu_1/4\pi\varepsilon_0 r^2$, (b) $V = -Q_2\mu_1 \cos\theta/4\pi\varepsilon_0 r^2$, and (c) $V = \mu_2\mu_1(1-3\cos^2\theta)/4\pi\varepsilon_0 r^3$.

35.2 Account for the theoretical conclusion that many attractive interactions between molecules vary with their separation as $1/r^6$.

35.3 Describe the formation of a hydrogen bond in terms of (a) electrostatic interactions and (b) molecular orbitals. How would you identify the better model?

35.4 Some polymers have unusual properties. For example, Kevlar (**4**) is strong enough to be the material of choice for bulletproof vests and is stable at temperatures up to 600 K. What molecular interactions contribute to the formation and thermal stability of this polymer?



4 Kevlar

Exercises

35.1(a) Calculate the molar energy required to reverse the direction of an H_2O molecule located 100 pm from a Li^+ ion. Take the magnitude of the dipole moment of water as 1.85 D.

35.2(b) Calculate the molar energy required to reverse the direction of an HCl molecule located 300 pm from a Mg^{2+} ion. Take the magnitude of the dipole moment of HCl as 1.08 D.

35.2(a) Calculate the potential energy of the interaction between two linear quadrupoles when they are collinear and their centres are separated by a distance *r*.

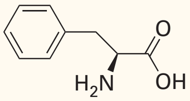
35.2(b) Calculate the potential energy of the interaction between two linear quadrupoles when they are parallel and separated by a distance *r*.

35.3(a) How much energy (in kJ mol⁻¹) is required to break the hydrogen bond in a vacuum ($\varepsilon_r = 1$)? (Use the electrostatic model of the hydrogen bond.)

35.3(b) How much energy (in kJ mol⁻¹) is required to break the hydrogen bond in water ($\varepsilon_r \approx 80.0$)? Use the electrostatic model of the hydrogen bond.

Problems

35.1 Phenylalanine (Phe, **5**) is a naturally occurring amino acid. What is the energy of interaction between its phenyl group and the electric dipole moment of a neighbouring peptide group? Take the distance between the groups as 4.0 nm and treat the phenyl group as a benzene molecule. The magnitude of the dipole moment of the peptide group is $\mu = 1.3$ D and the polarizability volume of benzene is $\alpha' = 1.04 \times 10^{-29}\,\mathrm{m}^3$.

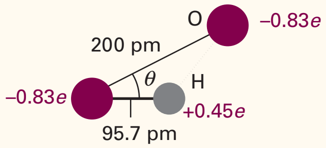


5 Phenylalanine

35.2 Now consider the London interaction between the phenyl groups of two Phe residues (see Problem 35.1). (a) Estimate the potential energy of interaction between two such rings (treated as benzene molecules) separated by 4.0 nm. For the ionization energy, use $I = 5.0$ eV. (b) Given that force is the negative slope of the potential, calculate the distance dependence of the force acting between two nonbonded groups of atoms, such as the phenyl groups of Phe, in a polypeptide chain that can have a London dispersion interaction with each other. What is the separation at which the force between the phenyl groups (treated as benzene molecules) of two Phe residues is zero? (*Hint*: Calculate the slope by considering the potential energy at r and $r + \delta r$, with $\delta r << r$, and evaluating $\{V(r+\delta r) - V(r)\}/\delta r$. At the end of the calculation, let δr become vanishingly small).

35.3 Given that $F = -\mathrm{d}V/\mathrm{d}r$, calculate the distance dependence of the force acting between two nonbonded groups of atoms in a polymer chain that have a London dispersion interaction with each other.

35.4 Consider the arrangement shown in **6** for a system consisting of an O–H group and an O atom, and then use the electrostatic model of the hydrogen bond to calculate the dependence of the molar potential energy of interaction on the angle θ.



6

35.5 The *cohesive energy density*, $\mathcal{U}$, is defined as U/V, where U is the mean potential energy of attraction within the sample and V its volume. Show that $\mathcal{U}=\frac{1}{2}\mathcal{N}\int V(R)\mathrm{d}\tau$, where $\mathcal{N}$ is the number density of the molecules and $V(R)$ is their attractive potential energy and where the integration ranges from d to infinity and over all angles. Go on to show that the cohesive energy density of a uniform distribution of molecules that interact by a van der Waals attraction of the form $-C_6/R^6$ is equal to $(2\pi/3)(N_A^2/d^3M^2)\rho^2C_6$, where ρ is the mass density of the solid sample and M is the molar mass of the molecules.

35.6 Suppose you distrusted the Lennard-Jones (12,6) potential for assessing a particular polypeptide conformation, and replaced the repulsive term by an exponential function of the form e^{-r/r_0}. (a) Sketch the form of the potential energy and locate the distance at which it is a minimum. (b) Identify the distance at which the exponential-6 potential is a minimum.

Topic 36 Real Gases

Discussion questions

36.1 Explain how the compression factor of a real gas varies with pressure and temperature, and describe how it reveals information about intermolecular interactions in real gases.

36.2 Describe and criticize the formulation of the van der Waals equation.

Exercises

36.1(a) What pressure would 3.15 g of nitrogen gas in a vessel of volume 2.05 dm^3 exert at 273 K if it obeyed the virial equation of state? What would be the pressure if it were a perfect gas?
36.1(b) What pressure would 4.56 g of carbon dioxide gas in a vessel of volume 2.25 dm^3 exert at 273 K if it obeyed the virial equation of state? What would be the pressure if it were a perfect gas?

36.2(a) What pressure would 4.56 g of carbon dioxide gas in a vessel of volume 2.25 dm^3 exert at its Boyle temperature?
36.2(b) What pressure would 3.01 g of oxygen gas in a vessel of volume 2.20 dm^3 exert at its Boyle temperature?

36.3(a) (i) What pressure would 131 g of xenon gas in a vessel of volume 1.0 dm^3 exert at 25 °C if it behaved as a perfect gas? (ii) What pressure would it exert if it behaved as a van der Waals gas?
36.3(b) (i) What pressure would 25 g of argon gas in a vessel of volume 1.5 dm^3 exert at 30 °C if it behaved as a perfect gas? (ii) What pressure would it exert if it behaved as a van der Waals gas?

36.4(a) Express the van der Waals parameters $a=0.751$ atm dm^6 mol^{-2} and $b=0.0226$ dm^3 mol^{-1} in SI base units.
36.4(b) Express the van der Waals parameters $a=1.32$ atm dm^6 mol^{-2} and $b=0.0436$ dm^3 mol^{-1} in SI base units.

36.5(a) A gas at 250 K and 12 atm has a molar volume 8.0 per cent smaller than that calculated from the perfect gas law. Calculate (a) the compression factor under these conditions and (b) the molar volume of the gas. Which are dominating in the sample, the attractive or the repulsive forces?
36.5(b) A gas at 350 K and 15 atm has a molar volume 15 per cent larger than that calculated from the perfect gas law. Calculate (a) the compression factor under these conditions and (b) the molar volume of the gas. Which are dominating in the sample, the attractive or the repulsive forces?

36.6(a) In an industrial process, nitrogen is heated to 500 K at a constant volume of 1.000 m^3. The gas enters the container at 300 K and 100 atm. The mass of the gas is 92.4 kg. Use the van der Waals equation to determine the approximate pressure of the gas at its working temperature of 500 K. For nitrogen, $a=1.39$ dm^6 atm mol^{-2}, $b=0.0391$ dm^3 mol^{-1}.
36.6(b) Cylinders of compressed gas are typically filled to a pressure of 200 bar. For oxygen, what would be the molar volume at this pressure and 25 °C based on (a) the perfect gas equation, (b) the van der Waals equation? For oxygen, $a=1.360$ dm^6 atm mol^{-2}, $b=3.183\times10^{-2}$ dm^3 mol^{-1}.

36.7(a) Use the van der Waals parameters for chlorine to estimate its Boyle temperature.
36.7(b) Use the van der Waals parameters for hydrogen sulfide to estimate its Boyle temperature.

36.8(a) Use the van der Waals parameters for chlorine to estimate the radius of a Cl_2 molecule regarded as a sphere.
36.8(b) Use the van der Waals parameters for hydrogen sulfide to estimate the radius of an H_2S molecule regarded as a sphere.

36.9(a) A certain gas obeys the van der Waals equation with $a=0.50$ m^6 Pa mol^{-2}. Its volume is found to be 5.00×10^{-4} m^3 mol^{-1} at 273 K and 3.0 MPa. From this information calculate the van der Waals constant b.
36.9(b) A certain gas obeys the van der Waals equation with $a=0.76$ m^6 Pa mol^{-2}. Its volume is found to be 4.00×10^{-4} m^3 mol^{-1} at 288 K and 4.0 MPa. From this information calculate the van der Waals constant b.

36.10(a) What is the compression factor for the gas described in Exercise 36.9(a) at the prevailing temperature and pressure?
36.10(b) What is the compression factor for the gas described in Exercise 36.9(b) at the prevailing temperature and pressure?

Problems

36.1 Derive an expression for the compression factor of a gas that obeys the equation of state $p(V - nb) = nRT$, where b and R are constants. If the pressure and temperature are such that $V_m = 10b$, what is the numerical value of the compression factor?

36.2 The second virial coefficient B' can be obtained from measurements of the density ρ of a gas at a series of pressures. Show that the graph of p/ρ against p should be a straight line with slope proportional to B'.

36.3 At 300 K and 20 atm, the compression factor of a gas is 0.86. Calculate (a) the volume occupied by 8.2 mmol of the gas under these conditions and (b) an approximate value of the second virial coefficient B at 300 K.

36.4 At 273 K measurements on argon gave $B = -21.7\,\text{cm}^3\,\text{mol}^{-1}$ and $C = 1200\,\text{cm}^6\,\text{mol}^{-2}$, where B and C are the second and third virial coefficients in the expansion of Z in powers of $1/V_m$. Assuming that the perfect gas law holds sufficiently well for the estimation of the second and third terms of the expansion, calculate the compression factor of argon at 100 atm and 273 K. From your result, estimate the molar volume of argon under these conditions.

36.5‡ The second virial coefficient of methane can be approximated by the empirical equation $B'(T) = a + be^{-c/T^2}$, where $a = -0.1993\,\text{bar}^{-1}$, $b = 0.2002\,\text{bar}^{-1}$, and $c = 1131\,\text{K}^2$ with $300\,\text{K} < T < 600\,\text{K}$. What is the Boyle temperature of methane according to this model?

36.6‡ A substance as elementary and well known as argon still receives research attention. A review of thermodynamic properties of argon has been published (R.B. Stewart and R.T. Jacobsen, *J. Phys. Chem. Ref. Data* **18**, 639 (1989)) which included the following 300 K isotherm:

p/MPa	0.4000	0.5000	0.6000	0.8000	1.000	1.500	2.000	2.500	3.000	4.000
$V_m/(\text{dm}^3\,\text{mol}^{-1})$	6.2208	4.9736	4.1423	3.1031	2.4795	1.6483	1.2328	0.98357	0.81746	0.60998

(a) Compute the second virial coefficient, B, at this temperature. (b) Use nonlinear curve-fitting software to compute the third virial coefficient, C, at this temperature.

36.7 Calculate the molar volume of chlorine gas on the basis of the van der Waals equation of state at 250 K and 150 kPa and calculate the percentage difference from the value predicted by the perfect gas equation.

36.8 Suppose that 10.0 mol C_2H_6(g) is confined to 4.860 dm³ at 27 °C. Use the perfect gas and van der Waals equations of state to calculate the compression factor based on these calculations. For ethane, $a = 5.489\,\text{dm}^6\,\text{atm}\,\text{mol}^{-2}$, $b = 0.06380\,\text{dm}^3\,\text{mol}^{-1}$.

36.9 Show that the van der Waals equation leads to values of $Z < 1$ and $Z > 1$, and identify the conditions for which these values are obtained.

36.10 Express the van der Waals equation of state as a virial expansion in powers of $1/V_m$ and obtain expressions for B and C in terms of the parameters a and b. The expansion you will need is $(1 - x)^{-1} = 1 + x + x^2 + \cdots$. Measurements on argon gave $B = -21.7\,\text{cm}^3\,\text{mol}^{-1}$ and $C = 1200\,\text{cm}^6\,\text{mol}^{-2}$ for the virial coefficients at 273 K. What are the values of a and b in the corresponding van der Waals equation of state?

Topic 37 Crystal structure

Discussion questions

37.1 Describe the relationship between the space lattice and unit cell.

37.2 Explain how planes of lattice points are labelled.

37.3 Describe the procedure for identifying the type and size of a cubic unit cell.

37.4 Discuss what is meant by 'scattering factor'. How is it related to the number of electrons in the atoms scattering X-rays?

37.5 Describe the consequences of the phase problem in determining structure factors, and how the problem is overcome.

Exercises

37.1(a) The orthorhombic unit cell of $NiSO_4$ has the dimensions $a = 634$ pm, $b = 784$ pm, and $c = 516$ pm, and the density of the solid is estimated as $3.9\,\text{g}\,\text{cm}^{-3}$. Determine the number of formula units per unit cell and calculate a more precise value of the density.

37.1(b) An orthorhombic unit cell of a compound of molar mass $135.01\,\text{g}\,\text{mol}^{-1}$ has the dimensions $a = 589$ pm, $b = 822$ pm, and $c = 798$ pm. The density of the solid is estimated as $2.9\,\text{g}\,\text{cm}^{-3}$. Determine the number of formula units per unit cell and calculate a more precise value of the density.

37.2(a) Find the Miller indices of the planes that intersect the crystallographic axes at the distances $(2a, 3b, 2c)$ and $(2a, 2b, \infty c)$.

37.2(b) Find the Miller indices of the planes that intersect the crystallographic axes at the distances $(-a, 2b, -c)$ and $(a, 4b, -4c)$.

37.3(a) Calculate the separations of the planes {112}, {110}, and {224} in a crystal in which the cubic unit cell has side 562 pm.

37.3(b) Calculate the separations of the planes {123}, {222}, and {246} in a crystal in which the cubic unit cell has side 712 pm.

37.4(a) The unit cells of $SbCl_3$ are orthorhombic with dimensions $a = 812$ pm, $b = 947$ pm, and $c = 637$ pm. Calculate the spacing, d, of the {321} planes.

37.4(b) An orthorhombic unit cell has dimensions $a = 769$ pm, $b = 891$ pm, and $c = 690$ pm. Calculate the spacing, d, of the {312} planes.

37.5(a) What are the values of the angle θ of the first three diffraction lines of bcc iron (atomic radius 126 pm) when the X-ray wavelength is 72 pm?

37.5(b) What are the values of the angle θ of the first three diffraction lines of fcc gold (atomic radius 144 pm) when the X-ray wavelength is 129 pm?

37.6(a) Potassium nitrate crystals have orthorhombic unit cells of dimensions $a = 542$ pm, $b = 917$ pm, and $c = 645$ pm. Calculate the values of θ for the (100), (010), and (111) reflections using radiation of wavelength 154 pm.

37.6(b) Calcium carbonate crystals in the form of aragonite have orthorhombic unit cells of dimensions $a = 574.1$ pm, $b = 796.8$ pm, and $c = 495.9$ pm. Calculate the values of θ for the (100), (010), and (111) reflections using radiation of wavelength 83.42 pm.

37.7(a) Radiation from an X-ray source consists of two components of wavelengths 154.433 pm and 154.051 pm. Calculate the difference in glancing angles (2θ) of the diffraction lines arising from the two components in a diffraction pattern from planes of separation 77.8 pm.

37.7(b) Consider a source that emits X-radiation at a range of wavelengths, with two components of wavelengths 93.222 and 95.123 pm. Calculate the separation of the glancing angles (2θ) arising from the two components in a diffraction pattern from planes of separation 82.3 pm.

37.8(a) What is the value of the scattering factor in the forward direction for Br^-?

37.8(b) What is the value of the scattering factor in the forward direction for Mg^{2+}?

37.9(a) The coordinates, in units of a, of the atoms in a primitive cubic unit cell are (0,0,0), (0,1,0), (0,0,1), (0,1,1), (1,0,0), (1,1,0), (1,0,1), and (1,1,1).Calculate the structure factors F_{hkl} when all the atoms are identical.

37.9(b) The coordinates, in units of a, of the atoms in a body-centred cubic unit cell are (0,0,0), (0,1,0), (0,0,1), (0,1,1), (1,0,0), (1,1,0), (1,0,1), (1,1,1), and $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$. Calculate the structure factors F_{hkl} when all the atoms are identical.

37.10(a) Calculate the structure factors for a face-centred cubic structure (C) in which the scattering factors of the ions on the two faces are twice that of the ions at the corners of the cube.

37.10(b) Calculate the structure factors for a body-centred cubic structure in which the scattering factor of the central ion is twice that of the ions at the corners of the cube.

37.11(a) In an X-ray investigation, the following structure factors were determined (with $F_{-h00} = F_{h00}$):

Construct the electron density along the corresponding direction.

37.11(b) In an X-ray investigation, the following structure factors were determined (with $F_{-h00} = F_{h00}$):

h	0	1	2	3	4	5	6	7	8	9
F_{h00}	10	−10	8	−8	6	−6	4	−4	2	−2

Construct the electron density along the corresponding direction.

37.12(a) Construct the Patterson synthesis from the information in Exercise 37.11(a).

h	0	1	2	3	4	5	6	7	8	9
F_{h00}	10	10	4	4	6	6	8	8	10	10

37.12(b) Construct the Patterson synthesis from the information in Exercise 37.11(b).

37.13(a) In a Patterson synthesis, the spots correspond to the lengths and directions of the vectors joining the atoms in a unit cell. Sketch the pattern that would be obtained for a planar, triangular isolated BF_3 molecule.

37.13(b) In a Patterson synthesis, the spots correspond to the lengths and directions of the vectors joining the atoms in a unit cell. Sketch the pattern that would be obtained from the C atoms in an isolated benzene molecule.

37.14(a) What speed should neutrons have if they are to have wavelength 65 pm?

37.14(b) What speed should electrons have if they are to have wavelength 105 pm?

37.15(a) Calculate the wavelength of neutrons that have reached thermal equilibrium by collision with a moderator at 350 K.

37.15(b) Calculate the wavelength of electrons that have reached thermal equilibrium by collision with a moderator at 380 K.

Problems

37.1 Although the crystallization of large biological molecules may not be as readily accomplished as that of small molecules, their crystal lattices are no different. Tobacco seed globulin forms face-centred cubic crystals with unit cell dimension of 12.3 nm and a density of 1.287 g cm^{-3}. Determine its molar mass.

37.2 Show that the volume of a monoclinic unit cell is $V = abc \sin \beta$.

37.3 Derive an expression for the volume of a hexagonal unit cell.

37.4 Show that the volume of a triclinic unit cell of sides a, b, and c and angles α, β, and γ is

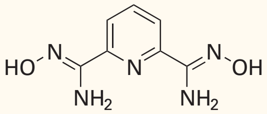
$$V = abc(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)^{1/2}$$

Use this expression to derive expressions for monoclinic and orthorhombic unit cells. For the derivation, it may be helpful to use the result from vector analysis that $V = \boldsymbol{a}\cdot\boldsymbol{b}\times\boldsymbol{c}$ and to calculate V^2 initially. The compound Rb_3TlF_6 has a *tetragonal* unit cell with dimensions $a = 651$ pm and $c = 934$ pm. Calculate the volume of the unit cell.

37.5 The volume of a monoclinic unit cell is $abc \sin \beta$ (see Problem 37.2). Naphthalene has a monoclinic unit cell with two molecules per cell and sides in the ratio 1.377:1:1.436. The angle β is 122.82° and the density of the solid is 1.152 g cm^{-3}. Calculate the dimensions of the cell.

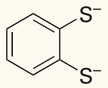
37.6 Fully crystalline polyethylene has its chains aligned in an orthorhombic unit cell of dimensions 740 pm × 493 pm × 253 pm. There are two repeating CH_2CH_2 units per unit cell. Calculate the theoretical mass density of fully crystalline polyethylene. The actual density ranges from 0.92 to 0.95 g cm^{-3}.

37.7‡ B.A. Bovenzi and G.A. Pearse, Jr. (*J. Chem. Soc. Dalton Trans.*, 2793 (1997)) synthesized coordination compounds of the tridentate ligand pyridine-2,6-diamidoxime (**7**, $C_7H_9N_5O_2$). The compound which they isolated from the reaction of the ligand with $CuSO_4(aq)$ did not contain a $[Cu(C_7H_9N_5O_2)_2]^{2+}$ complex cation as expected. Instead, X-ray diffraction analysis revealed a linear polymer of formula $[Cu(C_7H_9N_5O_2)(SO_4)\cdot 2H_2O]_n$, which features bridging sulfate groups. The unit cell was primitive monoclinic with $a = 1.0427$ nm, $b = 0.8876$ nm, $c = 1.3777$ nm, and $\beta = 93.254°$. The mass density of the crystals is 2.024 g cm^{-3}. How many monomer units are there in the unit cell?



7 Pyridine-2,6-diamidoxime

37.8‡ D. Sellmann, et al. (*Inorg. Chem.* **36**, 1397 (1997)) describe the synthesis and reactivity of the ruthenium nitrido compound $[N(C_4H_9)_4][Ru(N)(S_2C_6H_4)_2]$. The ruthenium complex anion has the two 1,2-benzenedithiolate ligands (**8**) at the base of a rectangular pyramid and the nitrido ligand at the apex. Compute the mass density of the compound given that it crystallizes into an orthorhombic unit cell with $a = 3.6881$ nm, $b = 0.9402$ nm, and $c = 1.7652$ nm and eight formula units per cell. Replacing the ruthenium with osmium results in a compound with the same crystal structure and a unit cell with a volume less than 1 per cent larger. Estimate the mass density of the osmium analogue.



8 1,2-Benzenedithiolate ion

37.9 Show that the separation of the {*hkl*} planes in an orthorhombic crystal with sides *a*, *b*, and *c* is given by eqn 37.1c.

37.10 In the early days of X-ray crystallography there was an urgent need to know the wavelengths of X-rays. One technique was to measure the diffraction angle from a mechanically ruled grating. Another method was to estimate the separation of lattice planes from the measured density of a crystal. The density of NaCl is 2.17 g cm^{-3} and the (100) reflection using radiation of a certain wavelength occurred at 6.0°. Calculate the wavelength of the X-rays.

37.11 The element polonium crystallizes in a cubic system. Bragg reflections, with X-rays of wavelength 154 pm, occur at $\sin\theta = 0.225$, 0.316, and 0.388 from the {100}, {110}, and {111} sets of planes. The separation between the sixth and seventh lines observed in the diffraction pattern is larger than between the fifth and sixth lines. Is the unit cell simple, body centred, or face centred? Calculate the unit cell dimension.

37.12 Elemental silver reflects X-rays of wavelength 154.18 pm at angles of 19.076°, 22.171°, and 32.256°. However, there are no other reflections at angles of less than 33°. Assuming a cubic unit cell, determine its type and dimension. Calculate the mass density of silver.

37.13 In their book *X-rays and crystal structures* (which begins 'It is now two years since Dr. Laue conceived the idea…') the Braggs give a number of simple examples of X-ray analysis. For instance, they report that the reflection from {100} planes in KCl occurs at 5° 23', but for NaCl it occurs at 6° 0' for X-rays of the same wavelength. If the side of the NaCl unit cell is 564 pm, what is the side of the KCl unit cell? The densities of KCl and NaCl are 1.99 g cm^{-3} and 2.17 g cm^{-3}, respectively. Do these values support the X-ray analysis?

37.14 Use mathematical software to draw a graph of the scattering factor *f* against $(\sin\theta)/\lambda$ for an atom of atomic number *Z* for which $\rho(r) = 3Z/4\pi R^3$ for $0 \le r \le R$ and $\rho(r) = 0$ for $r > R$, with *R* a parameter that represents the radius of the atom. Explore how *f* varies with *Z* and *R*.

37.15 The coordinates of the four I atoms in the unit cell of KIO_4 are $(0,0,0)$, $\left(0,\frac{1}{2},\frac{1}{2}\right)$, $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$, $\left(\frac{1}{2},0,\frac{3}{4}\right)$. By calculating the phase of the I reflection in the structure factor, show that the I atoms contribute no net intensity to the (114) reflection.

37.16 The coordinates, in units of *a*, of the A atoms, with scattering factor f_A, in a cubic lattice are (0,0,0), (0,1,0), (0,0,1), (0,1,1), (1,0,0), (1,1,0), (1,0,1), and (1,1,1). There is also a B atom, with scattering factor f_B, at $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$. Calculate the structure factors F_{hkl} and predict the form of the diffraction pattern when (a) $f_A = f$, $f_B = 0$, (b) $f_B = \frac{1}{2}f_A$, and (c) $f_A = f_B = f$.

37.17 Here we explore electron diffraction patterns. (a) Predict from the Wierl equation, eqn 37.9, the positions of the first maximum and first minimum in the neutron and electron diffraction patterns of a Br_2 molecule obtained with neutrons of wavelength 78 pm wavelength and electrons of wavelength 4.0 pm. (b) Use the Wierl equation to predict the appearance of the electron diffraction pattern of CCl_4 with an (as yet) undetermined C–Cl bond length but of known tetrahedral symmetry. Take $f_{Cl} = 17f$ and $f_C = 6f$ and note that $R(\text{Cl,Cl}) = (8/3)^{1/2}R(\text{C,Cl})$. Plot I/f^2 against positions of the maxima, which occurring at 3.17°, 5.37°, and 7.90° and minima, which occurring at 1.77°, 4.10°, 6.67°, and 9.17°. What is the C–Cl bond length in CCl_4?

Topic 38 Bonding in solids

Discussion questions

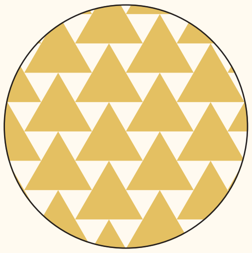
38.1 To what extent is the hard-sphere model of metallic solids deficient?

38.2 Describe the caesium chloride and rock salt structures in terms of the occupation of holes in expanded close-packed lattices.

Exercises

38.1(a) Calculate the packing fraction for close-packed cylinders. (For a generalization of this Exercise, see Problem 38.2.)

38.1(b) Calculate the packing fraction for equilateral triangular rods stacked as shown in **9**.



9

38.2(a) Calculate the packing fractions of (i) a primitive cubic unit cell, (ii) a bcc unit cell, (iii) an fcc unit cell composed of identical hard spheres.

38.2(b) Calculate the atomic packing factor for a side-centred (C) cubic unit cell.

38.3(a) From the data in Table 38.2 determine the radius of the smallest cation that can have (i) sixfold and (ii) eightfold coordination with the Cl$^-$ ion.

38.3(b) From the data in Table 38.2 determine the radius of the smallest cation that can have (i) sixfold and (ii) eightfold coordination with the Rb$^+$ ion.

38.4(a) Does titanium expand or contract as it transforms from hcp to body-centred cubic? The atomic radius of titanium is 145.8 pm in hcp but 142.5 pm in bcc.

38.4(b) Does iron expand or contract as it transforms from hcp to bcc? The atomic radius of iron is 126 in hcp but 122 pm in bcc.

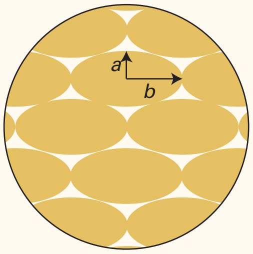
38.5(a) Calculate the lattice enthalpy of $CaCl_2$ from the following data:

	$\Delta H/(\text{kJ mol}^{-1})$
Sublimation of Ca(s)	+178
Ionization of Ca(g) to $Ca^{2+}(g)$	+1735
Dissociation of $Cl_2(g)$	+244
Electron attachment to Cl(g)	−349
Formation of $CaCl_2(s)$ from Ca(s) and $Cl_2(g)$	−796

Problems

38.1 Calculate the atomic packing factor for diamond.

38.2 Rods of elliptical cross-section with semi-minor and major axes a and b are close-packed, as shown in **10**. What is the packing fraction? Draw a graph of the packing fraction against the eccentricity ε of the ellipse. For an ellipse with semi-major axis a and semi-minor axis b, $\varepsilon = (1 - b^2/a^2)^{1/2}$.



10

38.3 The carbon–carbon bond length in diamond is 154.45 pm. If diamond were considered to be a close-packed structure of hard spheres with radii equal to half the bond length, what would be its expected density? The diamond lattice is face-centred cubic and its actual density is $3.516\,\text{g cm}^{-3}$. Can you explain the discrepancy?

38.4 When energy levels in a band form a continuum, the density of states $\rho(E)$, the number of levels in an energy range divided by the width of the range, may be written as $\rho(E) = \mathrm{d}k/\mathrm{d}E$, where $\mathrm{d}k$ is the change in the quantum number k and $\mathrm{d}E$ is the energy change. (a) Use eqn 38.1 to show that

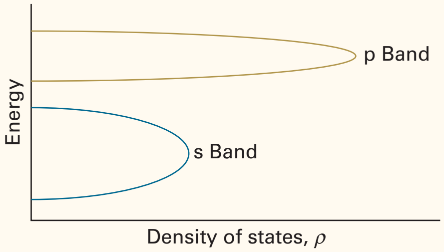
$$\rho(E) = -\frac{(N+1)/2\pi\beta}{\left\{1-\left(\dfrac{E-\alpha}{2\beta}\right)^2\right\}^{1/2}}$$

where k, N, α, and β have the meanings described in Topic 38. (b) Use this expression to show that $\rho(E)$ becomes infinite as E approaches $\alpha \pm 2\beta$. That is, show that the density of states increases towards the edges of the bands in a one-dimensional metallic conductor.

38.5 The treatment in Problem 38.4 applies only to one-dimensional solids. In three dimensions, the variation of density of states is more like that shown in (**11**). Account for the fact that in a three-dimensional solid the greatest density of states is near the centre of the band and the lowest density is at the edges.

38.5(b) Calculate the lattice enthalpy of $MgBr_2$ from the following data:

	$\Delta H/(\text{kJ mol}^{-1})$
Sublimation of Mg(s)	+148
Ionization of Mg(g) to $Mg^{2+}(g)$	+2187
Vaporization of $Br_2(l)$	+31
Dissociation of $Br_2(g)$	+193
Electron attachment to Br(g)	−331
Formation of $MgBr_2(s)$ from Mg(s) and $Br_2(l)$	−524



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38.6 The energy levels of N atoms in the tight-binding Hückel approximation are the roots of a tridiagonal determinant (eqn 38.1):

$$E_k = \alpha + 2\beta \cos\frac{k\pi}{N+1} \quad k = 1, 2, \ldots, N$$

If the atoms are arranged in a ring, the solutions are the roots of a 'cyclic' determinant:

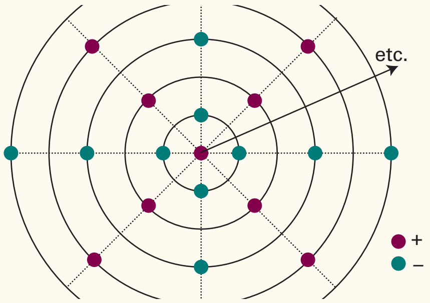
$$E_k = \alpha + 2\beta \cos\frac{2k\pi}{N} \quad k = 0, \pm 1, \pm 2, \ldots, \pm\tfrac{1}{2}N$$

(for N even). Discuss the consequences, if any, of joining the ends of an initially straight length of material.

38.7 Use the Born–Mayer equation for the lattice enthalpy and a Born–Haber cycle to show that formation of CaCl is an exothermic process (the sublimation enthalpy of Ca(s) is $176\,\text{kJ mol}^{-1}$). Show that an explanation for the nonexistence of CaCl can be found in the reaction enthalpy for the reaction $2\,CaCl(s) \rightarrow Ca(s) + CaCl_2$.

38.8 Derive the Born–Mayer equation (eqn 38.7) by calculating the energy at which $\mathrm{d}(E_P + E_P^*)/\mathrm{d}d = 0$, with E_P and E_P^* given by eqns 38.5 and 38.6, respectively.

38.9 Suppose that ions are arranged in a (somewhat artificial) two-dimensional lattice like the fragment shown in (**12**). Calculate the Madelung constant for this array.



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Topic 39 Electrical, optical, and magnetic properties of solids

Discussion questions

39.1 Describe the characteristics of the Fermi–Dirac distribution.

39.2 Is arsenic-doped germanium a p-type or n-type semiconductor?

Exercises

39.1(a) The promotion of an electron from the valence band into the conduction band in pure TIO_2 by light absorption requires a wavelength of less than 350 nm. Calculate the energy gap in electronvolts between the valence and conduction bands.
39.1(b) The band gap in silicon is 1.12 eV. Calculate the maximum wavelength of electromagnetic radiation that results in promotion of electrons from the valence to the conduction band.

39.2(a) The magnitude of the magnetic moment of $CrCl_3$ is $3.81\mu_B$. How many unpaired electrons does the Cr possess?
39.2(b) The magnitude of the magnetic moment of Mn^{2+} in its complexes is typically $5.3\mu_B$. How many unpaired electrons does the ion possess?

39.3(a) Calculate the molar susceptibility of benzene given that its volume susceptibility is -7.2×10^{-7} and its density 0.879 g cm^{-3} at 25 °C.
39.3(b) Calculate the molar susceptibility of cyclohexane given that its volume susceptibility is -7.9×10^{-7} and its density 811 kg m^{-3} at 25 °C.

39.4(a) Data on a single crystal of MnF_2 give $\chi_m = 0.1463$ cm^3 mol^{-1} at 294.53 K. Determine the effective number of unpaired electrons in this compound and compare your result with the theoretical value.
39.4(b) Data on a single crystal of $NiSO_4\cdot7H_2O$ give $\chi_m = 6.00\times10^{-8}$ m^3 mol^{-1} at 298 K. Determine the effective number of unpaired electrons in this compound and compare your result with the theoretical value.

39.5(a) Estimate the spin-only molar susceptibility of $CuSO_4{\cdot}5H_2O$ at 25 °C.
39.5(b) Estimate the spin-only molar susceptibility of $MnSO_4{\cdot}4H_2O$ at 298 K.

Problems

39.1 Refer to eqn 39.2 and express $f(E)$ as a function of the variables $(E-\mu)/\mu$ and μ/kT. Then, using mathematical software, display the set of curves shown in Fig. 39.3 as a single surface.

39.2 In this and the following problem we explore further some of the properties of the Fermi–Dirac distribution, eqn 39.2. For a three-dimensional solid of volume V, it turns out that $\rho(E) = CE^{1/2}$, with $C = 4\pi V(2m_e/h^2)^{3/2}$. Show that, at $T = 0$,

$$f(E)=1 \quad \text{for} \quad E<\mu \qquad f(E)=0 \text{ for } E>\mu$$

and deduce that $\mu(0) = (3\mathcal{N}/8\pi)^{2/3}(h^2/2m_e)$, where $\mathcal{N} = N/V$, the number density of electrons in the solid. Evaluate $\mu(0)$ for sodium (where each atom contributes one electron).

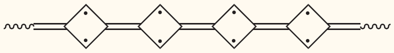
39.3 By inspection of eqn 39.2 and the expression for dN in eqn 39.1 (and without attempting to evaluate integrals explicitly), show that in order for N to remain constant as the temperature is raised, the chemical potential must decrease in value from $\mu(0)$.

39.4 In an intrinsic semiconductor, the band gap is so small that the Fermi–Dirac distribution results in some electrons populating the conduction band. It follows from the exponential form of the Fermi–Dirac distribution that the conductance G, the inverse of the resistance (with units of siemens, $1\,S = 1\,\Omega^{-1}$), of an intrinsic semiconductor should have an Arrhenius-like temperature dependence, shown in practice to have the form $G = G_0e^{-E_g/2kT}$, where E_g is the band gap. The conductance of a sample of germanium varied with temperature as indicated below. Estimate the value of E_g.

T/K	312	354	420
G/S	0.0847	0.429	2.86

39.5 A transistor is a semiconducting device that is commonly used either as a switch or as an amplifier of electrical signals. Prepare a brief report on the design of a nanometre-sized transistor that uses a carbon nanotube as a component. A useful starting point is the work summarized by Tans, et al. (*Nature* **393**, 49 (1998)).

39.6‡ J.J. Dannenberg, et al. (*J. Phys. Chem.* **100**, 9631 (1996)) carried out theoretical studies of organic molecules consisting of chains of unsaturated four-membered rings. The calculations suggest that such compounds have large numbers of unpaired spins, and that they should therefore have unusual magnetic properties. For example, the lowest energy state of the compound shown as **13** is computed to have $S = 3$, but the energies of $S = 2$ and $S = 4$ structures are each predicted to be 50 kJ mol^{-1} higher in energy. Compute the molar magnetic susceptibility of these three low-lying levels at 298 K. Estimate the molar susceptibility at 298 K if each level is present in proportion to its Boltzmann factor (effectively assuming that the degeneracy is the same for all three of these levels).



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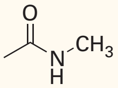
39.7 An NO molecule has thermally accessible electronically excited states. It also has an unpaired electron, and so may be expected to be paramagnetic. However, its ground state is not paramagnetic because the magnetic moment of the orbital motion of the unpaired electron almost exactly cancels the spin magnetic moment. The first excited state (at 121 cm^{-1}) is paramagnetic because the orbital magnetic moment adds to, rather than cancels, the spin magnetic moment. The upper state has a magnetic moment of magnitude $2\mu_B$. Because the upper state is thermally accessible, the paramagnetic susceptibility of NO shows a pronounced temperature dependence even near room temperature. Calculate the molar paramagnetic susceptibility of NO and plot it as a function of temperature.

39.8‡ P.G. Radaelli, et al. (*Science* **265**, 380 (1994)) reported the synthesis and structure of a material that becomes superconducting at temperatures below 45 K. The compound is based on a layered compound, $Hg_2Ba_2YCu_2O_{8-\delta}$, which has a tetragonal unit cell with $a = 0.38606$ nm and $c = 2.8915$ nm; each unit cell contains two formula units. The compound is made superconducting by partially replacing Y by Ca, accompanied by a change in unit cell volume by less than 1 per cent. Estimate the Ca content x in superconducting $Hg_2Ba_2Y_{1-x}Ca_xCu_2O_{7.55}$ given that the mass density of the compound is 7.651 g cm^{-3}.

Integrated activities

F8.1 The tip of a scanning tunnelling microscope can be used to move atoms on a surface. The movement of atoms and ions depends on their ability to leave one position and stick to another, and therefore on the energy changes that occur. As an illustration, consider a two-dimensional square lattice of univalent positive and negative ions separated by 200 pm, and consider a cation on top of this array. Calculate, by direct summation, its Coulombic interaction when it is in an empty lattice point directly above an anion.

F8.2 Molecular orbital calculations may be used to predict the dipole moments of molecules. (a) Using molecular modelling software and the computational method of your choice, calculate the dipole moment of the peptide link, modelled as a trans-*N*-methylacetamide (**14**). Plot the energy of interaction between these dipoles against the angle θ for $r = 3.0$ nm. (b) Compare the maximum value of the dipole–dipole interaction energy from part (a) to 20 kJ mol^{-1}, a typical value for the energy of a hydrogen bonding interaction in biological systems.



14 trans-*N*-methylacetamide

F8.3 Use eqn 34.7 to calculate the polarizability of a one-dimensional harmonic oscillator in its ground state when the field is applied (a) perpendicular to, (b) parallel to the oscillator. You will need the result:

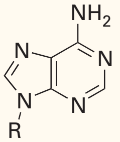
$$\mu_{z,01} = \mu_{z,10} = e\left(\frac{\hbar}{2m\omega}\right)^{1/2}$$

F8.4 Use eqn 34.7 to compute the polarizability of a hydrogen atom. For simplicity, confine the sum in eqn 34.7 to the np_z orbitals and use the following matrix element between the np_z and 1s orbitals:

$$\mu_{z,0n} = \mu_{z,n0} = -ea_0\left(\frac{2^8 n^7 (n-1)^{2n-5}}{3(n+1)^{2n+5}}\right)^{1/2}$$

F8.5 Show that the mean interaction energy of N atoms of diameter d interacting with a potential energy of the form C_6/R^6 is given by $U = -2N^2C_6/3Vd^3$, where V is the volume in which the molecules are confined and all effects of clustering are ignored. Hence, find a connection between the van der Waals parameter a and C_6, from $n^2a/V^2 = (\partial U/\partial V)_T$.

F8.6 Molecular orbital calculations may be used to predict structures of intermolecular complexes. Hydrogen bonds between purine and pyrimidine bases are responsible for the double helix structure of DNA. Consider methyladenine (**15**, with $R = CH_3$) and methylthymine (**16**, with $R = CH_3$) as models of two bases that can form hydrogen bonds in DNA. (a) Using molecular modelling software and the computational method of your choice, calculate the atomic charges of all atoms in methyladenine and methylthymine. (b) Based on your tabulation of atomic charges, identify the atoms in methyladenine and methylthymine that are likely to participate in hydrogen bonds. (c) Draw all possible adenine–thymine pairs that can be linked by hydrogen bonds, keeping in mind that linear arrangements of the A–H···B fragments are preferred in DNA. For this step, you may want to use your molecular modelling software to align the molecules properly. (d) Which of the pairs that you drew in part (c) occur naturally in DNA molecules? (e) Repeat parts (a)–(d) for cytosine and guanine, which also form base pairs in DNA.



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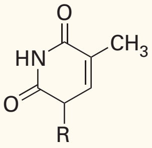

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F8.7 Calculate the thermal expansion coefficient, $\alpha = (\partial V/\partial T)_p/V$, of diamond given that the (111) reflection shifts from 22.0403° to 21.9664° on heating a crystal from 100 K to 300 K and 154.0562 pm X-rays are used.

F8.8 Calculate the scattering factor for a hydrogenic atom of atomic number Z in which the single electron occupies (a) the 1s orbital, (b) the 2s orbital. Plot f as a function of $(\sin\theta)/\lambda$. *Hint*: Interpret $4\pi\rho(r)r^2$ as the radial distribution function $P(r)$.

F8.9 Explore how the scattering factor of Problem F8.8 changes when the actual 1s wavefunction of a hydrogenic atom is replaced by a Gaussian function.

F8.10 The magnetizability, ξ, and the volume and molar magnetic susceptibilities can be calculated from the wavefunctions of molecules. For instance, the magnetizability of a hydrogenic atom is given by the expression $\xi = -(e^2/6m_e)\langle r^2\rangle$, where $\langle r^2\rangle$ is the (expectation) mean value of r^2 in the atom. Calculate ξ and χ_m for the ground state of a hydrogenic atom. Use $\chi = \mu_0\mathcal{N}\xi$.

Mathematical background 6 Fourier series and Fourier transforms

Some of the most versatile mathematical functions are the trigonometric functions sine and cosine. As a result, it is often very helpful to express a general function as a linear combination of these functions and then to carry out manipulations on the resulting series. Because sines and cosines have the form of waves, the linear combinations often have a straightforward physical interpretation. Throughout this discussion, the function $f(x)$ is real.

MB6.1 Fourier series

A *Fourier series* is a linear combination of sines and cosines that replicates a periodic function:

$$f(x)=\frac{1}{2}a_0+\sum_{n=1}^{\infty}\left\{a_n\cos\frac{n\pi x}{L}+b_n\sin\frac{n\pi x}{L}\right\}\qquad\text{(MB6.1)}$$

A periodic function is one that repeats periodically, such that $f(x+2L)=f(x)$ where $2L$ is the period. Although it is perhaps not surprising that sines and cosines can be used to replicate continuous functions, it turns out that—with certain limitations—they can also be used to replicate discontinuous functions. The coefficients in eqn MB6.1 are found by making use of the orthogonality of the sine and cosine functions

$$\int_{-L}^{L}\sin\frac{m\pi x}{L}\cos\frac{m\pi x}{L}\,\mathrm{d}x=0\qquad\text{(MB6.2a)}$$

and the integrals

$$\int_{-L}^{L}\sin\frac{m\pi x}{L}\sin\frac{n\pi x}{L}\,\mathrm{d}x=\int_{-L}^{L}\cos\frac{m\pi x}{L}\cos\frac{n\pi x}{L}\,\mathrm{d}x=L\delta_{mn}\qquad\text{(MB6.2b)}$$

where $\delta_{mn}=1$ if $m=n$ and 0 if $m\neq n$. Thus, multiplication of both sides of eqn MB6.1 by $\cos(k\pi x/L)$ and integration from $-L$ to L gives an expression for the coefficient a_k, and multiplication by $\sin(k\pi x/L)$ and integration likewise gives an expression for b_k:

$$\begin{aligned}a_k&=\frac{1}{L}\int_{-L}^{L}f(x)\cos\frac{k\pi x}{L}\,\mathrm{d}x\quad k=0,1,2,\ldots\\ b_k&=\frac{1}{L}\int_{-L}^{L}f(x)\sin\frac{k\pi x}{L}\,\mathrm{d}x\quad k=1,2,\ldots\end{aligned}\qquad\text{(MB6.3)}$$

Brief illustration MB6.1 A square wave

Figure MB6.1 shows a graph of a square wave of amplitude A that is periodic between $-L$ and L. The mathematical form of the wave is

$$f(x)=\begin{cases}-A & -L\le x<0\\ +A & 0\le x<L\end{cases}$$

The coefficients a are all zero because $f(x)$ is antisymmetric ($f(-x)=-f(x)$) whereas all the cosine functions are symmetric ($\cos(-x)=\cos(x)$) and so cosine waves make no contribution to the sum. The coefficients b are obtained from

$$\begin{aligned}b_k&=\frac{1}{L}\int_{-L}^{L}f(x)\sin\frac{k\pi x}{L}\,\mathrm{d}x\\ &=\frac{1}{L}\int_{-L}^{0}(-A)\sin\frac{k\pi x}{L}\,\mathrm{d}x+\frac{1}{L}\int_{0}^{L}A\sin\frac{k\pi x}{L}\,\mathrm{d}x\\ &=\frac{2A}{\pi}\frac{\{(1-(-1)^k)\}}{k}\end{aligned}$$

The final expression has been formulated to acknowledge that the two integrals cancel when k is even but add together when k is odd. Therefore,

$$f(x)=\frac{2A}{\pi}\sum_{k=1}^{N}\frac{1-(-1)^k}{k}\sin\frac{k\pi x}{L}=\frac{4A}{\pi}\sum_{n=1}^{N}\frac{1}{2n-1}\sin\frac{(2n-1)\pi x}{L}$$

with $N\to\infty$. The sum over n is the same as the sum over k; in the latter, terms with k even are all zero. This function is plotted in Fig. MB6.1 for two values of N to show how the series becomes more faithful to the original function as N increases.

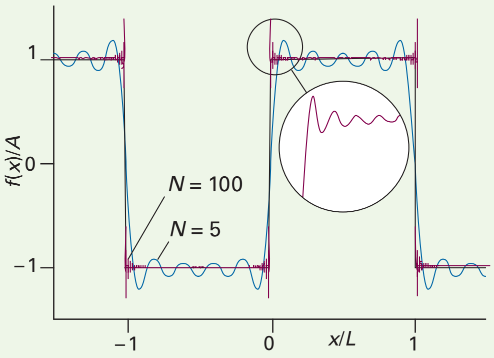

Figure MB6.1 A square wave and two successive approximations by Fourier series ($N=5$ and $N=100$). The inset shows a magnification of the $N=100$ approximation.

MB6.2 Fourier transforms

The Fourier series in eqn MB6.1 can be expressed in a more succinct manner if we allow the coefficients to be complex numbers and make use of *de Moivre's relation*

$$e^{\mathrm{i}n\pi x/L}=\cos\left(\frac{n\pi x}{L}\right)+\mathrm{i}\sin\left(\frac{n\pi x}{L}\right) \qquad \text{(MB6.4)}$$

for then we may write

$$f(x)=\sum_{n=-\infty}^{\infty}c_n e^{\mathrm{i}n\pi x/L} \qquad c_n=\frac{1}{2L}\int_{-L}^{L}f(x)e^{-\mathrm{i}n\pi x/L}\mathrm{d}x \qquad \text{(MB6.5)}$$

This complex formalism is well suited to the extension of this discussion to functions with periods that become infinite. If a period is infinite, then we are effectively dealing with a non-periodic function, such as the decaying exponential function e^{-x}.

We write $\delta k=\pi/L$ and consider the limit as $L\to\infty$ and therefore $\delta k\to 0$: that is, eqn MB6.5 becomes

$$\begin{aligned}f(x)&=\lim_{L\to\infty}\sum_{n=-\infty}^{\infty}\frac{1}{2L}\left\{\int_{-L}^{L}f(x')e^{-\mathrm{i}n\pi x'/L}\mathrm{d}x'\right\}e^{\mathrm{i}n\pi x/L}\\&=\lim_{\delta k\to 0}\sum_{n=-\infty}^{\infty}\frac{\delta k}{2\pi}\left\{\int_{-\pi/\delta k}^{\pi/\delta k}f(x')e^{-\mathrm{i}n\delta kx'}\mathrm{d}x'\right\}e^{\mathrm{i}n\delta kx/L}\\&=\lim_{\delta k\to 0}\sum_{n=-\infty}^{\infty}\frac{1}{2\pi}\left\{\int_{-\infty}^{\infty}f(x')e^{-\mathrm{i}n\delta k(x'-x)}\mathrm{d}x'\right\}\delta k\end{aligned} \qquad \text{(MB6.6)}$$

In the last line we have anticipated that the limits of the integral will become infinite. At this point we should recognize that a formal definition of an integral is the sum of the value of a function at a series of infinitesimally spaced points multiplied by the separation of each point (Fig. MB6.2; see *Mathematical background* 1):

$$\int_a^b F(k)\mathrm{d}k=\lim_{\delta k\to 0}\sum_{n=-\infty}^{\infty}F(n\delta k)\delta k \qquad \text{(MB6.7)}$$

Exactly this form appears on the right-hand side of eqn MB6.6, so we can write that equation as

$$f(x)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\tilde{f}(k)e^{\mathrm{i}kx}\mathrm{d}k \quad \text{where } \tilde{f}(k)=\int_{-\infty}^{\infty}f(x')e^{-\mathrm{i}kx'}\mathrm{d}x' \qquad \text{(MB6.8)}$$

At this stage we can drop the prime on x for $\tilde{f}(k)$. We call the function $\tilde{f}(k)$ the *Fourier transform* of $f(x)$; the original function $f(x)$ is the *inverse Fourier transform* of $\tilde{f}(k)$.

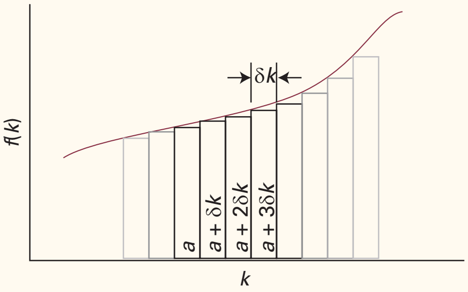

Figure MB6.2 The formal definition of an integral as the sum of the value of a function at a series of infinitesimally spaced points multiplied by the separation of each point.

Brief illustration MB6.2 A Fourier transform

The Fourier transform of the symmetrical exponential function $f(x)=e^{-a|x|}$ is

$$\begin{aligned}\tilde{f}(k)&=\int_{-\infty}^{\infty}f(x)e^{-\mathrm{i}kx}\mathrm{d}x=\int_{-\infty}^{\infty}e^{-a|x|-\mathrm{i}kx}\mathrm{d}x\\&=\int_{-\infty}^{0}e^{ax-\mathrm{i}kx}\mathrm{d}x+\int_{0}^{\infty}e^{-ax-\mathrm{i}kx}\mathrm{d}x\\&=\frac{1}{a-\mathrm{i}k}+\frac{1}{a+\mathrm{i}k}=\frac{2a}{a^2+k^2}\end{aligned}$$

The original function and its Fourier transform are drawn in Fig. MB6.3.

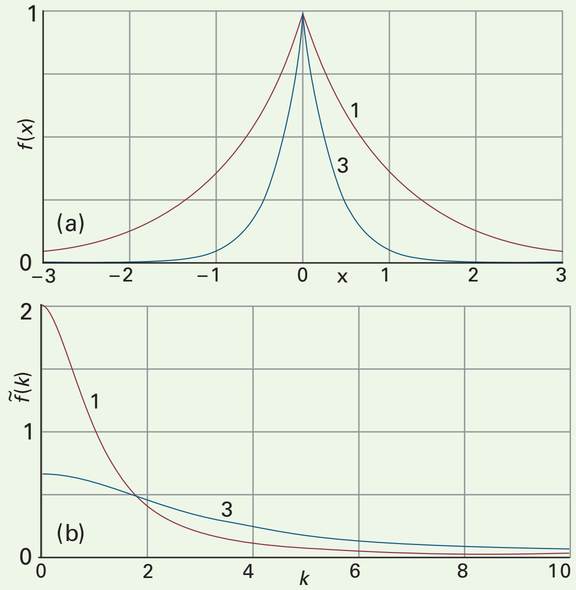

Figure MB6.3 (a) The symmetrical exponential function $f(x)=e^{-a|x|}$ and (b) its Fourier transform for two values of the decay constant *a*. Note how the function with the more rapid decay has a Fourier transform richer in short-wavelength (high *k*) components.

The physical interpretation of eqn MB6.8 is that $f(x)$ is expressed as a superposition of harmonic (sine and cosine) functions of wavelength $\lambda = 2\pi/k$, and that the weight of each constituent function is given by the Fourier transform at the corresponding value of k. This interpretation is consistent with the calculation in *Brief illustration* MB6.2. As we see from Fig. MB6.3, when the exponential function falls away rapidly with time, the Fourier transform is extended to high values of k, corresponding to a significant contribution from short-wavelength waves. When the exponential function decays only slowly, the most significant contributions to the superposition come from low-frequency components, which is reflected in the Fourier transform, with its predominance of small-k contributions in this case. In general, a slowly varying function has a Fourier transform with significant contributions from small-k components.

MB6.3 The convolution theorem

A final point concerning the properties of Fourier transforms is the **convolution theorem**, which states that if a function is the 'convolution' of two other functions, that is, if

$$F(x) = \int_{-\infty}^{\infty} f_1(x')f_2(x-x')\,\mathrm{d}x' \qquad \text{(MB6.9a)}$$

then the Fourier transform of $F(x)$ is the product of the Fourier transforms of its component functions:

$$\tilde{F}(k) = \tilde{f}_1(k)\tilde{f}_2(k) \qquad \text{(MB6.9b)}$$

Brief illustration MB6.3 Convolutions

Suppose that $F(x)$ is the convolution of two Gaussian functions:

$$F(x) = \int_{-\infty}^{\infty} \mathrm{e}^{-a^2x'^2}\mathrm{e}^{-b^2(x-x')^2}\,\mathrm{d}x'$$

The Fourier transform of a Gaussian function is itself a Gaussian function:

$$\tilde{f}(k) = \int_{-\infty}^{\infty} \mathrm{e}^{-c^2x^2}\mathrm{e}^{-\mathrm{i}kx}\,\mathrm{d}x = \left(\frac{\pi}{c^2}\right)^{1/2}\mathrm{e}^{-k^2/4c^2}$$

Therefore, the transform of $F(x)$ is the product

$$\tilde{F}(k) = \left(\frac{\pi}{a^2}\right)^{1/2}\mathrm{e}^{-k^2/4a^2}\left(\frac{\pi}{b^2}\right)^{1/2}\mathrm{e}^{-k^2/4b^2} = \frac{\pi}{ab}\mathrm{e}^{-(k^2/4)(1/a^2+1/b^2)}$$

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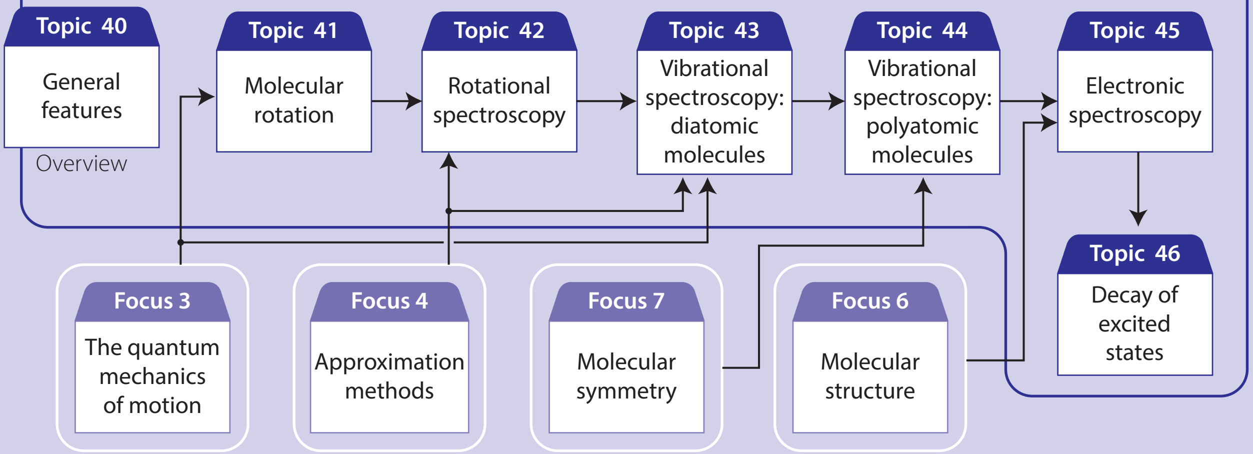
FOCUS 9 ON Molecular spectroscopy



The origin of spectral lines in molecular spectroscopy is the absorption, emission, or scattering of a photon when the energy of a molecule changes. The difference from atomic spectroscopy is that the energy of a molecule can change not only as a result of electronic transitions but also because it can undergo changes of rotational and vibrational state. Molecular spectra are therefore more complex than atomic spectra. However, they also contain information relating to more properties, and their analysis leads to values of bond strengths, lengths, and angles. They also provide a way of determining a variety of molecular properties, such as dipole moments. The general strategy we adopt in this cluster of topics is to set up expressions for the energy levels of molecules and then infer the form of molecular spectra observed from the microwave to the ultraviolet regions of the electromagnetic spectrum. Throughout our exploration we use 'time-dependent perturbation theory' (*Approximation methods*) to develop a quantum mechanical treatment of 'selection rules' for the observation of spectroscopic transitions.

Topic 40 begins with a discussion of the features of instrumentation used to monitor the absorption, emission, and scattering of radiation spanning a wide range of frequencies. Then we describe the theory of absorption and emission of radiation, leading to the factors that determine the intensities and widths of spectral lines.

In **Topic 41** we use knowledge of *The quantum mechanics of motion* to derive expressions for the rotational energy levels of diatomic and polyatomic molecules. The most direct procedure, which we adopt, is to identify the expressions for the energy and angular momentum obtained in classical physics, and then to transform these expressions into their quantum mechanical counterparts. The stage is then set for the study of pure rotational and rotational Raman spectra, in which only the rotational state of a molecule changes (**Topic 42**).

Topic 43 considers the vibrational energy levels of diatomic molecules and shows that we can use the properties of 'harmonic oscillators' (*The quantum mechanics of motion*). It also shows that it is important to take into account deviations from harmonic oscillation. We see that vibrational spectra of gaseous samples show features that arise from the rotational transitions that accompany the excitation of vibrations. Our discussion of the vibrational spectra of polyatomic molecules is based on the approach employed for diatomic molecules (**Topic 44**). We also see that *Molecular symmetry* is helpful for deciding which modes of vibration can be studied spectroscopically.

Unlike for rotational and vibrational modes, simple analytical expressions for the electronic energy levels of molecules cannot be given. Therefore, we concentrate on the qualitative features of electronic transitions that arise from a knowledge of *Atomic structure and spectra* and *Molecular structure*. A common theme is that electronic transitions occur within a stationary nuclear framework. **Topic 45** begins with a discussion of the electronic spectra of diatomic molecules, and we see that in the gas phase it is possible to observe simultaneous vibrational and rotational transitions that accompany the electronic transition. Then we describe features of the electronic spectra of polyatomic molecules. In **Topic 46** we discuss spontaneous emission by molecules, including the phenomena of 'fluorescence' and 'phosphorescence'. Then we see how nonradiative decay of excited states can result in transfer of energy as heat to the surroundings or result in molecular dissociation. A very important example of stimulated radiative decay is that responsible for the action of 'lasers'.

What is the impact of this material?

Molecular spectroscopy is useful to astrophysicists and environmental scientists. In *Impact* 9.1 we see how the identities of molecules found in interstellar space can be inferred from their rotational and vibrational spectra. In *Impact* 9.2 we turn our attention back towards the Earth and see how the vibrational properties of its atmospheric constituents can affect its climate. Absorption and emission spectroscopy is also useful to biochemists. In *Impact* 9.3 we describe how the absorption of visible radiation by special molecules in the eye initiates the process of vision. In *Impact* 9.4 we see how fluorescence techniques can be used to make very small samples visible, ranging from specialized compartments inside biological cells to single molecules.

To read more about the impact of this material, scan the QR code or go to http://bcs.whfreeman.com/webpub/chemistry/qmc2e/impact/qchem_impact9.html.

TOPIC 40

General features

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➤ Why do you need to know this material?

To interpret data from the wide range of varieties of molecular spectroscopy, you need to understand the experimental and theoretical features that all types of spectra have in common. This Topic lays the foundation for the following ten.

➤ What is the key idea?

Different arrangements of light sources, wavelength analysers, and detectors make possible the study of absorption, emission, and scattering of electromagnetic radiation by molecules in gaseous, liquid, and solid samples.

➤ What do you need to know already?

You need to be familiar with quantization of energy in molecules (Topics 9–14), and the general principles governing the intensities of spectroscopic transitions (Topic 16).

In **emission spectroscopy**, a molecule undergoes a transition from a state of high energy E_1 to a state of lower energy E_2 and emits the excess energy as a photon. In **absorption spectroscopy**, the net absorption of incident radiation is monitored as its frequency is varied. We say *net* absorption, because, when a sample is irradiated, both absorption and emission at a given frequency are stimulated (Topic 16), and the detector measures the difference, the net absorption. In **Raman spectroscopy**, changes in molecular state are explored by examining the frequencies present in the radiation scattered by molecules.

The energy, $h\nu$, of the photon emitted or absorbed, and therefore the frequency ν of the radiation emitted or absorbed, is given by the Bohr frequency condition (Topic 4, $h\nu = E_1 - E_2$). Emission and absorption spectroscopy give the same information about electronic, vibrational, or rotational energy level separations, but practical considerations generally determine which technique is employed. In Raman spectroscopy the difference between the frequencies of the scattered and incident radiation is determined by the transitions that take place within the molecule; this technique is used to study molecular vibrations and rotations.

Atomic spectroscopy is discussed in Topic 21. Here we set the stage for detailed discussion of rotational (Topics 41 and 42), vibrational (Topics 43 and 44), and electronic (Topics 45 and 46) transitions in molecules. Techniques that probe transitions between spin states of electrons and nuclei are also useful. They rely on special experimental approaches described in Topics 47–50.

40.1 Spectrometers

Common to all spectroscopic techniques is a **spectrometer**, an instrument that detects the characteristics of radiation scattered, emitted, or absorbed by atoms and molecules. As an example, Fig. 40.1 shows the general layout of an absorption spectrometer. Radiation from an appropriate source is directed toward a sample and the radiation transmitted strikes a device that separates it into different frequencies. The intensity of radiation at each frequency is then analysed by a suitable detector.

(a) Sources of radiation

Sources of radiation are either *monochromatic*, those spanning a very narrow range of frequencies around a central value, or *polychromatic*, those spanning a wide range of frequencies. Monochromatic sources that can be tuned over a range of frequencies include the *klystron* and the *Gunn diode*, which operate in the microwave range, and lasers (Topic 46).

Polychromatic sources that take advantage of black-body radiation from hot materials (Topic 4) can be used from the infrared to the ultraviolet regions of the electromagnetic spectrum. Examples include mercury arcs inside a quartz envelope ($35\,\mathrm{cm^{-1}} < \tilde{\nu} < 200\,\mathrm{cm^{-1}}$), *Nernst filaments* and *globars* ($4000\,\mathrm{cm^{-1}} < \tilde{\nu} < 31\,000\,\mathrm{cm^{-1}}$), and *quartz–tungsten–halogen lamps* ($320\,\mathrm{nm} < \lambda < 2500\,\mathrm{nm}$).

A *gas discharge lamp* is a common source of ultraviolet and visible radiation. In a *xenon discharge lamp*, an electrical discharge excites xenon atoms to excited states, which then emit ultraviolet radiation. In a *deuterium lamp*, excited D_2 molecules dissociate into electronically excited D atoms, which emit intense radiation in the range 200–400 nm ($25\,000\,\mathrm{cm^{-1}} < \tilde{\nu} < 40\,000\,\mathrm{cm^{-1}}$).

For certain applications, synchrotron radiation is generated in a *synchrotron storage ring*, which consists of an electron beam travelling in a circular path with a circumference of up to several hundred metres. As electrons travelling in a circle are constantly accelerated by the forces that constrain them to their path, they generate radiation (Fig. 40.2). Synchrotron radiation spans a wide range of frequencies, including the infrared and X-rays. Except in the microwave region, synchrotron radiation is much more intense than can be obtained by most conventional sources.

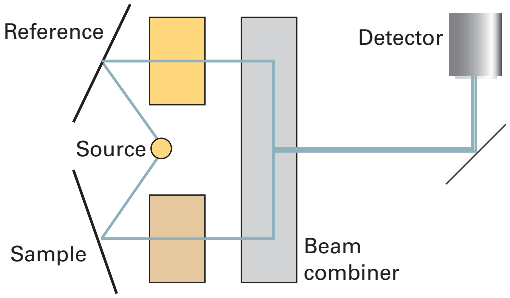

Figure 40.1 The layout of a typical absorption spectrometer, in which the exciting beams of radiation pass alternately through a sample and a reference cell, and the detector is synchronized with them so that the relative absorption can be determined.

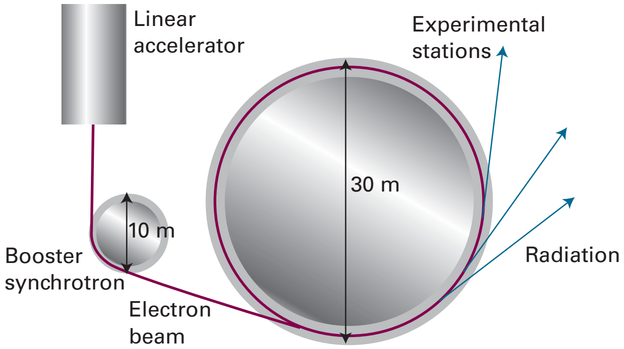

Figure 40.2 A synchrotron storage ring. The electrons injected into the ring from the linear accelerator and booster synchrotron are accelerated to high speed in the main ring. An electron in a curved path is subject to constant acceleration, and an accelerated charge radiates electromagnetic energy.

(b) Spectral analysis

A common device for the analysis of the wavelengths (or wavenumbers) in a beam of radiation is a *diffraction grating*, which consists of a glass or ceramic plate into which fine grooves have been cut and covered with a reflective aluminium coating. For work in the visible region of the spectrum, the grooves are cut about 1000 nm apart (a spacing comparable to the wavelength of visible light). The grating causes interference between waves reflected from its surface, and constructive interference occurs at specific angles that depend on the frequency of the radiation being used. Thus, each wavelength of light is directed into a specific direction (Fig. 40.3). In a *monochromator*, a narrow exit slit allows only a narrow range of wavelengths to reach the detector. Turning the grating around an axis perpendicular to the incident and diffracted beams allows different wavelengths to be analysed; in this way, the absorption spectrum is built up one narrow wavelength range at a time. In a *polychromator*, there is no slit and a broad range of wavelengths can be analysed simultaneously by *array detectors*, such as those discussed below.

Many spectrometers, particularly those operating in the infrared and near-infrared, now almost always use **Fourier transform techniques** of spectral detection and analysis. The heart of a Fourier transform spectrometer is a *Michelson interferometer*, a device for analysing the frequencies present in a composite signal. The total signal from a sample is like a chord played on a piano, and the Fourier transform of the signal is equivalent to the separation of the chord into its individual notes, its spectrum.

The Michelson interferometer works by splitting the beam from the sample into two and introducing a varying path

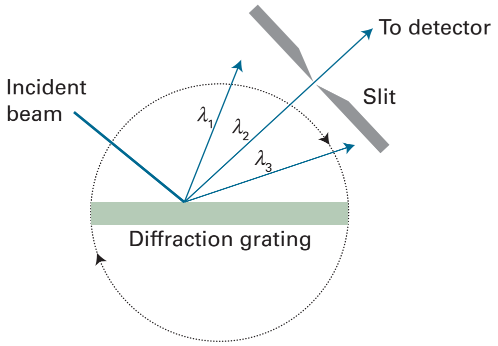

Figure 40.3 A polychromatic beam is dispersed by a diffraction grating into three component wavelengths λ_1, λ_2, and λ_3. In the configuration shown, only radiation with λ_2 passes through a narrow slit and reaches the detector. Rotating the diffraction grating (as shown by the arrows on the dotted circle) allows λ_1 or λ_3 to reach the detector.

difference, p, into one of them (Fig. 40.4). When the two components recombine, there is a phase difference between them, and they interfere either constructively or destructively depending on the difference in path lengths. The detected signal oscillates as the two components alternately come into and out of phase as the path difference is changed (Fig. 40.5). If the radiation has wavenumber $\tilde{\nu}$, the intensity of the detected signal due to radiation in the range of wavenumbers $\tilde{\nu}$ to $\tilde{\nu}+\mathrm{d}\tilde{\nu}$, which we denote $I(p,\tilde{\nu})\mathrm{d}\tilde{\nu}$, varies with p as

$$I(p,\tilde{\nu})\mathrm{d}\tilde{\nu}=I(\tilde{\nu})(1+\cos 2\pi\tilde{\nu}p)\mathrm{d}\tilde{\nu} \qquad (40.1)$$

Hence, the interferometer converts the presence of a particular wavenumber component in the signal into a variation in intensity of the radiation reaching the detector. An actual signal consists of radiation spanning a large number of wavenumbers, and the total intensity at the detector, which we write $I(p)$, is the sum of contributions from all the wavenumbers present in the signal:

$$I(p)=\int_0^\infty I(p,\tilde{\nu})\mathrm{d}\tilde{\nu}=\int_0^\infty I(\tilde{\nu})(1+\cos 2\pi\tilde{\nu}p)\mathrm{d}\tilde{\nu} \qquad (40.2)$$

The problem is to find $I(\tilde{\nu})$, the variation of intensity with wavenumber, which is the spectrum we require, from the record of values of $I(p)$. This step is a standard technique of mathematics, and is the 'Fourier transformation' step from which this form of spectroscopy takes its name (see *Mathematical background* 6). Specifically,

$$I(\tilde{\nu})=4\int_0^\infty \left\{I(p)-\tfrac{1}{2}I(0)\right\}\cos 2\pi\tilde{\nu}p\,\mathrm{d}p \qquad (40.3)$$

Fourier transformation

where $I(0)$ is given by eqn 40.2 with $p=0$. This integration is carried out numerically in a computer connected to the spectrometer, and the output, $I(\tilde{\nu})$, is the transmission spectrum of the sample.

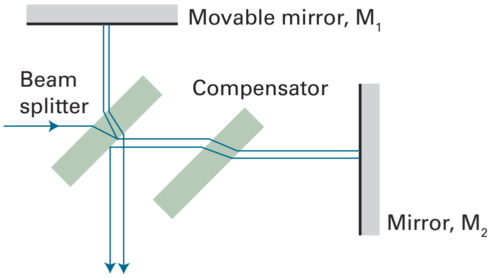

Figure 40.4 A Michelson interferometer. The beam-splitting element divides the incident beam into two beams with a path difference that depends on the location of the mirror M_1. The compensator ensures that both beams pass through the same thickness of material.

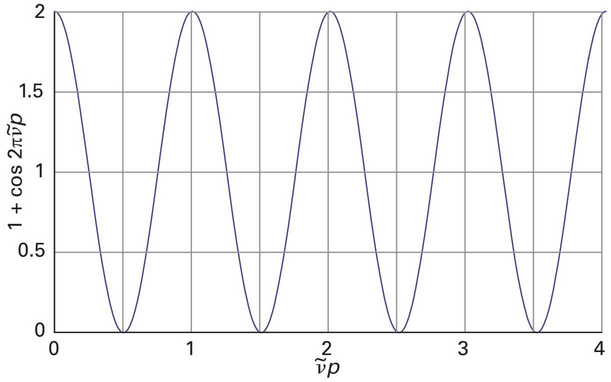

Figure 40.5 An interferogram produced as the path length p is changed in the interferometer shown in Fig. 40.4. Only a single frequency component is present in the signal, so the graph is a plot of the function $I(p)=I_0(1+\cos 2\tilde{\nu}p)$, where I_0 is the intensity of the radiation.

Example 40.1 Calculating a Fourier transform

Consider a signal consisting of three monochromatic beams with the following characteristics:

$\tilde{\nu}_i/\mathrm{cm}^{-1}$	150	250	450
I_i	1	3	6

where the intensities are relative to the intensity I_1 of the beam with $\tilde{\nu}_1=150\ \mathrm{cm}^{-1}$. Plot the interferogram associated with this signal. Then calculate and plot the Fourier transform of the interferogram.

Method For a signal consisting of only a few monochromatic beams, the integrals in eqns 40.2 and 40.3 can be replaced by a sum over the finite number of wavenumbers. It follows that the interferogram is

$$I(p)=\sum_i I(\tilde{\mathbf{n}}_i)(1+\cos 2\pi\tilde{\nu}_i p) \qquad (40.4)$$

where the path difference p does not vary continuously: it increases from zero by an increment determined by details of the design of the interferometer. It also follows that the Fourier transform is

$$I(\tilde{\nu})=4\sum_j\left\{I(p_j)-\tfrac{1}{2}I(0)\right\}\cos 2\pi\tilde{\nu}p_j \qquad (40.5)$$

Answer From the data and eqn 40.4, the interferogram is

$$\begin{aligned}I(p_j)&=(1+\cos 2\pi\tilde{\nu}_1 p)+3\times(1+\cos 2\pi\tilde{\nu}_2 p)+6\times(1+\cos 2\pi\tilde{\nu}_3 p)\\&=10+\cos 2\pi\tilde{\nu}_1 p+3\cos 2\pi\tilde{\nu}_2 p+6\cos 2\pi\tilde{\nu}_3 p\end{aligned}$$

where intensities are relative to I_1. This function is plotted in Fig. 40.6. The calculation of the Fourier transform from eqn 40.5, with $I(0)=20$, is made easier by the use of mathematical software. The result is shown in Fig. 40.7.

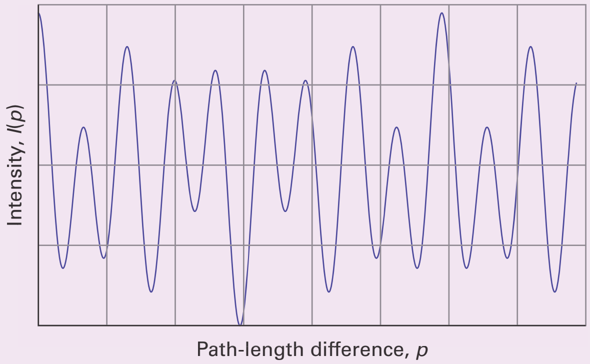

Figure 40.6 The interferogram calculated from data in Example 40.1.

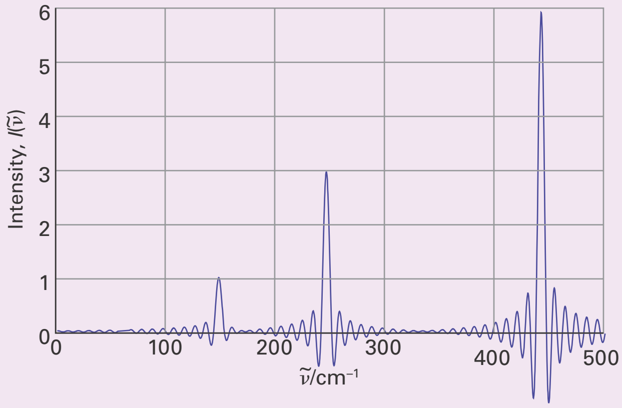

Figure 40.7 The Fourier transform of the interferogram shown in Fig. 40.6.

Self-test 40.1 Explore the effect of varying the wavenumbers of the three components of the radiation on the shape of the interferogram by changing the value of $\tilde{\nu}_3$ to 550 cm^{-1}.

Answer: See Fig. 40.8

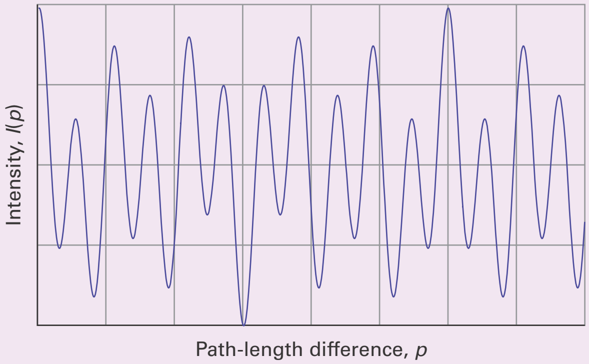

Figure 40.8 The interferogram calculated from data in Self-test 40.1.

(c) Detectors

A **detector** is a device that converts radiation into an electric current or potential difference for appropriate signal processing and display. Detectors may consist of a single radiation sensing element or of several small elements arranged in one or two-dimensional arrays.

A microwave detector is typically a *crystal diode* consisting of a tungsten tip in contact with a semiconductor. The most common detectors found in commercial infrared spectrometers are sensitive in the mid-infrared region. In a *photovoltaic device* the potential difference changes upon exposure to infrared radiation. In a *pyroelectric device* the capacitance is sensitive to temperature and hence the presence of infrared radiation.

A common detector for work in the ultraviolet and visible ranges is the *photomultiplier tube* (PMT), in which the photoelectric effect (Topic 4) is used to generate an electrical signal proportional to the intensity of light that strikes the detector. A common, but less sensitive, alternative to the PMT is the *photodiode*, a solid-state device that conducts electricity when struck by photons because light-induced electron transfer reactions in the detector material create mobile charge carriers (negatively charged electrons and positively charged 'holes').

The *charge-coupled device* (CCD) is a two-dimensional array of several million small photodiode detectors. A CCD detects simultaneously a wide range of wavelengths that emerge from a polychromator, thus eliminating the need to measure light intensity one narrow wavelength range at a time. CCD detectors are the imaging devices in digital cameras, but are also used widely in spectroscopy to measure absorption, emission, and Raman scattering.

40.2 Absorption spectroscopy

With a proper choice of spectrometer, absorption spectroscopy can probe electronic, vibrational, and rotational transitions in molecules. While radiation sources and detection schemes vary with specific applications of the technique, the quantitative interpretation of the intensity of transmitted radiation uses a simple, common approach.

(a) The Beer–Lambert law

It is found empirically that the transmitted intensity I varies with the length, L, of the sample and the molar concentration, [J], of the absorbing species J in accord with the **Beer–Lambert law**:

$$I = I_0 10^{-\varepsilon[\mathrm{J}]L} \qquad \text{Beer–Lambert law} \qquad (40.6)$$

where I_0 is the incident intensity. The quantity ε (epsilon) is called the **molar absorption coefficient** (formerly, and still widely, the 'extinction coefficient'). The molar absorption coefficient depends on the frequency of the incident radiation and is greatest where the absorption is most intense. Its dimensions are 1/(concentration × length), and it is normally convenient to express it in cubic decimetres per mole per centimetre ($\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$); in SI base units it is expressed in metres-squared per mole ($\mathrm{m^2\,mol^{-1}}$). The latter units imply that ε may be regarded as a (molar) cross-section for absorption and that the greater the cross-sectional area of the molecule for absorption, the greater is its ability to block the passage of the incident radiation at a given frequency. The Beer–Lambert law is an empirical result. However, it is simple to account for its form, as we show in the following *Justification*.

Justification 40.1 The Beer–Lambert law

We think of the sample as consisting of a stack of infinitesimal slices, like sliced bread (Fig. 40.9). The thickness of each layer is dx. The change in intensity, dI, that occurs when electromagnetic radiation passes through one particular slice is proportional to the thickness of the slice, the concentration of the absorber J, and the intensity of the incident radiation at that slice of the sample, so $\mathrm{d}I \propto [\mathrm{J}]I\mathrm{d}x$. Because d$I$ is negative (the intensity is reduced by absorption), we can write

$$\mathrm{d}I = -\kappa[\mathrm{J}]I\mathrm{d}x$$

where κ (kappa) is the proportionality coefficient. Division of both sides by I gives

$$\frac{\mathrm{d}I}{I} = -\kappa[\mathrm{J}]\mathrm{d}x$$

This expression applies to each successive slice.

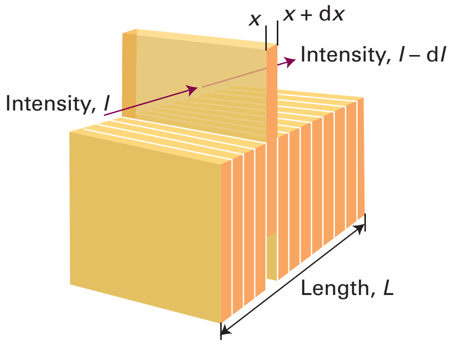

Figure 40.9 To establish the Beer–Lambert law, the sample is supposed to be sliced into a large number of planes. The reduction in intensity caused by one plane is proportional to the intensity incident on it (after passing through the preceding planes), the thickness of the plane, and the concentration of absorbing species.

To obtain the intensity that emerges from a sample of thickness L when the intensity incident on one face of the sample is I_0, we sum all the successive changes. Because a sum over infinitesimally small increments is an integral, we write

$$\overbrace{\int_{I_0}^{I}\frac{\mathrm{d}I}{I}}^{\ln(I/I_0)\,\text{(Integral A.2)}} = -\kappa\int_0^L[\mathrm{J}]\int\mathrm{d}x \overset{[\mathrm{J}]\,\text{uniform}}{\overbrace{=}} -\kappa[\mathrm{J}]\overbrace{\int_0^L\mathrm{d}x}^{L\,\text{(Integral A.1)}}$$

In the second step we have supposed that the concentration is uniform, so [J] is independent of x and can be taken outside the integral. Therefore

$$\ln\frac{I}{I_0} = -\kappa[\mathrm{J}]L$$

Because $\ln x = (\ln 10)\log x$, we can write $\varepsilon = \kappa/\ln 10$ and obtain

$$\log\frac{I}{I_0} = -\varepsilon[\mathrm{J}]L$$

which, on taking (common) antilogarithms, is the Beer–Lambert law (eqn 40.6).

The spectral characteristics of a sample are commonly reported as the **transmittance**, T, of the sample at a given frequency:

$$T = \frac{I}{I_0} \qquad \textit{Definition} \quad \text{Transmittance} \qquad (40.7)$$

and the **absorbance**, A, of the sample:

$$A = \log\frac{I_0}{I} \qquad \textit{Definition} \quad \text{Absorbance} \qquad (40.8)$$

The two quantities are related by $A = -\log T$ (note the common logarithm) and the Beer–Lambert law becomes

$$A = \varepsilon[J]L \qquad (40.9)$$

The product $\varepsilon[\mathrm{J}]L$ was known formerly as the *optical density* of the sample.

Example 40.2 Determining a molar absorption coefficient

Radiation of wavelength 280 nm was passed through 1.0 mm of a solution that contained an aqueous solution of the amino acid tryptophan at a concentration of 0.50 mmol dm⁻³. The light intensity is reduced to 54 per cent of its initial value (so $T = 0.54$). Calculate the absorbance and the molar absorption coefficient of tryptophan at 280 nm. What would be the transmittance through a cell of thickness 2.0 mm?

Method From $A = -\log T = \varepsilon[\mathrm{J}]L$, it follows that $\varepsilon = -\log T/[\mathrm{J}]L$. For the transmittance through the thicker cell, we use $T = 10^{-A}$ and the value of ε calculated here.

Answer The molar absorption coefficient is

$$\varepsilon = -\frac{\log 0.54}{(5.0\times10^{-4}\ \mathrm{mol\ dm^{-3}})\times(1.0\ \mathrm{mm})}$$
$$= 5.4\times10^{2}\ \mathrm{dm^{3}\ mol^{-1}\ mm^{-1}}$$

These units are convenient for the rest of the calculation (but the outcome could be reported as $5.4\times10^{3}\ \mathrm{dm^{3}\ mol^{-1}\ cm^{-1}}$ if desired). The absorbance is

$$A = -\log 0.54 = 0.27$$

The absorbance of a sample of length 2.0 mm is

$$A = (5.4\times10^{2}\ \mathrm{dm^{3}\ mol^{-1}\ mm^{-1}})\times(5.0\times10^{-4}\ \mathrm{mol\ dm^{-3}})$$
$$\times(2.0\ \mathrm{mm}) = 0.54$$

It follows that the transmittance is now

$$T = 10^{-A} = 10^{-0.54} = 0.29$$

That is, the emergent light is reduced to 29 per cent of its incident intensity.

Self-test 40.2 The transmittance of an aqueous solution that contained the amino acid tyrosine at a molar concentration of 0.10 mmol dm⁻³ was measured as 0.14 at 240 nm in a cell of length 5.0 mm. Calculate the molar absorption coefficient of tyrosine at that wavelength and the absorbance of the solution. What would be the transmittance through a cell of length 1.0 mm?

Answer: $1.7\times10^{3}\ \mathrm{dm^{3}\ mol^{-1}\ mm^{-1}}$, $A = 0.85$, $T = 0.68$

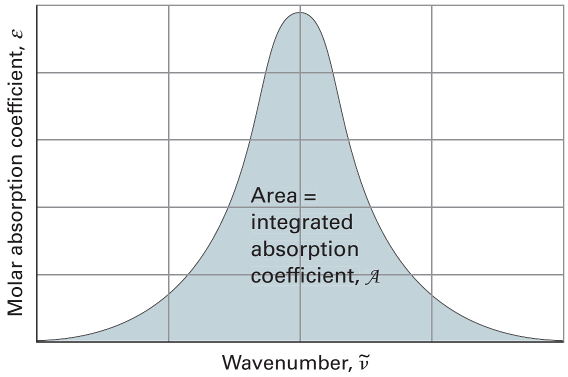

Figure 40.10 The integrated absorption coefficient of a transition is the area under a plot of the molar absorption coefficient against the wavenumber of the incident radiation.

The maximum value of the molar absorption coefficient, $\varepsilon_{\max}$, is an indication of the intensity of a transition. However, as absorption bands generally spread over a range of wavenumbers, quoting the absorption coefficient at a single wavenumber might not give a true indication of the intensity of a transition. The **integrated absorption coefficient**, $\mathcal{A}$, is the sum of the absorption coefficients over the entire band (Fig. 40.10), and corresponds to the area under the plot of the molar absorption coefficient against wavenumber:

$$\mathcal{A} = \int_{\text{band}} \varepsilon(\tilde{\nu})\mathrm{d}\tilde{\nu} \qquad \textit{Definition} \qquad \text{Integrated absorption coefficient} \qquad (40.10)$$

For lines of similar widths, the integrated absorption coefficients are proportional to the heights of the lines.

(b) Special techniques

The separation of rotational energy levels ($\Delta E \approx 1$ zJ, corresponding to about 1 kJ mol⁻¹) is smaller than that of vibrational energy levels ($\Delta E \approx 10$ zJ, corresponding to 10 kJ mol⁻¹), which itself is smaller than that of electronic energy levels ($\Delta E \approx 1$ aJ, corresponding to about 10^{3} kJ mol⁻¹) (*Foundations*, Topic 2). From $\nu = \Delta E/h$, it follows that rotational, vibrational, and electronic transitions result from the absorption or emission of microwave, infrared, and ultraviolet to far-infrared radiation, respectively (see Topics 42–45).

In Section 40.1, we discussed options for the construction of spectrometers that monitor different regions of the electromagnetic spectrum. Often it is necessary to modify the general design of Fig. 40.1 in order to detect weak signals. For instance, to detect rotational transitions with a microwave spectrometer it is often useful to modulate the transmitted intensity by varying the energy levels with an oscillating electric field. In this **Stark modulation**, an electric field of about $10^{5}\ \mathrm{V\ m^{-1}}$ and a frequency of between 10 and 100 kHz is applied to the sample.

Virtually every commercial spectrometer operating in the infrared region and designed for the study of vibrational transitions uses the Fourier transform techniques described in Section 40.1b. A major advantage of the Fourier transform procedure is that all the radiation emitted by the source is monitored continuously, in contrast to a spectrometer in which a monochromator discards most of the generated radiation. As a result, Fourier transform spectrometers have a higher sensitivity than conventional spectrometers.

The ability of lasers to produce pulses of very short duration (Topic 46) is particularly useful in chemistry when we want to monitor processes in time. In **time-resolved spectroscopy**, laser pulses are used to obtain the spectrum of reactants, intermediates, products, and even transition states of reactions. The arrangement shown in Fig. 40.11 is often used to study ultrafast chemical reactions that can be initiated by light and monitored by electronic spectroscopy (Topic 45). A strong and short laser pulse, the *pump*, promotes a molecule A to an excited electronic state A^* that can either emit a photon or react with another species B to yield a product C:

$$\begin{aligned} &A + h\nu \rightarrow A^* && \text{(absorption)} \\ &A^* \rightarrow A && \text{(emission)} \\ &A^* + B \rightarrow [AB] \rightarrow C && \text{(reaction)} \end{aligned}$$

Here [AB] denotes either an intermediate or an activated complex, a high-energy cluster of atoms. The rates of appearance and disappearance of the various species are determined by observing time-dependent changes in the electronic absorption spectrum of the sample during the course of the reaction. This monitoring is done by passing a weak pulse of white light, the *probe*, through the sample at different times after the laser pulse. Pulsed 'white' light can be generated directly from the laser pulse by the phenomenon of **continuum generation**, in which focusing a short laser pulse on a vessel containing water, carbon tetrachloride, or sapphire results in an outgoing beam with a wide distribution of frequencies. A time delay between the strong laser pulse and the 'white' light pulse can be introduced by allowing one of the beams to travel a longer distance before reaching the sample. For example, a difference in travel distance of $\Delta d = 3\,\text{mm}$ corresponds to a time delay $\Delta t = \Delta d/c \approx 10\,\text{ps}$ between two beams, where c is the speed of light. The relative distances travelled by the two beams in Fig 40.11 are controlled by directing the 'white' light beam to a motorized stage carrying a pair of mirrors.

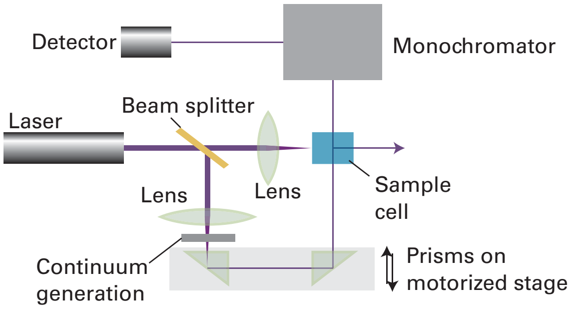

Figure 40.11 A configuration used for time-resolved absorption spectroscopy, in which the same pulsed laser is used to generate a monochromatic pump pulse and, after continuum generation in a suitable liquid, a 'white' light probe pulse. The time delay between the pump and probe pulses may be varied.

40.3 Emission spectroscopy

Rotational, vibrational, and electronic transitions can be studied by monitoring the spectrum of radiation emitted by a sample. Studies of spontaneous emission by electronic excited states of molecules are particularly useful in chemistry and biochemistry, and in Topic 46 we discuss the origins of two processes, namely fluorescence, which ceases within a few nanoseconds of the exciting radiation being extinguished, and phosphorescence, which may persist for long periods. We confine our short remarks at this stage to fluorescence because it is the basis of a number of sensitive techniques for chemical and biochemical analysis.

In a conventional fluorescence experiment, the source is tuned, often with the use of a monochromator, to a wavelength that causes electronic excitation of the molecule. Typically, the emitted radiation is detected perpendicular to the direction of the exciting beam of radiation, and analysed with a second monochromator (Fig. 40.12).

40.4 Raman spectroscopy

In a typical Raman spectroscopy experiment, a monochromatic incident laser beam is passed through the sample and the radiation scattered from the front face of the sample is monitored (Fig. 40.13). Lasers (Topic 46) are used as the source of

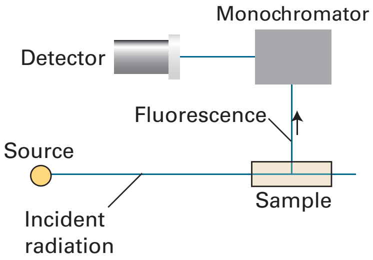

Figure 40.12 A simple emission spectrometer for monitoring fluorescence, where light emitted by the sample is detected at right angles to the direction of propagation of an incident beam of radiation.

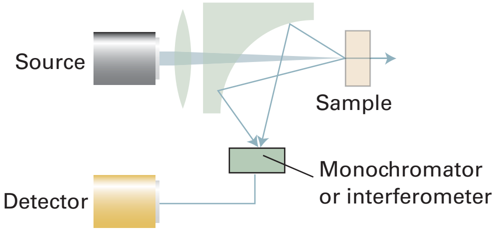

Figure 40.13 A common arrangement adopted in Raman spectroscopy. A laser beam first passes through a lens and then through a small hole in a mirror with a curved reflecting surface. The focused beam strikes the sample and scattered light is both deflected and focused by the mirror. The spectrum is analysed by a monochromator or an interferometer.

the incident radiation because an intense beam increases the intensity of scattered radiation. The monochromaticity of laser radiation makes possible the observation of frequencies of scattered light that differs only slightly from that of the incident radiation. Such high resolution is particularly useful for observing rotational transitions by Raman spectroscopy. The monochromaticity of laser radiation also allows observations to be made very close to absorption frequencies. Fourier transform instruments are common, as are spectrometers using polychromators connected to CCD detectors.

In Raman spectroscopy, about 1 in 10^7 of the incident photons collide with the molecules, give up some of their energy, and emerge with a lower energy. These scattered photons constitute the lower-frequency **Stokes radiation** from the sample (Fig. 40.14). Other incident photons may collect energy from the molecules (if they are already excited), and emerge as higher-frequency **anti-Stokes radiation**. The component of radiation scattered without change of frequency is called **Rayleigh radiation**.

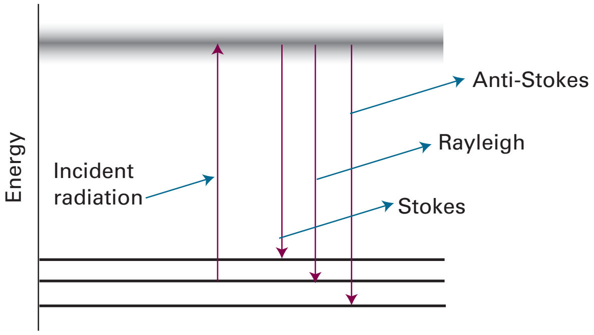

Figure 40.14 In Raman spectroscopy, an incident photon is scattered from a molecule with either an increase in frequency (if the radiation collects energy from the molecule) or with a lower frequency (if it loses energy to the molecule) to give the anti-Stokes and Stokes lines, respectively. Scattering without a change of frequency results in the Rayleigh lines. The process can be regarded as taking place by an excitation of the molecule to a wide range of states (represented by the shaded band), and the subsequent return of the molecule to a lower state; the net energy change is then carried away by the photon.

Raman spectroscopy can be used to study rotational and vibrational transitions in molecules. Most commercial instruments are designed for vibrational studies, which lead to applications in biochemistry, art restoration, and monitoring of industrial processes. Raman spectrometers can also be coupled to microscopes, resulting in spectra of very small regions of a sample.

Many special techniques are based on the arrangement just discussed. By far the most common variation uses incident radiation that nearly coincides with the frequency of an electronic transition of the sample (Fig. 40.15). The technique is then called **resonance Raman spectroscopy**. It is characterized by a much greater intensity in the scattered radiation. Furthermore, because it is often the case that only a few vibrational modes contribute to the more intense scattering, the spectrum is greatly simplified.

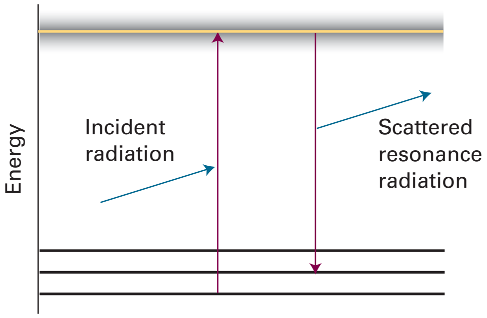

Figure 40.15 In the resonance Raman effect the incident radiation has a frequency close to an actual electronic excitation of the molecule. A photon is emitted when the excited state returns to a state close to the ground state.

Brief illustration 40.1 Resonance Raman spectroscopy

Figure 40.16 shows the resonance Raman spectra of a protein that binds β-carotene and chlorophyll and captures solar energy during plant photosynthesis. Only vibrational transitions from the few pigment molecules are observed because water (the solvent), amino acid residues, and the peptide group do not have electronic transitions at the laser wavelengths used in the experiment. Comparison of the spectra in Figs 40.16a and 40.16b also shows that, with proper choice of excitation wavelength, it is possible to examine individual classes of pigments bound to the same protein: excitation at 488 nm, where β-carotene absorbs strongly, shows vibrational bands from β-carotene only, whereas excitation at 407 nm, where chlorophyll a and β-carotene absorb, reveals features from both types of pigments.

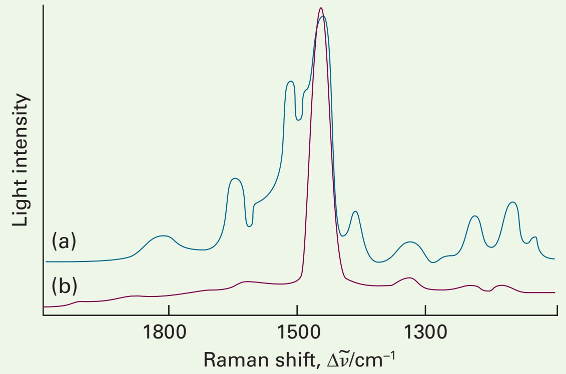

Figure 40.16 The resonance Raman spectra of a protein complex that is responsible for some of the initial electron transfer events in plant photosynthesis. (a) Laser excitation of the sample at 407 nm shows Raman bands due to both chlorophyll *a* and β-carotene bound to the protein because both pigments absorb light at this wavelength. (b) Laser excitation at 488 nm shows Raman bands from β-carotene only because chlorophyll *a* does not absorb light very strongly at this wavelength. (Adapted from D.F. Ghanotakis, et al., *Biochim. Biophys. Acta* **974**, 44 (1989).)

Self-test 40.3 What process might contribute to signals where resonance Raman scattering is expected?

Answer: Spontaneous emission (such as fluorescence), which also originates from excitation of an electronic transition

40.5 Spectral linewidths

A number of effects contribute to the widths of spectroscopic lines. Some contributions to linewidths can be modified by changing the conditions, and to achieve high resolutions we need to know how to minimize these contributions. Other contributions cannot be changed, and represent an inherent limitation on resolution.

(a) Doppler broadening

One important broadening process in gaseous samples is the **Doppler effect**, in which radiation is shifted in frequency when the source is moving towards or away from the observer. When a source emitting electromagnetic radiation of frequency ν moves with a speed s relative to an observer, the observer detects radiation of frequency

$$\nu_{\text{receding}} = \nu\left(\frac{1-s/c}{1+s/c}\right)^{1/2} \qquad \nu_{\text{approaching}} = \nu\left(\frac{1+s/c}{1-s/c}\right)^{1/2} \qquad (40.11\text{a})$$

Doppler shifts

where c is the speed of light. For nonrelativistic speeds ($s \ll c$), these expressions simplify to

$$\nu_{\text{receding}} \approx \frac{\nu}{1+s/c} \qquad \nu_{\text{approaching}} \approx \frac{\nu}{1-s/c} \qquad (40.11\text{b})$$

Atoms and molecules reach high speeds in all directions in a gas, and a stationary observer detects the corresponding Doppler-shifted range of frequencies. Some molecules approach the observer, some move away; some move quickly, others slowly. The detected spectral 'line' is the absorption or emission profile arising from all the resulting Doppler shifts. As shown in the following *Justification*, the profile reflects the distribution of velocities parallel to the line of sight, which is a bell-shaped Gaussian curve. The Doppler line shape is therefore also a Gaussian (Fig. 40.17), and we show in the *Justification* that, when the temperature is T and the mass of the atom or molecule is m, then the observed width of the line at half-height (in terms of frequency or wavelength) is

$$\delta\nu_{\text{obs}} = \frac{2\nu}{c}\left(\frac{2kT\ln 2}{m}\right)^{1/2} \qquad \delta\lambda_{\text{obs}} = \frac{2\lambda}{c}\left(\frac{2kT\ln 2}{m}\right)^{1/2} \qquad (40.12)$$

Doppler broadening

Doppler broadening increases with temperature because the molecules acquire a wider range of speeds. Therefore, to obtain spectra of maximum sharpness, it is best to work with cool samples.

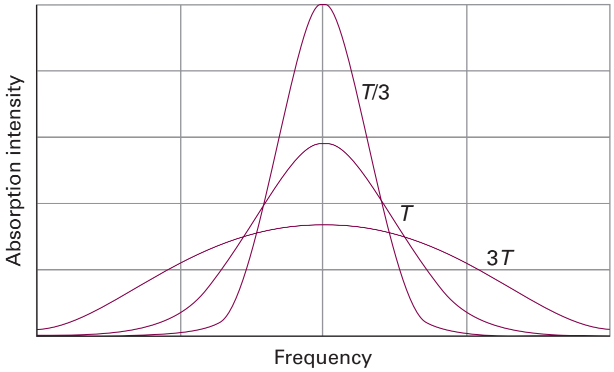

Figure 40.17 The Gaussian shape of a Doppler-broadened spectral line reflects the Maxwell distribution of speeds in the sample at the temperature of the experiment. Notice that the line broadens as the temperature is increased.

Brief illustration 40.2 Doppler broadening

For N_2 of mass $28.02m_u$ at $T=300\,\mathrm{K}$,

$$\frac{\delta\nu_{\mathrm{obs}}}{\nu}=\frac{2}{c}\left(\frac{2kT\ln 2}{m_{N_2}}\right)^{1/2}$$

$$=\frac{2}{2.998\times10^{8}\,\mathrm{m\,s^{-1}}}\times\left(\frac{2\times\left(1.380\times10^{-23}\,\overset{\mathrm{kg\,m^2\,s^{-2}}}{\overbrace{\mathrm{J}}}\,\mathrm{K^{-1}}\right)\times(300\,\mathrm{K})\times\ln 2}{4.653\times10^{-26}\,\mathrm{kg}}\right)^{1/2}$$

$$=2.34\times10^{-6}$$

For a transition wavenumber of $2331\,\mathrm{cm^{-1}}$ (from the Raman spectrum of N_2), corresponding to a frequency of 69.9 THz (1 THz $=10^{12}$ Hz), the linewidth is 164 MHz.

Self-test 40.4 What is the Doppler-broadened linewidth of the 821 nm transition in atomic hydrogen at 300 K?

Answer: 4.38 GHz

Justification 40.2 Doppler broadening

It follows from the Boltzmann distribution (Foundations Topic 2, and Topic 51) that the probability that an atom or molecule of mass m and speed s in a gas-phase sample at a temperature T has kinetic energy $E_k=\frac{1}{2}ms^2$ is proportional to $e^{-ms^2/2kT}$. The observed frequencies, ν_{obs}, emitted or absorbed by the molecule are related to its speed by eqn 40.11a. When $s\ll c$, the Doppler shift in the frequency is

$$\nu_{\mathrm{obs}}-\nu\approx\pm\nu s/c$$

More specifically, the intensity I of a transition at ν_{obs} is proportional to the probability of there being an atom that emits or absorbs at ν_{obs}, so it follows from the Boltzmann distribution and the expression for the Doppler shift, in the form $s=\pm(\nu_{\mathrm{obs}}-\nu)c/\nu$, that

$$I(\nu_{\mathrm{obs}})\propto e^{-mc^2(\nu_{\mathrm{obs}}-\nu)^2/2\nu^2kT} \qquad (40.13)$$

which has the form of a Gaussian function. Because the width at half-height of a Gaussian function $ae^{-(x-b)^2/2\sigma^2}$ (where a, b, and σ are constants) is $\delta x=2\sigma(2\ln 2)^{1/2}$, $\delta\nu_{\mathrm{obs}}$ can be inferred directly from the exponent of eqn 40.13 to give eqn 40.12.

(b) Lifetime broadening

It is found that spectroscopic lines from gas-phase samples are not infinitely sharp even when Doppler broadening has been largely eliminated by working at low temperatures. This residual broadening is due to quantum mechanical effects. Specifically, when the Schrödinger equation is solved for a system that is changing with time, it is found that it is impossible to specify the energy levels exactly (Topic 16). If on average a system survives in a state for a time τ, the lifetime of the state, then its energy levels are blurred to an extent of order $\delta E\approx\hbar/\tau$ (eqn 16.9). With the energy spread expressed as a wavenumber through $\delta E=hc\delta\tilde{\nu}$, and the values of the fundamental constants introduced, this relation becomes

$$\delta\tilde{\nu}\approx\frac{5.3\,\mathrm{cm^{-1}}}{\tau/\mathrm{ps}} \qquad \text{Lifetime broadening} \qquad (40.14)$$

and gives an indication of **lifetime broadening** of spectral lines. No excited state has an infinite lifetime; therefore, all states are subject to some lifetime broadening and the shorter the lifetimes of the states involved in a transition the broader the corresponding spectral lines.

Brief illustration 40.3 Lifetime broadening

A typical electronic excited-state lifetime is about $\tau=10^{-8}\,\mathrm{s}=1.0\times10^{4}\,\mathrm{ps}$, corresponding to a linewidth of

$$\delta\tilde{\nu}\approx\frac{5.3\,\mathrm{cm^{-1}}}{1.0\times10^{4}}=5.3\times10^{-4}\,\mathrm{cm^{-1}}$$

which corresponds to 16 MHz.

Self-test 40.5 A typical lifetime of a molecular rotation is about 10^3 s. What is the linewidth of the spectral line?

Answer: $5\times10^{-15}\,\mathrm{cm^{-1}}$ (of the order of 10^{-4} Hz)

Two processes are responsible for the finite lifetimes of excited states. The dominant one for low-frequency transitions is **collisional deactivation**, which arises from collisions between atoms or with the walls of the container. If the **collisional lifetime**, the mean time between collisions, is τ_{col}, the resulting collisional linewidth is $\delta E_{\mathrm{col}}\approx\hbar/\tau_{\mathrm{col}}$. Because $\tau_{\mathrm{col}}=1/z$, where z is the collision frequency, and the kinetic model of gases (Topic 78) implies that z is proportional to the pressure, we conclude that the collisional linewidth is proportional to the pressure. The collisional linewidth can therefore be minimized by working at low pressures.

The rate of spontaneous emission cannot be changed (Topic 16). Hence it is a natural limit to the lifetime of an excited state, and the resulting lifetime broadening is the **natural linewidth** of the transition, which cannot be changed by modifying the conditions. Because the rate of spontaneous emission increases as ν^3 (Topic 16), the lifetime of the excited state decreases as ν^3, and the natural linewidth increases with the transition frequency. Thus, rotational (microwave) transitions occur at much lower frequencies than vibrational (infrared) transitions and consequently have much longer lifetimes and hence much smaller natural linewidths: at low pressures rotational linewidths are due principally to Doppler broadening.

Checklist of concepts

☐ 1. In **emission spectroscopy**, a molecule undergoes a transition from a state of high energy to a state of lower energy, and emits the excess energy as a photon.

☐ 2. In **absorption spectroscopy**, the net absorption of incident radiation is monitored as its frequency is varied.

☐ 3. **A spectrometer** is an instrument that detects the characteristics of radiation scattered, emitted, or absorbed by atoms and molecules.

☐ 4. In **Raman spectroscopy,** changes in molecular state are explored by examining the frequencies present in the radiation scattered by molecules.

☐ 5. **Stokes radiation** is the result of Raman scattering of photons that give up some of their energy during (and emerge with lower frequency after) collisions with molecules.

☐ 6. **Anti-Stokes radiation** is the result of Raman scattering of photons that collect some energy during (and emerge with higher frequency after) collisions with molecules.

☐ 7. The component of radiation scattered without change of frequency is called **Rayleigh radiation.**

☐ 8. **Doppler broadening** of a spectral line is caused by the distribution of molecular and atomic speeds in a sample.

☐ 9. **Lifetime broadening** arises from the finite lifetime of an excited state and a consequent blurring of energy levels.

☐ 10. Collisions between atoms can affect excited-state lifetimes and spectral linewidths.

☐ 11. The **natural linewidth** of a transition is an intrinsic property that depends on the rate of spontaneous emission at the transition frequency.

Checklist of equations

Property	Equation	Comment	Equation number
Fourier transformation	$I(\tilde{\nu})=4\int_0^\infty\left\{I(p)-\frac{1}{2}I(0)\right\}\cos 2\pi\tilde{\nu}p\,\mathrm{d}p$	Spectral data collected with a Michelson interferometer	40.3
Beer–Lambert law	$I=I_0 10^{-\varepsilon[J]L}$	Uniform medium	40.6
Absorbance	$A=\log(I_0/I)=-\log T$	Definitions	40.8
Integrated absorption coefficient	$\mathcal{A}=\int_{\text{band}}\varepsilon(\tilde{\nu})\mathrm{d}\tilde{\nu}$	Definition	40.10
Doppler broadening	$\delta\nu_{\text{obs}}=2\nu/c(2kT\ln 2/m)^{1/2}$ $\delta\lambda_{\text{obs}}=2\lambda/c(2kT\ln 2/m)^{1/2}$		40.12
Lifetime broadening	$\delta\tilde{\nu}\approx(5.3\,\text{cm}^{-1})/(\tau/\text{ps})$		40.14

TOPIC 41

Molecular rotation

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(b) Symmetric rotors 392

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(d) Centrifugal distortion 394

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➤ Why do you need to know this material?

To understand the origin of microwave spectra and to derive useful information, such as bond lengths, about molecules from them, you need to understand the quantum mechanical treatment of rotation of polyatomic molecules.

➤ What is the key idea?

The energy levels of a molecule modelled as a rigid rotor may be expressed in terms of quantum numbers and parameters related to its moments of inertia.

➤ What do you need to know already?

You need to be familiar with the classical description of rotational motion (*Foundations*, Topic 2). You also need to be familiar with the particle on a ring (Topic 13) and particle on a sphere (Topic 14) as quantum mechanical models of rotational motion.

Topics 13 and 14 explore the rotational states of diatomic molecules by using the particle on a ring and particle on a sphere, respectively, as models. Here we use a more sophisticated model that can be applied to the rotation of polyatomic molecules.

41.1 Moments of inertia

The key molecular parameter we shall need for the description of molecular rotation is the **moment of inertia**, I, of the molecule (see Topic 13). The moment of inertia of a molecule is defined as the mass of each atom multiplied by the square of its distance from the rotational axis passing through the centre of mass of the molecule (Fig. 41.1):

$$I=\sum_i m_i x_i^2 \qquad \textit{Definition} \quad \text{Moment of inertia} \qquad (41.1)$$

where x_i is the perpendicular distance of the atom i from the axis of rotation. The moment of inertia depends on the masses of the atoms present and the molecular geometry, so we can

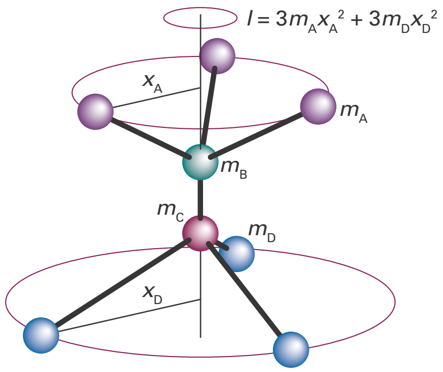


Figure 41.1 The definition of moment of inertia. In this molecule there are three identical atoms attached to the B atom and three different but mutually identical atoms attached to the C atom. In this example, the centre of mass lies on an axis passing through the B and C atoms, and the perpendicular distances are measured from this axis.

suspect (and see explicitly in Topic 42) that microwave spectroscopy will give information about bond lengths and bond angles.

In general, the rotational properties of any molecule can be expressed in terms of the moments of inertia about three perpendicular axes set in the molecule (Fig. 41.2). The convention is to label the moments of inertia I_a, I_b, and I_c, with the axes chosen so that $I_c \geq I_b \geq I_a$. For linear molecules, the moment of inertia around the internuclear axis is zero (because $x_i = 0$ for all the atoms). The explicit expressions for the moments of inertia of some symmetrical molecules are given in Table 41.1.

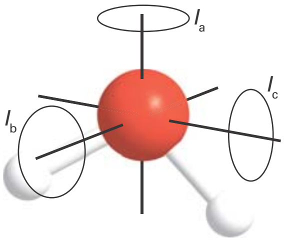
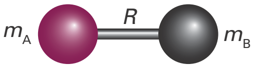
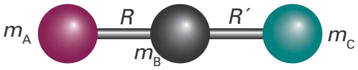
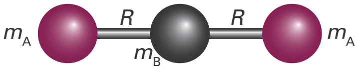
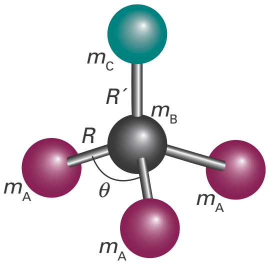
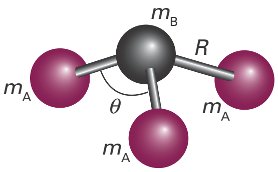
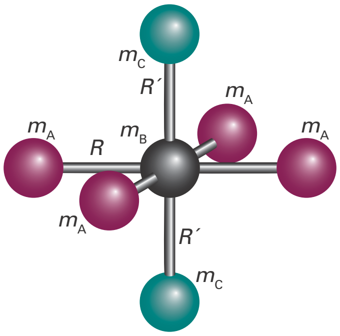
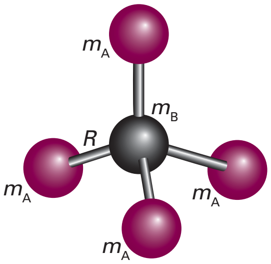


Figure 41.2 An asymmetric rotor has three different moments of inertia; all three rotation axes coincide at the centre of mass of the molecule.

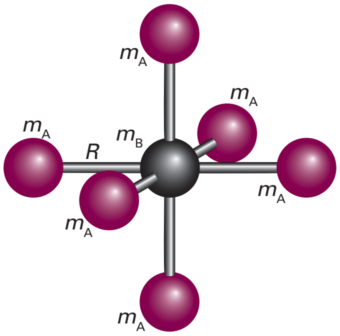
Table 41.1 Moments of inertia*

1. *Diatomic molecules*	
	$I = \mu R^2 \quad \mu = \frac{m_A m_B}{m}$
2. *Triatomic linear rotors*	
	$I = m_A R^2 + m_C R'^2 - \frac{(m_A R - m_C R')^2}{m}$
	$I = 2m_A R^2$
3. *Symmetric rotors*	
	$I_{\parallel} = 2m_A(1-\cos\theta)R^2$ $I_{\perp} = m_A(1-\cos\theta)R^2 + \frac{m_A}{m}(m_B + m_A)(1+2\cos\theta)R^2 + \frac{m_C}{m}\left\{(3m_A + m_B)R' + 6m_A R\left[\frac{1}{3}(1+2\cos\theta)\right]^{1/2}\right\}R'$
	$I_{\parallel} = 2m_A(1-\cos\theta)R^2$ $I_{\perp} = m_A(1-\cos\theta)R^2 + \frac{m_A m_B}{m}(1+2\cos\theta)R^2$
	$I_{\parallel} = 4m_A R^2$ $I_{\perp} = 2m_A R^2 + 2m_C R'^2$

4. *Spherical rotors*



$I=\frac{8}{3}m_AR^2$



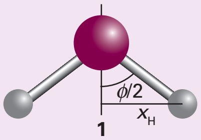
$I=4m_AR^2$

---

* In each case, m is the total mass of the molecule.

Example 41.1 Calculating the moment of inertia of a molecule

Calculate the moment of inertia of an H_2O molecule around the axis defined by the bisector of the HOH angle (**1**). The HOH bond angle is 104.5° and the bond length is 95.7 pm.



1

Method According to eqn 41.1, the moment of inertia is the sum of the masses multiplied by the squares of their distances from the axis of rotation. The latter can be expressed by using trigonometry and the bond angle and bond length.

> *A note on good practice* The mass to use in the calculation of the moment of inertia is the actual atomic mass, not the element's molar mass; don't forget to convert from relative masses to actual masses by using the atomic mass constant m_u.

Answer From eqn 41.1,

$$I=\sum_i m_ix_i^2=m_Hx_H^2+0+m_Hx_H^2=2m_Hx_H^2$$

If the bond half-angle of the molecule is denoted ϕ and the bond length is R, trigonometry gives $x_H=R\sin\frac{1}{2}\phi$. It follows that

$$I=2m_HR^2\sin^2\tfrac{1}{2}\phi$$

Substitution of the data gives

$$\begin{aligned}I&=2\times(1.67\times10^{-27}\,\text{kg})\times(9.57\times10^{-11}\,\text{m})^2\times\sin^2(\tfrac{1}{2}\times104.5°)\\&=1.91\times10^{-47}\text{ kg m}^2\end{aligned}$$

Note that the mass of the O atom makes no contribution to the moment of inertia for this mode of rotation as the O atom is immobile while the H atoms circulate around it.

Self-test 41.1 Calculate the moment of inertia of a $CH^{35}Cl_3$ molecule around a rotational axis that contains the C—H bond. The C—Cl bond length is 177 pm and the HCCl angle is 107°; $m(^{35}Cl)=34.97m_u$.

Answer: 4.99×10^{-45} kg m^2

We shall suppose initially that molecules are **rigid rotors**, bodies that do not distort under the stress of rotation. Rigid rotors can be classified into four types (Fig. 41.3):

Spherical rotors have three equal moments of inertia (examples: CH_4, SiH_4, and SF_6).

Symmetric rotors have two equal moments of inertia and a third that is nonzero (examples: NH_3, CH_3Cl, and CH_3CN).

Linear rotors have two equal moments of inertia and a third that is zero (examples: CO_2, HCl, OCS, and HC≡CH).

Asymmetric rotors have three different and nonzero moments of inertia (examples: H_2O, H_2CO, and CH_3OH).

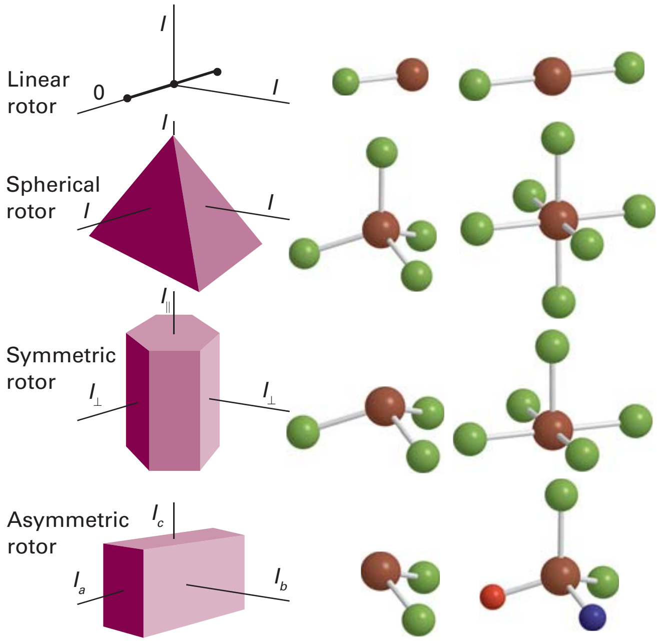


Figure 41.3 A schematic illustration of the classification of rigid rotors.

Spherical, symmetric, and asymmetric rotors are also called *spherical tops*, *symmetric tops*, and *asymmetric tops*.

41.2 The rotational energy levels

The rotational energy levels of a rigid rotor may be obtained by solving the appropriate Schrödinger equation. Fortunately, however, there is a much less onerous shortcut to the exact expressions that depends on noting the classical expression for the energy of a rotating body, expressing it in terms of the angular momentum, and then importing the quantum mechanical properties of angular momentum into the equations.

The classical expression for the energy of a body rotating about an axis a is

$$E_a = \tfrac{1}{2} I_a \omega_a^2 \tag{41.2}$$

where ω_a is the angular velocity (in rad s^{-1}) about that axis and I_a is the corresponding moment of inertia. A body free to rotate about three axes has an energy

$$E = \tfrac{1}{2} I_a \omega_a^2 + \tfrac{1}{2} I_b \omega_b^2 + \tfrac{1}{2} I_c \omega_c^2 \tag{41.3}$$

Because the classical angular momentum about the axis a is $J_a = I_a\omega_a$, with similar expressions for the other axes, it follows that

$$E = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c} \qquad \textit{Classical expression} \qquad \text{Rotational energy} \tag{41.4}$$

This is the key equation, which can be used in conjunction with the quantum mechanical properties of angular momentum developed in Topic 14.

(a) Spherical rotors

When all three moments of inertia are equal to some value I, as in CH_4 and SF_6, the classical expression for the energy is

$$E = \frac{J_a^2 + J_b^2 + J_c^2}{2I} = \frac{J^2}{2I} \tag{41.5}$$

where $J^2 = J_a^2 + J_b^2 + J_c^2$ is the square of the magnitude of the angular momentum. We can immediately find the quantum expression by making the replacement

$$J^2 \rightarrow J(J+1)\hbar^2 \qquad J = 0, 1, 2, \ldots$$

where J is the angular momentum quantum number. Therefore, the energy of a spherical rotor is confined to the values

$$E_J = J(J+1)\frac{\hbar^2}{2I} \qquad J = 0,1,2,\ldots \qquad \textit{Spherical rotor} \qquad \text{Rotational energy levels} \tag{41.6}$$

The resulting ladder of energy levels is illustrated in Fig. 41.4.

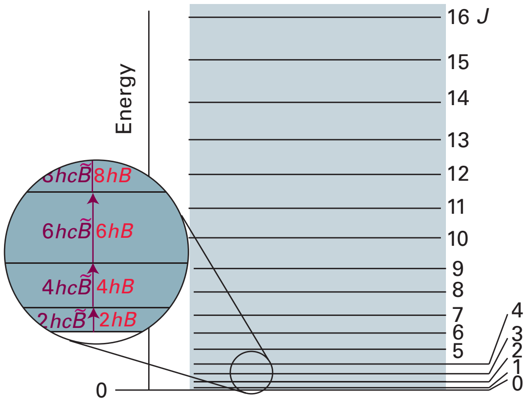


Figure 41.4 The rotational energy levels of a linear or spherical rotor. Note that the energy separation between neighbouring levels increases as J increases.

The energy is normally expressed in terms of the **rotational constant**, $\tilde{B}$, of the molecule, where

$$hc\tilde{B}=\frac{\hbar^2}{2I} \quad \text{so} \quad \tilde{B}=\frac{\hbar}{4\pi cI} \qquad \textit{Spherical rotor} \quad \text{Rotational constant} \qquad (41.7)$$

It follows that $\tilde{B}$ is a wavenumber. The expression for the energy is then

$$E_J=hc\tilde{B}J(J+1) \quad J=0,1,2,\ldots \qquad \textit{Spherical rotor} \quad \text{Energy levels} \qquad (41.8)$$

It is also common to define the rotational constant as a frequency and to denote it simply as B. Then $B=\hbar/4\pi I$ and the energy is $E=hBJ(J+1)$. The two quantities are related by $B=c\tilde{B}$.

The energy of a rotational state is normally reported as the **rotational term**, $\tilde{F}(J)$, a wavenumber, by division of both sides of eqn 41.8 by hc:

$$\tilde{F}(J)=\tilde{B}J(J+1) \qquad \textit{Spherical rotor} \quad \text{Rotational terms} \qquad (41.9)$$

To express the rotational term as a frequency, we use $F=c\tilde{F}$. The separation of adjacent levels is

$$\tilde{F}(J+1)-\tilde{F}(J)=\tilde{B}(J+1)(J+2)-\tilde{B}J(J+1)=2\tilde{B}(J+1) \qquad (41.10)$$

Because the rotational constant is inversely proportional to I, large molecules have closely spaced rotational energy levels.

Brief illustration 41.1 Spherical rotors

Consider $^{12}C^{35}Cl_4$: from Table 41.1, the C—Cl bond length ($R_{C-Cl}=177$ pm) and the mass of the ^{35}Cl nuclide ($m(^{35}Cl)=34.97m_u$), we find

$$I=\frac{8}{3}m(^{35}\mathrm{Cl})R_{\mathrm{C-Cl}}^2=\frac{8}{3}\times\overbrace{(5.807\times10^{-26}\ \mathrm{kg})}^{34.97\times(1.66054\times10^{-27}\ \mathrm{kg})}\times(1.77\times10^{-10}\ \mathrm{m})^2$$
$$=4.85\times10^{-45}\ \mathrm{kg\ m^2}$$

and, from eqn 41.7,

$$\tilde{B}=\frac{1.05457\times10^{-34}\ \overset{\mathrm{kg\,m^2s^{-2}}}{\widehat{\mathrm{J}}}\ \mathrm{s}}{4\pi\times(2.998\times10^8\ \mathrm{m\ s^{-1}})\times4.85\times10^{-45}\ \mathrm{kg\ m^2}}$$
$$=5.77\ \mathrm{m^{-1}}=0.0577\ \mathrm{cm^{-1}}$$

It follows from eqn 41.10 that the energy separation between the $J=0$ and $J=1$ levels is $\tilde{F}(1)-\tilde{F}(0)=2\tilde{B}=0.1154\ \mathrm{cm^{-1}}$.

Self-test 41.2 Calculate $\tilde{F}(2)-\tilde{F}(0)$ for $^{12}C^{35}Cl_4$.

Answer: $6\tilde{B}=0.3462\ \mathrm{cm^{-1}}$.

(b) Symmetric rotors

In symmetric rotors, all three moments of inertia are nonzero but two are the same and different from the third (as in CH_3Cl, NH_3, and C_6H_6); the unique axis of the molecule is its **principal axis** (or *figure axis*). We shall write the unique moment of inertia (that about the principal axis) as $I_{\parallel}$ and the other two as $I_{\perp}$. If $I_{\parallel}>I_{\perp}$, the rotor is classified as **oblate** (like a pancake, and C_6H_6); if $I_{\parallel}<I_{\perp}$ it is classified as **prolate** (like a cigar, and CH_3Cl). The classical expression for the energy, eqn 41.4, becomes

$$E=\frac{J_b^2+J_c^2}{2I_{\perp}}+\frac{J_a^2}{2I_{\parallel}} \qquad (41.11)$$

Again, this expression can be written in terms of $J^2=J_a^2+J_b^2+J_c^2$:

$$E=\frac{J^2-J_a^2}{2I_{\perp}}+\frac{J_a^2}{2I_{\parallel}}=\frac{J^2}{2I_{\perp}}+\left(\frac{1}{2I_{\parallel}}-\frac{1}{2I_{\perp}}\right)J_a^2 \qquad (41.12)$$

Now we generate the quantum expression by replacing J^2 by $J(J+1)\hbar^2$. We also know from the quantum theory of angular momentum (Topic 14) that the component of angular momentum about any axis is restricted to the values $K\hbar$, with $K=0, \pm1, \ldots, \pm J$. (K is the quantum number used to signify a component on the principal axis; M_J is reserved for a component on an externally defined axis.) Therefore, we also replace J_a^2 by $K^2\hbar^2$. It follows that the rotational terms are

$$\tilde{F}(J,K)=\tilde{B}J(J+1)+(\tilde{A}-\tilde{B})K^2 \quad J=0,1,2,\ldots \quad K=0,\pm1,\ldots,\pm J \qquad \textit{Symmetric rotor} \quad \text{Rotational terms} \qquad (41.13)$$

with

$$\tilde{A}=\frac{\hbar}{4\pi cI_{\parallel}} \qquad \tilde{B}=\frac{\hbar}{4\pi cI_{\perp}} \qquad (41.14)$$

Equation 41.13 matches what we should expect for the dependence of the energy levels on the two distinct moments of inertia of the molecule:

Physical interpretation

- When $K=0$, there is no component of angular momentum about the principal axis, and the energy levels depend only on $I_{\perp}$ (Fig. 41.5).
- When $K=\pm J$, almost all the angular momentum arises from rotation around the principal axis, and the energy levels are determined largely by $I_{\parallel}$.
- The sign of K does not affect the energy because opposite values of K correspond to opposite senses of rotation, and the energy does not depend on the sense of rotation.

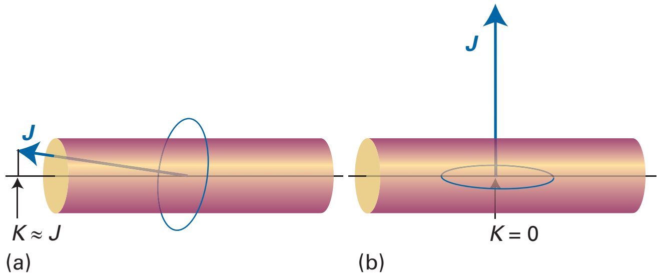


Figure 41.5 The significance of the quantum number K. (a) When $|K|$ is close to its maximum value, J, most of the molecular rotation is around the figure axis. (b) When $K=0$ the molecule has no angular momentum about its principal axis: it is undergoing end-over-end rotation.

Example 41.2 Calculating the rotational energy levels of a symmetric rotor

A $^{14}NH_3$ molecule is a symmetric rotor with bond length 101.2 pm and HNH bond angle 106.7°. Calculate its rotational terms.

> *A note on good practice* To calculate moments of inertia precisely, it is necessary to specify the nuclide.

Method Begin by calculating the rotational constants $\tilde{A}$ and $\tilde{B}$ by using the expressions for moments of inertia given in Table 41.1 and eqn 41.14. Then use eqn 41.13 to find the rotational terms.

Answer Substitution of $m_A = 1.0078m_u$, $m_B = 14.0031m_u$, $R=101.2$ pm, and $\theta=106.7°$ into the second of the symmetric rotor expressions in Table 41.1 gives $I_{\parallel}=4.4128\times10^{-47}$ kg m^2 and $I_{\perp}=2.8059\times10^{-47}$ kg m^2. Hence, by the same kind of calculations as in *Brief illustration* 41.1, $\tilde{A}=6.344$ cm^{-1} and $\tilde{B}=9.977$ cm^{-1}. It follows from eqn 41.13 that

$$\tilde{F}(J,K)/\text{cm}^{-1}=9.977\times J(J+1)-3.933K^2$$

Multiplication by c converts $\tilde{F}(J,K)$ to a frequency, denoted $F(J,K)$:

$$F(J,K)/\text{GHz}=299.1\times J(J+1)-108.9K^2$$

For $J=1$, the energy needed for the molecule to rotate mainly about its figure axis ($K=\pm J$) is equivalent to 16.32 cm^{-1} (489.3 GHz), but end-over-end rotation ($K=0$) corresponds to 19.95 cm^{-1} (598.1 GHz).

Self-test 41.3 A $CH_3{}^{35}Cl$ molecule has a C–Cl bond length of 178 pm, a C–H bond length of 111 pm, and an HCH angle of 110.5°. Calculate its rotational energy terms.

Answer: $\tilde{F}(J,K)/\text{cm}^{-1}=0.444J(J+1)+4.58K^2$;
also $F(J,K)/\text{GHz}=13.3J(J+1)+137K^2$

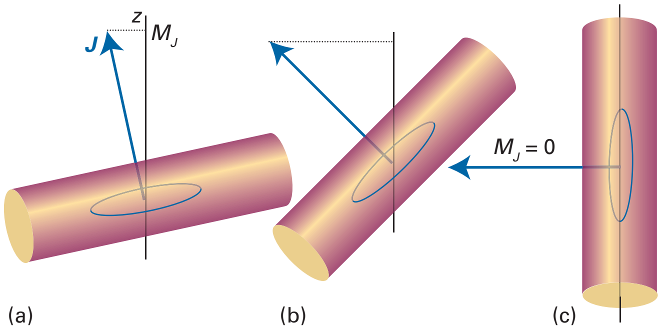


Figure 41.6 The significance of the quantum number M_J. (a) When M_J is close to its maximum value, J, most of the molecular rotation is around the laboratory z-axis. (b) An intermediate value of M_J. (c) When $M_J=0$ the molecule has no angular momentum about the z-axis. All three diagrams correspond to a state with $K=0$; there are corresponding diagrams for different values of K, in which the angular momentum makes a different angle to the molecule's principal axis.

The energy of a symmetric rotor depends on J and K, and each level except those with $K=0$ is doubly degenerate: the states with K and $-K$ have the same energy. However, we must not forget that the angular momentum of the molecule has a component on an external, laboratory-fixed axis. This component is quantized, and its permitted values are $M_J\hbar$, with $M_J=0$, $\pm1, \ldots, \pm J$, giving $2J+1$ values in all (Fig. 41.6). The quantum number M_J does not appear in the expression for the energy, but it is necessary for a complete specification of the state of the rotor. Consequently, all $2J+1$ orientations of the rotating molecule have the same energy. It follows that a symmetric rotor level is $2(2J+1)$-fold degenerate for $K\neq0$ and $(2J+1)$-fold degenerate for $K=0$. A linear rotor has K fixed at 0, but the angular momentum may still have $2J+1$ components on the laboratory axis, so its degeneracy is $2J+1$.

A spherical rotor can be regarded as a version of a symmetric rotor in which $\tilde{A}=\tilde{B}$. The quantum number K may still take any one of $2J+1$ values, but the energy is independent of which value it takes. Therefore, as well as having a $(2J+1)$-fold degeneracy arising from its orientation in space, the rotor also has a $(2J+1)$-fold degeneracy arising from its orientation with respect to an arbitrary axis in the molecule. The overall degeneracy of a symmetric rotor with quantum number J is therefore $(2J+1)^2$. This degeneracy increases very rapidly: when $J=10$, for instance, there are 441 states of the same energy.

(c) Linear rotors

For a linear rotor (such as CO_2, HCl, and C_2H_2), in which the nuclei are regarded as mass points, the rotation occurs only about an axis perpendicular to the line of atoms and there is zero angular momentum around the line. Therefore, the component of angular momentum around the figure axis of a linear rotor is identically zero, and $K \equiv 0$ in eqn 41.13. The rotational terms of a linear molecule are therefore

$$\tilde{F}(J) = \tilde{B}J(J+1) \qquad J = 0,1,2,\ldots \qquad \textit{Linear rotor} \quad \text{Rotational terms} \qquad (41.15)$$

This expression is the same as eqn 41.9 but we have arrived at it in a significantly different way: here $K \equiv 0$ but for a spherical rotor $\tilde{A} = \tilde{B}$. Note that it is important to set K identically equal to 0 in eqn 41.13 so that the second term vanishes identically; there is then no need to worry about the consequences of $\tilde{A} \propto 1/I_{||}$ approaching infinity as $I_{||}$ approaches 0.

Brief illustration 41.2 Linear rotors

Equation 41.10 for the energy separation of adjacent levels of a spherical rotor also applies to linear rotors. For $^1H^{35}Cl$, $\tilde{F}(3) - \tilde{F}(2) = 63.56\ \text{cm}^{-1}$, and it follows that $6\tilde{B} = 63.56\ \text{cm}^{-1}$ and $\tilde{B} = 10.59\ \text{cm}^{-1}$.

Self-test 41.4 For $^1H^{81}Br$, $\tilde{F}(1) - \tilde{F}(0) = 16.93\ \text{cm}^{-1}$. Determine the value of $\tilde{B}$.

Answer: $8.465\ \text{cm}^{-1}$

(d) Centrifugal distortion

We have treated molecules as rigid rotors. However, the atoms of rotating molecules are subject to centrifugal forces that tend to distort the molecular geometry and change the moments of inertia (Fig. 41.7). The effect of centrifugal distortion on a diatomic molecule is to stretch the bond and hence to increase the moment of inertia. As a result, centrifugal distortion reduces the rotational constant and consequently the energy levels are slightly closer than the rigid-rotor expressions predict. The effect is usually taken into account largely empirically by subtracting a term from the energy and writing

$$\tilde{F}(J) = \tilde{B}J(J+1) - \tilde{D}_J J^2(J+1)^2 \qquad \text{Rotational terms affected by centrifugal distortion} \qquad (41.16)$$

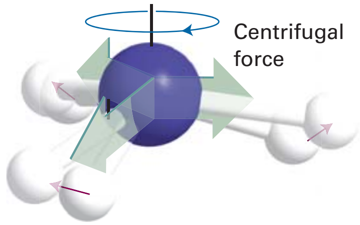


Figure 41.7 The effect of rotation on a molecule. The centrifugal force arising from rotation distorts the molecule, opening out bond angles and stretching bonds slightly. The effect is to increase the moment of inertia of the molecule and hence to decrease its rotational constant.

The parameter $\tilde{D}_J$ is the **centrifugal distortion constant**. It is large when the bond is easily stretched. The centrifugal distortion constant of a diatomic molecule is related to the vibrational wavenumber of the bond, $\tilde{\nu}$ (which, as we see in Topic 43, is a measure of its stiffness), through the approximate relation (see Problem F9.2)

$$\tilde{D}_J = \frac{4\tilde{B}^3}{\tilde{\nu}^2} \qquad \text{Centrifugal distortion constant} \qquad (41.17)$$

Hence the observation of the convergence of the rotational levels as J increases can be interpreted in terms of the rigidity of the bond.

Brief illustration 41.3 The effect of centrifugal distortion

For $^{12}C^{16}O$, $\tilde{B} = 1.931\ \text{cm}^{-1}$ and $\tilde{\nu} = 2170\ \text{cm}^{-1}$. It follows that

$$\tilde{D}_J = \frac{4 \times (1.931\ \text{cm}^{-1})^3}{(2170\ \text{cm}^{-1})^2} = 6.116 \times 10^{-6}\ \text{cm}^{-1}$$

and that, because $\tilde{D}_J \ll \tilde{B}$, centrifugal distortion has a very small effect on the energy levels.

Self-test 41.5 Does centrifugal distortion increase or decrease the separation between adjacent energy levels?

Answer: decreases

Checklist of concepts

☐ 1. A **rigid rotor** is a body that does not distort under the stress of rotation.

☐ 2. Rigid rotors are classified as **spherical, symmetric, linear**, or **asymmetric** by noting the number of equal principal moments of inertia.

☐ 3. **Symmetric rotors** are classified as prolate or oblate.

☐ 4. A linear rotor rotates only about an axis perpendicular to the line of atoms.

☐ 5. The degeneracies of spherical, symmetric ($K \neq 0$), and linear rotors are $(2J+1)^2$, $2(2J+1)$, and $2J+1$, respectively.

☐ 6. **Centrifugal distortion** arises from forces that change the geometry of a molecule.

Checklist of equations

Property	Equation	Comment	Equation number
Moment of inertia	$I=\sum_i m_i x_i^2$	x_i is perpendicular distance of atom i from the axis of rotation	41.1
Rotational terms of a spherical or linear rotor	$\tilde{F}(J)=\tilde{B}J(J+1)$	$J=0, 1, 2, \ldots,$ $\tilde{B}=\hbar/4\pi cI$	41.9, 41.15
Rotational terms of a symmetric rotor	$\tilde{F}(J,K)=\tilde{B}J(J+1)+(\tilde{A}-\tilde{B})K^2$	$J=0, 1, 2, \ldots$ $K=0, \pm 1, \ldots, \pm J$ $\tilde{A}=\hbar/4\pi cI_{\parallel}$ $\tilde{B}=\hbar/4\pi cI_{\perp}$	41.13, 41.14
Rotational terms of a spherical or linear rotor affected by centrifugal distortion	$\tilde{F}(J)=\tilde{B}J(J+1)-\tilde{D}_J J^2(J+1)^2$	$\tilde{D}_J=4\tilde{B}^3/\tilde{\nu}^2$	41.16, 41.17

TOPIC 42

Rotational spectroscopy

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➤ Why do you need to know this material?

You need to be familiar with rotational spectroscopy because it is well suited for the study of molecules and reactions in gas-phase systems, such as the atmosphere, and also provides highly precise data on bond lengths and bond angles of molecules.

➤ What is the key idea?

The frequencies of rotational transitions depend on the moments of inertia of molecules and their intensities depend on the magnitudes of permanent molecular dipole moments.

➤ What do you need to know already?

You should be familiar with the general principles of molecular spectroscopy (Topic 40) and the quantum mechanical treatment of molecular rotation (Topic 41). The derivation of selection rules draws on the concepts of time-dependent perturbation theory introduced in Topic 16.

Pure rotational spectra, in which only the rotational state of a molecule changes, can be observed only in the gas phase (Topic 40). In spite of this limitation, rotational spectroscopy can provide a wealth of information about molecules, including precise bond lengths and dipole moments. Our approach to the description of rotational spectra consists of developing the gross and specific selection rules for rotational transitions, examining the appearance of rotational spectra, and exploring the information that can be obtained from the spectra. This material also informs the discussion of the fine details observed in infrared spectra (Topics 43–44) and electronic spectra (Topics 45–46).

42.1 Microwave spectroscopy

Typical values of the rotational constant $\tilde{B}$ for small molecules are in the region of 0.1–10 cm^{-1} (Topic 41); for example, 0.356 cm^{-1} for NF_3 and 10.59 cm^{-1} for HCl. It follows that rotational transitions can be studied with **microwave spectroscopy**, a technique that monitors the absorption or emission of radiation in the microwave region of the spectrum.

(a) Selection rules

We show in the following *Justification* that the gross selection rule for the observation of a pure rotational transition in a microwave spectrum is that a molecule must have a permanent electric dipole moment. That is, *to absorb or emit microwave radiation and undergo a pure rotational transition, a molecule must be polar*. The classical basis of this rule is that a polar molecule appears to possess a fluctuating dipole when rotating but a nonpolar molecule does not (Fig. 42.1). The permanent dipole can be regarded as a handle with which the molecule stirs the electromagnetic field into oscillation (and vice versa for absorption).

The specific rotational selection rules are found by evaluating the transition dipole moment (Topic 16) between rotational states. We show in the following *Justification* that, for a linear molecule, the transition moment vanishes unless the following conditions are fulfilled:

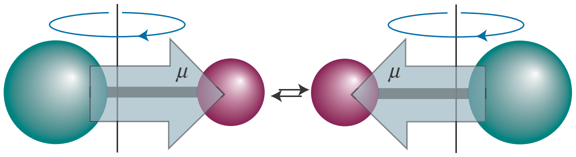

Figure 42.1 To a stationary observer, a rotating polar molecule looks like an oscillating dipole which can stir the electromagnetic field into oscillation (and vice versa for absorption). This picture is the classical origin of the gross selection rule for rotational transitions.

Brief illustration 42.1 Gross selection rules for microwave spectroscopy

Homonuclear diatomic molecules and nonpolar polyatomic molecules such as CO_2, $CH_2{=}CH_2$, and C_6H_6, are rotationally inactive. On the other hand, OCS and H_2O are polar, and have microwave spectra. Spherical rotors cannot have electric dipole moments unless they become distorted by rotation, so they are rotationally inactive except in special cases. An example of a spherical rotor that does become sufficiently distorted for it to acquire a dipole moment is SiH_4, which has a dipole moment with a magnitude of about 8.3 μD by virtue of its rotation when $J \approx 10$ (for comparison, HCl has a permanent dipole moment of magnitude 1.1 D; molecular dipole moments and their units are discussed in Topic 34).

Self-test 42.1 Which of the molecules H_2, NO, N_2O, CH_4 can have a pure rotational spectrum?

Answer: NO, N_2O

$$\Delta J = \pm 1 \qquad \Delta M_J = 0, \pm 1 \tag{42.1}$$

Linear rotors Rotational selection rules

The transition $\Delta J = +1$ corresponds to absorption and the transition $\Delta J = -1$ corresponds to emission. The allowed change in J in each case arises from the conservation of angular momentum when a photon, a spin-1 particle, is emitted or absorbed (Fig. 42.2).

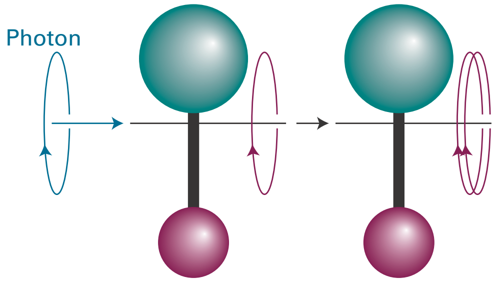

Figure 42.2 When a photon is absorbed by a molecule, the angular momentum of the combined system is conserved. If the molecule is rotating in the same sense as the spin of the incoming photon, then J increases by 1.

Justification 42.1 Selection rules: microwave spectra

The starting point for any discussion about selection rules is the total wavefunction for a molecule, which can be written as $\psi_{\text{total}} = \psi_{\text{cm}}\psi$, where ψ_{cm} describes the motion of the centre of mass and ψ describes the internal motion of the molecule. The Born–Oppenheimer approximation (Topic 22) allows us to write ψ as the product of an electronic part, ψ_ε, a vibrational part, ψ_v, and a rotational part, which for a diatomic molecule can be represented by the spherical harmonics $Y_{J,M_J}(\theta,\phi)$ (Topic 14). The transition dipole moment for the spectroscopic transition i → f can now be written as

$$\boldsymbol{\mu}_{\text{fi}} = \int \psi^\star_{\varepsilon_\text{f}}\psi^\star_{v_\text{f}} Y^\star_{J_\text{f},M_{J,\text{f}}}\hat{\boldsymbol{\mu}}\psi_{\varepsilon_\text{i}}\psi_{v_\text{i}}Y_{J_\text{i},M_{J,\text{i}}}\,\mathrm{d}\tau \tag{42.2}$$

and our task is to explore conditions under which this integral vanishes or has a nonzero value.

For a pure rotational transition the initial and final electronic and vibrational states are the same, and we identify $\boldsymbol{\mu}_\text{i} = \int \psi^\star_{\varepsilon_\text{i}}\psi^\star_{v_\text{i}}\hat{\boldsymbol{\mu}}\psi_{\varepsilon_\text{i}}\psi_{v_\text{i}}\,\mathrm{d}\tau$ with the *permanent* electric dipole moment of the molecule in the state i. Equation 42.2 then becomes

$$\boldsymbol{\mu}_{\text{fi}} = \int Y^\star_{J_\text{f},M_{J,\text{f}}}\boldsymbol{\mu}_\text{i} Y_{J_\text{i},M_{J,\text{i}}}\,\mathrm{d}\tau \tag{42.3}$$

The remaining integration is over the angles representing the orientation of the molecule. We see immediately that the molecule must have a permanent dipole moment in order to have a microwave spectrum. This is the gross selection rule for microwave spectroscopy.

From this point on, the deduction of the specific selection rules proceeds as in the case of atomic transitions (Topic 21), and makes use of the fact that the three components of the dipole moment (Fig. 42.3) are

$$\mu_{\text{i},x} = \mu_0 \sin\theta\cos\phi \qquad \mu_{\text{i},y} = \mu_0\sin\theta\sin\phi \qquad \mu_{\text{i},z} = \mu_0\cos\theta \tag{42.4}$$

and can be expressed in terms of the spherical harmonics $Y_{j,m}$, with $j=1$ and $m=0,\pm1$ (see *Justification* 21.1). Then, the condition for the non-vanishing of the integral over the product of three spherical harmonics, which is described in Topic 33, implies that

$$\int Y^\star_{J_\text{f},M_{J,\text{f}}} Y_{j,m} Y_{J_\text{i},M_{J,\text{i}}}\,\mathrm{d}\tau_{\text{angles}} = 0 \tag{42.5}$$

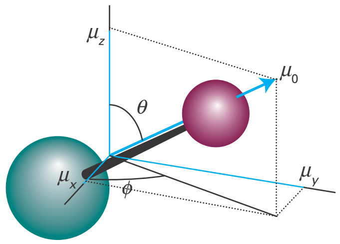

Figure 42.3 The axis system used in the calculation of the transition dipole moment.

unless $M_{J,\mathrm{f}} = M_{J,\mathrm{i}} + m$ and lines of length J_f, J_i, and j can form a triangle (such as 1, 2, and 3, or 1, 1, and 1, but not 1, 2, and 4). By exactly the same argument as presented in *Justification* 21.1 (and developed in Problem 21.7), we conclude that $J_\mathrm{f} - J_\mathrm{i} = \pm 1$ and $M_{J,\mathrm{f}} - M_{J,\mathrm{i}} = 0$ or ± 1.

In Topic 16 it is shown that the intensity of a spectral line is proportional to the square modulus of the transition dipole moment. When the transition moment is evaluated for all possible relative orientations of the molecule to the line of flight of the photon, it is found that the total $J+1 \leftrightarrow J$ transition intensity is proportional to

$$\left|\mu_{J+1,J}\right|^2 = \left(\frac{J+1}{2J+1}\right)\mu_0^2 \qquad (42.6)$$

where μ_0 is the magnitude of the permanent electric dipole moment of the molecule. The intensity is proportional to the square of the magnitude of the permanent electric dipole moment, so strongly polar molecules give rise to much more intense rotational lines than less polar molecules.

For symmetric rotors, an additional selection rule states that $\Delta K = 0$. To understand this rule, consider the symmetric rotor NH_3, where the electric dipole moment lies parallel to the figure axis. Such a molecule cannot be accelerated into different states of rotation around the figure axis by the absorption of radiation, so $\Delta K = 0$. Therefore, for symmetric rotors the selection rules are

$$\Delta J = \pm 1 \quad \Delta M_J = 0, \pm 1 \quad \Delta K = 0 \qquad (42.7)$$

Symmetric rotors

Rotational selection rules

The degeneracy associated with the quantum number M_J (the orientation of the rotation in space) is partly removed when an electric field is applied to a polar molecule (for example, HCl or NH_3), as illustrated in Fig. 42.4. The splitting of states by an electric field is called the Stark effect (Topic 40). The energy shift depends on the permanent electric dipole moment, μ_0, so the observation of the Stark effect can be used to measure the magnitudes (not the sign) of electric dipole moments with a rotational spectrum.

(b) The appearance of microwave spectra

When the selection rules are applied to the expressions for the energy levels of a rigid spherical or linear rotor, it follows that the wavenumbers of the allowed $J+1 \leftarrow J$ absorptions are

$$\begin{aligned}\tilde{\nu}(J+1 \leftarrow J) &= \tilde{F}(J+1) - \tilde{F}(J) \\ &= 2\tilde{B}(J+1) \\ J &= 0, 1, 2, \ldots\end{aligned} \qquad (42.8a)$$

Linear and spherical rotors

Wavenumbers of rotational transitions

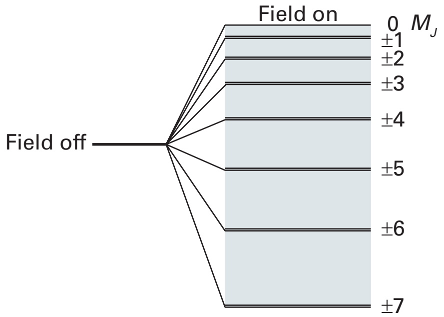

Figure 42.4 The effect of an electric field on the energy levels of a polar linear rotor. All levels are doubly degenerate except that with $M_J = 0$.

where the terms $\tilde{F}(J) = \tilde{B}J(J+1)$ are introduced in Topic 41. When centrifugal distortion (Topic 41) is taken into account, the corresponding expression obtained from eqn 41.16, $\tilde{F}(J) = \tilde{B}J(J+1) - \tilde{D}_J J^2(J+1)^2$, is

$$\tilde{\nu}(J+1 \leftarrow J) = 2\tilde{B}(J+1) - 4\tilde{D}_J(J+1)^3 \qquad (42.8b)$$

However, because the second term is typically very small compared with the first (see *Brief illustration* 41.3), the appearance of the spectrum closely resembles that predicted from eqn 42.8a.

Example 42.1 Predicting the appearance of a rotational spectrum

Predict the form of the rotational spectrum of $^{14}NH_3$.

Method The energy levels are calculated in Example 41.2. The $^{14}NH_3$ molecule is a polar symmetric rotor, so the rotational terms are given by eqn 41.13 ($\tilde{F}(J,K) = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2$). Because $\Delta J = \pm 1$ and $\Delta K = 0$, the expression for the wavenumbers of the rotational transitions is identical to eqn 42.8a and depends only on $\tilde{B}$. For absorption, $\Delta J = +1$.

Answer Because $\tilde{B} = 9.977\ \mathrm{cm}^{-1}$, we can draw up the following table for the $J+1 \leftarrow J$ transitions:

J	0	1	2	3	…
$\tilde{\nu}/\mathrm{cm}^{-1}$	19.95	39.91	59.86	79.82	…
ν/GHz	598.1	1197	1795	2393	…

The line spacing is $19.95\ \mathrm{cm}^{-1}$ (598.1 GHz).

Self-test 42.2 Repeat the problem for $CH_3{}^{35}Cl$ (see Self-test 41.3 for details).

Answer: Lines of separation $0.888\ \mathrm{cm}^{-1}$ (26.6 GHz)

The form of the spectrum predicted by eqn 42.8 is shown in Fig. 42.5. The most significant feature is that it consists of a series of lines with wavenumbers $2\tilde{B}$, $4\tilde{B}$, $6\tilde{B}$, …, and of separation $2\tilde{B}$. The measurement of the line spacing gives $\tilde{B}$, and hence the moment of inertia perpendicular to the principal axis of the molecule. Because the masses of the atoms are known, it is a simple matter to deduce the bond length of a diatomic molecule. However, in the case of a polyatomic molecule such as OCS or NH_3, the analysis gives only a single quantity, $I_\perp$, and it is not possible to infer both bond lengths (in OCS) or the bond length and bond angle (in NH_3). This difficulty can be overcome by using isotopically substituted molecules, such as ABC and A′BC; then, by assuming that $R(\text{A–B})=R(\text{A}'\text{–B})$, both A–B and B–C bond lengths can be extracted from the two moments of inertia. A famous example of this procedure is the study of OCS; the actual calculation is worked through in Problem 42.5. The assumption that bond lengths are unchanged by isotopic substitution is only an approximation, but it is a good approximation in most cases. Nuclear spin (Topic 47), which differs from one isotope to another, also affects the appearance of high-resolution rotational spectra because spin is a source of angular momentum and can couple with the rotation of the molecule itself and hence affect the rotational energy levels.

The intensities of spectral lines increase with increasing J and pass through a maximum before tailing off as J becomes large. The most important reason for the maximum in intensity is the existence of a maximum in the population of rotational levels. The Boltzmann distribution (*Foundations*, Topic 2, and Topic 51) implies that the population of each state decays exponentially with increasing J, but the degeneracy of the levels increases, and these two opposite trends result in the population of the energy levels (as distinct from the individual states) passing through a maximum. Specifically, the population of a rotational energy level J is given by the Boltzmann expression

$$N_J \propto N g_J \mathrm{e}^{-E_J/kT}$$

where N is the total number of molecules and g_J is the degeneracy of the level J. The value of J corresponding to a maximum of this expression is found by treating J as a continuous variable, differentiating with respect to J, and then setting the result equal to zero. The result is (see Problem 42.9)

$$J_{\max} \approx \left(\frac{kT}{2hc\tilde{B}}\right)^{1/2} - \tfrac{1}{2} \qquad (42.9)$$

Linear rotors

Rotational state with largest population

For a typical molecule (for example, OCS, with $\tilde{B}=0.2\,\mathrm{cm}^{-1}$) at room temperature, $kT\approx 1000hc\tilde{B}$, so $J_{\max}\approx 30$. However, it must be recalled that the intensity of each transition also depends on the value of J (eqn 42.6) and on the population difference between the two states involved in the transition. Hence the value of J corresponding to the most intense line is not quite the same as the value of J for the most highly populated level.

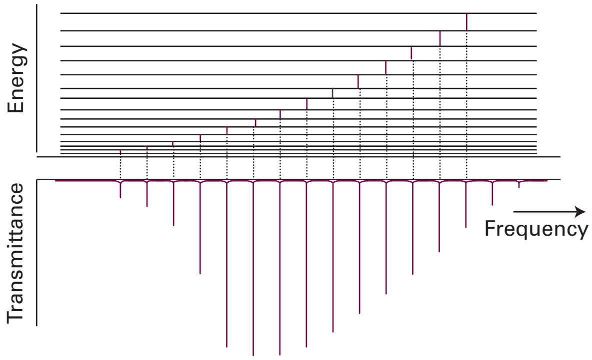

Figure 42.5 The rotational energy levels of a linear rotor, the transitions allowed by the selection rule $\Delta J=+1$, and a typical pure rotational absorption spectrum (displayed here in terms of the radiation transmitted through the sample). The intensities reflect the populations of the initial level in each case and the strengths of the transition dipole moments.

42.2 Rotational Raman spectroscopy

Raman scattering (Topic 40) can also lead to rotational transitions. The gross selection rule for rotational Raman transitions is *that the polarizability of the molecule must be anisotropic*. The distortion of a molecule in an electric field is determined by its polarizability, α (Topic 34). More precisely, if the strength of the field is $\mathcal{E}$, then the molecule acquires an induced dipole moment of magnitude

$$\mu = \alpha\mathcal{E} \qquad (42.10)$$

in addition to any permanent dipole moment it may have. An atom is isotropically polarizable. That is, the same distortion is induced whatever the direction of the applied field. The polarizability of a spherical rotor is also isotropic. However, non-spherical rotors have polarizabilities that do depend on the direction of the field relative to the molecule, so these molecules are anisotropically polarizable (Fig. 42.6). The electron distribution in H_2, for example, is more distorted when the field is applied parallel to the bond than when it is applied perpendicular to it, and we write $\alpha_{\parallel} > \alpha_{\perp}$.

All linear molecules and diatomics (whether homonuclear or heteronuclear) have anisotropic polarizabilities, and so are rotationally Raman active. This activity is one reason for the

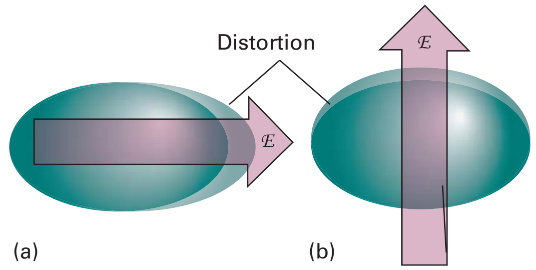

Figure 42.6 An electric field applied to a molecule results in its distortion, and the distorted molecule acquires a contribution to its dipole moment (even if it is nonpolar initially). The polarizability may be different when the field is applied (a) parallel or (b) perpendicular to the molecular axis (or, in general, in different directions relative to the molecule); if that is so, then the molecule has an anisotropic polarizability.

importance of rotational Raman spectroscopy, for the technique can be used to study many of the molecules that are inaccessible to microwave spectroscopy. Spherical rotors such as CH_4 and SF_6, however, are rotationally Raman inactive as well as microwave inactive. This inactivity does not mean that such molecules are never found in rotationally excited states. Molecular collisions do not have to obey such restrictive selection rules, and hence collisions between molecules can result in the population of any rotational state.

The specific rotational Raman selection rules are

$$\begin{array}{ll} \text{Linear rotors:} & \Delta J = 0, \pm 2 \\ \text{Symmetric rotors:} & \Delta J = 0, \pm 1, \pm 2 \\ & \Delta K = 0 \end{array} \qquad (42.11)$$

Rotational Raman selection rules

The $\Delta J = 0$ transitions do not lead to a shift in frequency of the scattered photon in pure rotational Raman spectroscopy, and contribute to the unshifted radiation (the Rayleigh radiation, Topic 40). The specific selection rule for linear rotors is explored in the following *Justification*.

Justification 42.2 Selection rules: rotational Raman spectra

We can understand the origin of the gross and specific selection rules for rotational Raman spectroscopy by using a diatomic molecule as an example. The incident electric field of magnitude $\mathcal{E}$ of a wave of electromagnetic radiation of frequency ω_i induces a molecular dipole moment with a magnitude given by

$$\mu_{\text{ind}} = \alpha\mathcal{E}(\text{t}) = \alpha\mathcal{E}\cos\omega_i t \qquad (42.12)$$

If the molecule is rotating at a circular frequency ω_R, to an external observer its polarizability is also time-dependent (if it is anisotropic), and we can write

$$\alpha = \alpha_0 + \Delta\alpha\cos 2\omega_R t \qquad (42.13)$$

where $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$ and α ranges from $\alpha_0 + \Delta\alpha$ to $\alpha_0 - \Delta\alpha$ as the molecule rotates. The 2 appears because the polarizability returns to its initial value twice each revolution (Fig. 42.7). Substituting this expression into the expression for the magnitude of the induced dipole moment gives

$$\begin{aligned}\mu_{\text{ind}} &= (\alpha_0 + \Delta\alpha\cos 2\omega_R t)\times(\mathcal{E}\cos\omega_i t)\\ &= \alpha_0\mathcal{E}\cos\omega_i t + \mathcal{E}\Delta\alpha\cos 2\omega_R t\cos\omega_i t\\ &= \alpha_0\mathcal{E}\cos\omega_i t + \tfrac{1}{2}\mathcal{E}\Delta\alpha\{\cos(\omega_i + 2\omega_R)t\\ &\quad + \cos(\omega_i - 2\omega_R)t\}\end{aligned} \qquad (42.14)$$

where we have used the trigonometric identity $\cos x\cos y = \frac{1}{2}\{\cos(x+y) + \cos(x-y)\}$. This calculation shows that the induced dipole has a component oscillating at the incident frequency (which generates Rayleigh radiation), and that it also has two components at $\omega_i \pm 2\omega_R$, which give rise to the shifted Raman lines. These lines appear only if $\Delta\alpha \neq 0$; hence the polarizability must be anisotropic for there to be Raman lines. This is the gross selection rule for rotational Raman spectroscopy.

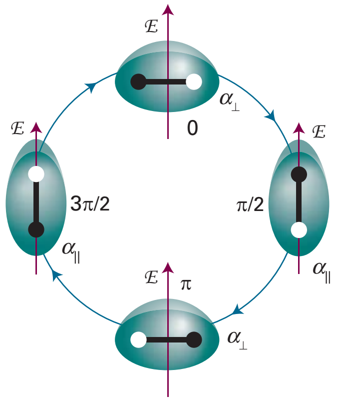

Figure 42.7 The distortion induced in a molecule by an applied electric field returns the polarizability to its initial value after a rotation of only 180° (that is, twice a revolution). This doubling of the apparent rate of rotation is the origin of the $\Delta J = \pm 2$ selection rule in rotational Raman spectroscopy.

We also see that the distortion induced in the molecule by the incident electric field returns to its initial value after a rotation of 180° (that is, twice a revolution). This is the classical origin of the specific selection rule $\Delta J = \pm 2$.[1]

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[1] See our *Molecular quantum mechanics*, Oxford University Press (2011) for the quantum mechanical calculation of the selection rules for rotational Raman spectroscopy.

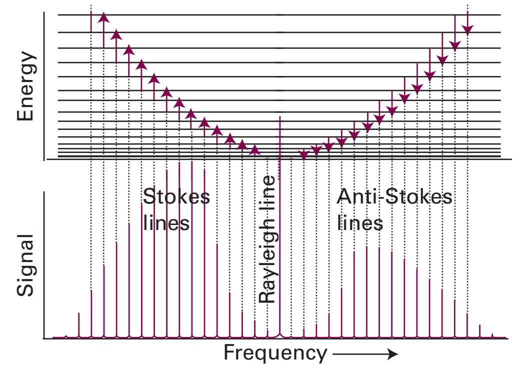

Figure 42.8 The rotational energy levels of a linear rotor and the transitions allowed by the $\Delta J = \pm 2$ Raman selection rules. The form of a typical rotational Raman spectrum is also shown. The Rayleigh line is much stronger than depicted in the figure; it is shown as a weaker line to improve visualization of the Raman lines.

We can predict the form of the Raman spectrum of a linear rotor by applying the selection rule $\Delta J = \pm 2$ to the rotational energy levels (Fig. 42.8). When the molecule makes a transition with $\Delta J = +2$, the scattered radiation leaves the molecule in a higher rotational state, so the wavenumber of the incident radiation, initially $\tilde{\nu}_i$, is decreased. These transitions account for the Stokes lines (the lines at lower than the incident frequency, Topic 40) in the spectrum:

$$\begin{aligned}\tilde{\nu}(J+2 \leftarrow J) &= \tilde{\nu}_i - \{\tilde{F}(J+2) - \tilde{F}(J)\} \\ &= \tilde{\nu}_i - 2\tilde{B}(2J+3)\end{aligned} \qquad \text{Linear rotors} \quad \text{Wavenumbers of Stokes lines} \qquad (42.15a)$$

The Stokes lines appear at lower frequencies than the incident radiation and at displacements $6\tilde{B}$, $10\tilde{B}$, $14\tilde{B}$, … from $\tilde{\nu}_i$ for $J = 0, 1, 2, \ldots$. When the molecule makes a transition with $\Delta J = -2$, the scattered photon emerges with increased energy. These transitions account for the anti-Stokes lines (the lines at higher than the incident frequency, Topic 40) of the spectrum:

$$\begin{aligned}&\tilde{\nu}(J-2 \leftarrow J) \\ &= \tilde{\nu}_i + \{\tilde{F}(J) - \tilde{F}(J-2)\} \\ &= \tilde{\nu}_i + 2\tilde{B}(2J-1)\end{aligned} \qquad \text{Linear rotors} \quad \text{Wavenumbers of anti-Stokes lines} \qquad (42.15b)$$

The anti-Stokes lines occur at displacements of $6\tilde{B}$, $10\tilde{B}$, $14\tilde{B}$, … (for $J = 2, 3, 4, \ldots$; $J = 2$ is the lowest state that can contribute under the selection rule $\Delta J = -2$) at higher frequencies than the incident radiation. The separation of adjacent lines in both the Stokes and the anti-Stokes regions is $4\tilde{B}$, so from its measurement $I_\perp$ can be determined and then used to find the bond lengths, exactly as in the case of microwave spectroscopy.

Example 42.2 Predicting the form of a Raman spectrum

Predict the form of the rotational Raman spectrum of $^{14}N_2$, for which $\tilde{B} = 1.99\,\text{cm}^{-1}$, when it is exposed to 336.732 nm laser radiation.

Method The molecule is rotationally Raman active because end-over-end rotation modulates its polarizability as viewed by a stationary observer. The Stokes and anti-Stokes lines are given by eqn 42.15.

Answer Because $\lambda_i = 336.732\,\text{nm}$ corresponds to $\tilde{\nu}_i = 29\,697.2\,\text{cm}^{-1}$, eqns 42.15a and 42.15b give the following line positions:

J	0	1	2	3
Stokes lines				
$\tilde{\nu}/\text{cm}^{-1}$	29 685.3	29 677.3	29 669.3	29 661.4
λ/nm	336.867	336.958	337.048	337.139
Anti-Stokes lines				
$\tilde{\nu}/\text{cm}^{-1}$			29 709.1	29 717.1
λ/nm			336.597	336.507

There will be a strong central line at 336.732 nm accompanied on either side by lines of increasing and then decreasing intensity (as a result of transition moment and population effects). The spread of the entire spectrum is very small, so the incident light must be highly monochromatic.

Self-test 42.3 Repeat the calculation for the rotational Raman spectrum of a molecule with $\tilde{B} = 9.977\,\text{cm}^{-1}$.

Answer: Stokes lines at 29 637.3, 29 597.4, 29 557.5, 29 517.6 cm^{-1}, anti-Stokes lines at 29 757.1, 29 797.0 cm^{-1}

42.3 Nuclear statistics and rotational states

If eqn 42.15 is used in conjunction with the rotational Raman spectrum of CO_2, the rotational constant is inconsistent with other measurements of C—O bond lengths. The results are consistent only if it is supposed that the molecule can exist in states with even values of J, so the Stokes lines are $2 \leftarrow 0$, $4 \leftarrow 2$, … and not $5 \leftarrow 3$, $3 \leftarrow 1$, ….

The explanation of the missing lines is the Pauli principle (Topic 19) and the fact that ^{16}O nuclei are spin-0 bosons (Topic 47): just as the Pauli principle excludes certain electronic states, so too does it exclude certain molecular rotational states. The form of the Pauli principle given in Topic 19 states that, when two identical bosons are exchanged, the overall wavefunction must remain unchanged in every respect, including sign. When

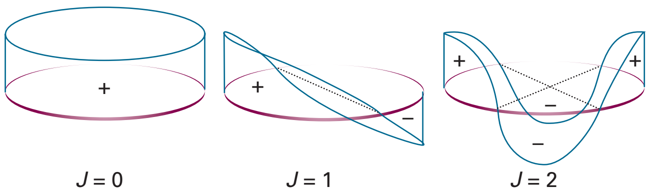

Figure 42.9 The symmetries of rotational wavefunctions (shown here, for simplicity as a two-dimensional rotor) under a rotation through 180°. Wavefunctions with *J* even do not change sign; those with *J* odd do change sign.

a CO_2 molecule rotates through 180°, two identical O nuclei are interchanged, so the overall wavefunction of the molecule must remain unchanged. However, inspection of the form of the rotational wavefunctions (which have the same form as the s, p, etc. orbitals of atoms) shows that they change sign by $(-1)^J$ under such a rotation (Fig. 42.9). Therefore, only even values of *J* are permissible for CO_2, and hence the Raman spectrum shows only alternate lines.

The selective occupation of rotational states that stems from the Pauli principle is termed **nuclear statistics**. Nuclear statistics must be taken into account whenever a rotation interchanges equivalent nuclei. However, the consequences are not always as simple as for CO_2 because there are complicating features when the nuclei have nonzero spin: there may be several different relative nuclear spin orientations consistent with even values of *J* and a different number of spin orientations consistent with odd values of *J*. For molecular hydrogen and fluorine, for instance, with their two identical spin-$\frac{1}{2}$ nuclei, we show in the following *Justification* that there are three times as many ways of achieving a state with odd *J* as with even *J*, and there is a corresponding 3:1 alternation in intensity in their rotational Raman spectra (Fig. 42.10). In general, for a homonuclear diatomic molecule with nuclei of spin *I*, the numbers of ways of achieving states of odd and even *J* are in the ratio

$$\frac{\text{Number of ways of achieving odd } J}{\text{Number of ways of achieving even } J} = \begin{cases} (I+1)/I & \text{for half-integral spin nuclei} \\ I/(I+1) & \text{for integral spin nuclei} \end{cases} \qquad (42.16)$$

Homonuclear diatomic molecules Nuclear statistics

For hydrogen, $I=\frac{1}{2}$, and the ratio is 3:1. For N_2, with $I=1$, the ratio is 1:2.

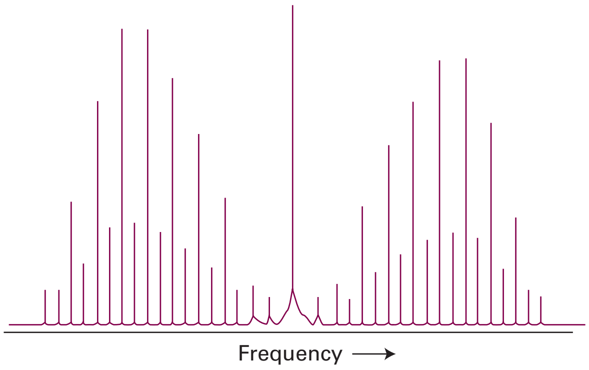

Figure 42.10 The rotational Raman spectrum of a diatomic molecule with two identical spin-$\frac{1}{2}$ nuclei shows an alternation in intensity as a result of nuclear statistics. The Rayleigh line is much stronger than depicted in the figure; it is shown as a weaker line to improve visualization of the Raman lines.

Justification 42.3 The effect of nuclear statistics on rotational spectra

Hydrogen nuclei are fermions, so the Pauli principle requires the overall wavefunction to change sign under particle interchange. However, the rotation of an H_2 molecule through 180° has a more complicated effect than merely relabelling the nuclei, because it also interchanges their spin states if the nuclear spins are paired ($\uparrow\downarrow$; $I_{\text{total}}=0$) but not if they are parallel ($\uparrow\uparrow$, $I_{\text{total}}=1$).

First, consider the case when the spins are parallel and their state is $\alpha(\text{A})\alpha(\text{B})$, $\alpha(\text{A})\beta(\text{B})+\alpha(\text{B})\beta(\text{A})$, or $\beta(\text{A})\beta(\text{B})$. The $\alpha(\text{A})\alpha(\text{B})$ and $\beta(\text{A})\beta(\text{B})$ combinations are unchanged when the molecule rotates through 180° so the rotational wavefunction must change sign to achieve an overall change of sign. Hence, only odd values of *J* are allowed. Although at first sight the spins must be interchanged in the combination $\alpha(\text{A})\beta(\text{B})+\alpha(\text{B})\beta(\text{A})$ so as to achieve a simple $\text{A}\leftrightarrow\text{B}$ interchange of labels (Fig. 42.11), $\beta(\text{A})\alpha(\text{B})+\beta(\text{B})\alpha(\text{A})$ is the same as $\alpha(\text{A})\beta(\text{B})+\alpha(\text{B})\beta(\text{A})$ apart from the order of terms, so only odd values of *J* are allowed for it too. In contrast, if the nuclear spins are paired, their wavefunction is $\alpha(\text{A})\beta(\text{B})-\alpha(\text{B})\beta(\text{A})$. This combination changes sign when α and β are exchanged (in order to achieve a simple $\text{A}\leftrightarrow\text{B}$ interchange overall). Therefore, for the overall wavefunction to change sign in this case requires the rotational wavefunction *not* to change sign. Hence, only even values of *J* are allowed if the nuclear spins are paired. In accord with the prediction of eqn 42.16, there are three ways of achieving odd *J* but only one way of achieving even *J*.

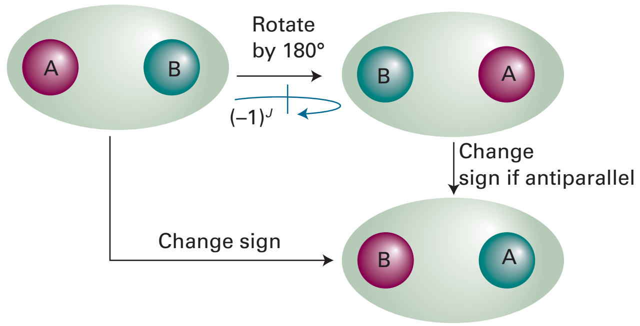

Figure 42.11 The interchange of two identical fermion nuclei results in the change in sign of the overall wavefunction. The relabelling can be thought of as occurring in two steps: the first is a rotation of the molecule; the second is the interchange of unlike spins (represented by the different colours of the nuclei). The wavefunction changes sign in the second step if the nuclei have antiparallel spins.

Brief illustration 42.2 *Ortho*- and *para*-hydrogen

Different relative nuclear spin orientations change into one another only very slowly, so an H_2 molecule with parallel nuclear spins remains distinct from one with paired nuclear spins for long periods. The form with parallel nuclear spins is called ***ortho*-hydrogen** and the form with paired nuclear spins is called ***para*-hydrogen**. Because *ortho*-hydrogen cannot exist in a state with $J=0$, it continues to rotate at very low temperatures and has an effective rotational zero-point energy (Fig. 42.12).

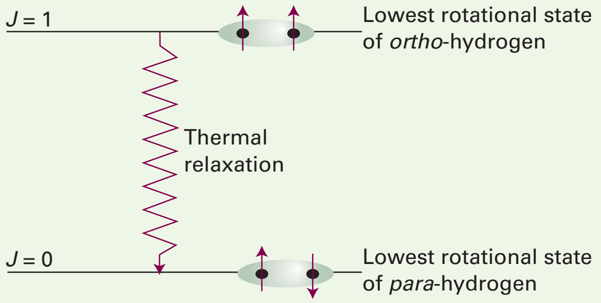

Figure 42.12 When hydrogen is cooled, the molecules with parallel nuclear spins accumulate in their lowest available rotational state, the one with $J=1$. They can enter the lowest rotational state ($J=0$) only if the spins change their relative orientation and become antiparallel. This is a slow process under normal circumstances, so energy is slowly released.

Self-test 42.4 Does BeF_2 exist in *ortho* and *para* forms? *Hints*: (a) Determine the geometry of BeF_2, then (b) decide whether fluorine nuclei are fermions or bosons.

Answer: Yes

Checklist of concepts

☐ 1. Pure rotational transitions can be studied with **microwave spectroscopy** and **rotational Raman spectroscopy.**

☐ 2. For a molecule to give a pure rotational spectrum, it must be polar.

☐ 3. The specific selection rules for microwave spectroscopy are $\Delta J=\pm1$; $\Delta M_J=0,\pm1$; $\Delta K=0$.

☐ 4. Bond lengths and dipole moments may be obtained from analysis of rotational spectra.

☐ 5. A molecule must be anisotropically polarizable for it to be rotationally Raman active.

☐ 6. The specific selection rules for rotational Raman spectroscopy are: (i) linear rotors, $\Delta J=0,\pm2$; (ii) symmetric rotors, $\Delta J=0,\pm1,\pm2$; $\Delta K=0$.

☐ 7. The appearance of rotational spectra is affected by **nuclear statistics**, the selective occupation of rotational states that stems from the Pauli principle.

Checklist of equations

Property	Equation	Comment	Equation number
Wavenumbers of rotational transitions	$\tilde{\nu}J+1\leftarrow J)=2\tilde{B}(J+1)$	$J=0, 1, 2, \ldots$; spherical and linear rotors (ignoring centrifugal distortion)	42.8a
Rotational state with largest population	$J_{\max}\approx(kT/2hc\tilde{B})^{1/2}-\frac{1}{2}$	Linear rotors	42.9

Property	Equation	Comment	Equation number
Wavenumbers of (i) Stokes and (ii) anti-Stokes lines in the rotational Raman spectrum of linear rotors	(i) $\tilde{\nu}(J+2\leftarrow J)=\tilde{\nu}_\mathrm{i}-2\tilde{B}(2J+3)$ (ii) $\tilde{\nu}(J-2\leftarrow J)=\tilde{\nu}_\mathrm{i}+2\tilde{B}(2J-1)$	$J=0, 1, 2, \ldots$ (ignoring centrifugal distortion)	42.15
Nuclear statistics	$\dfrac{\text{Number of ways of achieving odd } J}{\text{Number of ways of achieving even } J}=\begin{cases}(I+1)/I \text{ for half-integral spin nuclei}\\ I/(I+1) \text{ for integral spin nuclei}\end{cases}$	Homonuclear diatomic molecules	42.16

TOPIC 43

Vibrational spectroscopy: diatomic molecules

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➤ Why do you need to know this material?

The observation of the frequencies of vibrational transitions gives very valuable information about the identity of molecules and provides quantitative information about the flexibility of their bonds.

➤ What is the key idea?

The vibrational spectrum of a diatomic molecule can be interpreted by using the harmonic oscillator model, with suitable modifications to account for bond dissociation and the coupling of rotational and vibrational motion.

➤ What do you need to know already?

You need to be familiar with the harmonic oscillator (Topic 12) and rigid rotor (Topic 41) models of molecular motion, general principles of spectroscopy (Topic 40), and the interpretation of pure rotational spectra (Topic 42). The derivation of selection rules draws from the discussion of transitions in Topic 16.

Here we explore the vibrational energy levels of diatomic molecules and establish the selection rules for spectroscopic transitions between these levels. We also see how the simultaneous excitation of rotation modifies the appearance of a vibrational spectrum and is used to obtain information about the lengths of bonds as well as their stiffness. This material sets the stage for the discussion of vibrations of polyatomic molecules in Topic 44.

43.1 Vibrational motion of diatomic molecules

We base our discussion on Fig. 43.1, which shows a typical potential energy curve (as in Fig. 22.1) of a diatomic molecule. In regions close to R_e (at the minimum of the curve) the potential energy can be approximated by a parabola, so we can write

$$V=\tfrac{1}{2}k_f x^2 \qquad x=R-R_e \qquad \text{Parabolic potential energy} \qquad (43.1)$$

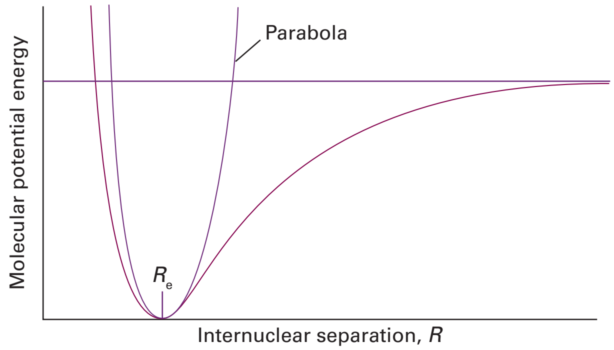

Figure 43.1 A molecular potential energy curve can be approximated by a parabola near the bottom of the well. The parabolic potential leads to harmonic oscillations. At high excitation energies the parabolic approximation is poor (the true potential is less confining), and is totally wrong near the dissociation limit.

where k_f is the **force constant** of the bond. The steeper the walls of the potential (the stiffer the bond), the greater the force constant.

To see the connection between the shape of the molecular potential energy curve and the value of k_f, note that we can expand the potential energy around its minimum by using a series (*Mathematical background* 1), which is a common way of expressing how a function varies near a selected point (in this case, the minimum of the curve at $x=0$):

$$V(x)=V(0)+\left(\frac{\mathrm{d}V}{\mathrm{d}x}\right)_0 x+\frac{1}{2}\left(\frac{\mathrm{d}^2V}{\mathrm{d}x^2}\right)_0 x^2+\dots \qquad (43.2)$$

The notation $(\dots)_0$ means that the derivatives are first evaluated and then x is set equal to 0. The term $V(0)$ can be set arbitrarily to zero. The first derivative of V is zero at the minimum. Therefore, the first surviving term is proportional to the square of the displacement. For small displacements we can ignore all the higher terms, and so write

$$V(x)\approx\frac{1}{2}\left(\frac{\mathrm{d}^2V}{\mathrm{d}x^2}\right)_0 x^2 \qquad (43.3)$$

Therefore, the first approximation to a molecular potential energy curve is a parabolic potential, and we can identify the force constant as

$$k_f=\left(\frac{\mathrm{d}^2V}{\mathrm{d}x^2}\right)_0 \qquad (43.4)$$

Formal definition Force constant

We see that if the potential energy curve is sharply curved close to its minimum, then k_f will be large and the bond stiff. Conversely, if the potential energy curve is wide and shallow, then k_f will be small and the bond easily stretched or compressed (Fig. 43.2).

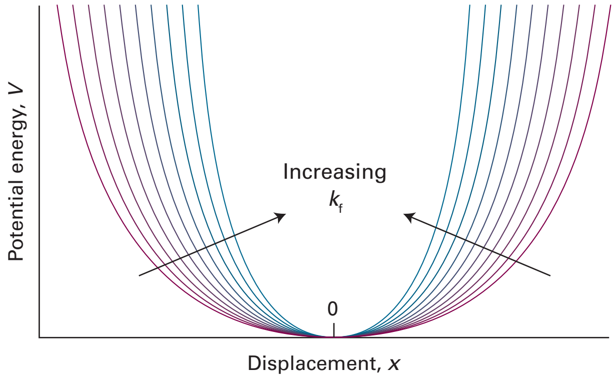

Figure 43.2 The force constant is a measure of the curvature of the potential energy close to the equilibrium extension of the bond. A strongly confining well (one with steep sides, a stiff bond) corresponds to high values of k_f.

The Schrödinger equation for the relative motion of two atoms of masses m_1 and m_2 with a parabolic potential energy is

$$-\frac{\hbar^2}{2m_{\mathrm{eff}}}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+\tfrac{1}{2}k_f x^2\psi=E\psi \qquad (43.5)$$

where m_{eff} is the **effective mass**:

$$m_{\mathrm{eff}}=\frac{m_1m_2}{m_1+m_2} \qquad (43.6)$$

Definition Effective mass

These equations are derived in the same way as in Topic 11, but here the separation of variables procedure is used to separate the relative motion of the atoms from the motion of the molecule as a whole.

> *A note on good practice* Distinguish *effective mass* from *reduced mass*. The former is a measure of the mass that is moved during a vibration. The latter is the quantity that emerges from the separation of relative internal and overall translational motion. For a diatomic molecule the two are the same, but that is not true in general for vibrations of polyatomic molecules. Many, however, do not make this useful distinction and refer to both quantities as the 'reduced mass'.

The Schrödinger equation in eqn 43.5 is the same as eqn 12.3 for a particle of mass m undergoing harmonic motion. Therefore, we can use the results of Topic 12 to write down the permitted vibrational energy levels:

$$E_v=\left(v+\frac{1}{2}\right)\hbar\omega \qquad \omega=\left(\frac{k_f}{m_{\mathrm{eff}}}\right)^{1/2} \qquad v=0,1,2,\dots \qquad (43.7)$$

Diatomic molecule Vibrational energy levels

The **vibrational terms** of a molecule, the energies of its vibrational states expressed as wavenumbers, are denoted $\tilde{G}(v)$, with $E_v = hc\tilde{G}(v)$, so

$$\tilde{G}(v)=\left(v+\frac{1}{2}\right)\tilde{\nu} \qquad \tilde{\nu}=\frac{1}{2\pi c}\left(\frac{k_\mathrm{f}}{m_\mathrm{eff}}\right)^{1/2} \tag{43.8}$$

Diatomic molecule Vibrational terms

The vibrational wavefunctions are the same as those discussed in Topic 12 for a harmonic oscillator.

It is important to note that the vibrational terms depend on the *effective* mass of the molecule, not directly on its total mass. This dependence is physically reasonable, for if atom 1 were as heavy as a brick wall, then we would find $m_\mathrm{eff} \approx m_2$, the mass of the lighter atom. The vibration would then be that of a light atom relative to that of a stationary wall (this is approximately the case in HI, for example, where the I atom barely moves and $m_\mathrm{eff} \approx m_\mathrm{H}$). For a homonuclear diatomic molecule, $m_1 = m_2$, and the effective mass is half the total mass: $m_\mathrm{eff} = \frac{1}{2}m$.

Brief illustration 43.1 The vibrational frequency of a diatomic molecule

The force constant of the bond in HCl is 516 N m^{-1}, a reasonably typical value for a single bond. The effective mass of $^1H^{35}Cl$ is 1.63×10^{-27} kg (note that this mass is very close to the mass of the hydrogen atom, 1.67×10^{-27} kg, so the Cl atom is acting like a brick wall). These values imply

$$\omega=\left(\frac{516\ \overbrace{\mathrm{N}}^{\mathrm{kg\,m\,s^{-2}}}\ \mathrm{m^{-1}}}{1.63\times10^{-27}\ \mathrm{kg}}\right)^{1/2}=5.63\times10^{14}\ \mathrm{s^{-1}}$$

or $\nu = \omega/2\pi = 89.5$ THz (1 THz $= 10^{12}$ Hz).

Self-test 43.1 The vibrational frequency ν of $^{35}Cl_2$ is 16.94 THz. What is the force constant of the bond?

Answer: 327.8 N m^{-1}

43.2 Infrared spectroscopy

The gross selection rule for a change in vibrational state brought about by absorption or emission of radiation is that *the electric dipole moment of the molecule must change when the atoms are displaced relative to one another*. Such vibrations are said to be **infrared active**. The classical basis of this rule is that the molecule can shake the electromagnetic field into oscillation if its dipole moment changes as it vibrates, and vice versa (Fig. 43.3); its formal basis is given in the following *Justification*. Note that the molecule need not have a permanent dipole moment: the rule requires only a *change* in dipole moment, possibly from zero. Some vibrations do not affect the molecule's dipole moment (for instance, the stretching motion of a homonuclear diatomic molecule), so they neither absorb nor generate radiation: such vibrations are said to be **infrared inactive**.

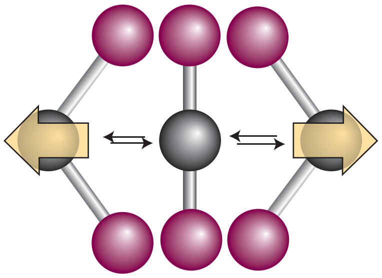

Figure 43.3 The oscillation of a molecule, even if it is nonpolar, may result in an oscillating dipole that can interact with the electromagnetic field.

Brief illustration 43.2 The gross selection rule for infrared spectroscopy

Homonuclear diatomic molecules are infrared inactive because their dipole moments remain zero however long the bond; heteronuclear diatomic molecules are infrared active. Weak infrared transitions can be observed from homonuclear diatomic molecules trapped within various nanomaterials. For instance, when incorporated into solid C_{60}, H_2 molecules interact through van der Waals forces with the surrounding C_{60} molecules and acquire dipole moments, with the result that they have observable infrared spectra.

Self-test 43.2 Identify the infrared active molecules in the group: N_2, NO, and CO.

Answer: NO and CO

The specific selection rule, which is obtained from an analysis of the expression for the transition moment and the properties of integrals over harmonic oscillator wavefunctions (as shown in the following *Justification*), is

$$\Delta v = \pm 1 \tag{43.9}$$

Infrared spectroscopy Specific selection rule

Justification 43.1 Gross and specific selection rules for infrared spectra

The gross selection rule for infrared spectroscopy is based on an analysis of the transition dipole moment $\boldsymbol{\mu}_\mathrm{fi} = \int \psi^*_{v_\mathrm{f}} \hat{\boldsymbol{\mu}} \psi_{v_\mathrm{i}} \mathrm{d}\tau$ (Topic 42), which arises from eqn 42.2 ($\boldsymbol{\mu}_\mathrm{fi} = \int \psi^*_{\varepsilon_\mathrm{f}} \psi^*_{v_\mathrm{f}} Y^*_{J_\mathrm{f},M_{J,\mathrm{f}}} \hat{\boldsymbol{\mu}} \psi_{\varepsilon_\mathrm{i}} \psi_{v_\mathrm{i}} Y_{J_\mathrm{i},M_{J,\mathrm{i}}} \mathrm{d}\tau$) when the molecule does not change electronic or rotational states. For simplicity, we consider a one-dimensional oscillator (like a diatomic molecule). The electric dipole moment depends on the location of

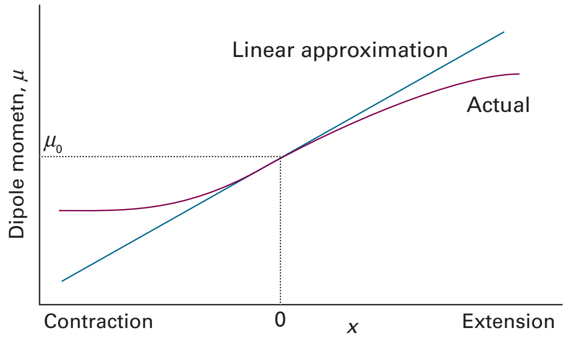

Figure 43.4 The magnitude of the electric dipole moment of a heteronuclear diatomic molecule varies as shown by the purple curve. For small displacements the change in the magnitude of the dipole moment is proportional to the displacement.

all the electrons and all the nuclei in the molecule, so it varies as the internuclear separation changes (Fig. 43.4). We can write its variation with displacement from the equilibrium separation, x, as

$$\mu=\mu_0+\left(\frac{\mathrm{d}\mu}{\mathrm{d}x}\right)_0 x+\ldots \tag{43.10}$$

where μ_0 is the electric dipole moment when the nuclei have their equilibrium separation. It then follows that, with $\mathrm{f}\neq\mathrm{i}$ and keeping only the term linear in the small displacement x,

$$\mu_{\mathrm{fi}}=\mu_0\overbrace{\int\psi^*_{v_\mathrm{f}}\psi_{v_\mathrm{i}}\,\mathrm{d}x}^{0}+\left(\frac{\mathrm{d}\mu}{\mathrm{d}x}\right)_0\int\psi^*_{v_\mathrm{f}}x\psi_{v_\mathrm{i}}\,\mathrm{d}x$$

The term multiplying μ_0 is zero because the states with different values of v are orthogonal (Topic 12). It follows that the transition dipole moment is

$$\mu_{\mathrm{fi}}=\left(\frac{\mathrm{d}\mu}{\mathrm{d}x}\right)_0\int\psi^*_{v_\mathrm{f}}x\psi_{v_\mathrm{i}}\,\mathrm{d}x \tag{43.11}$$

We see that the right-hand side is zero unless the dipole moment varies with displacement. This is the gross selection rule for infrared spectroscopy.

The specific selection rule is determined by considering the value of $\int\psi^*_{v_\mathrm{f}}x\psi_{v_\mathrm{i}}\,\mathrm{d}x$. We need to write out the wavefunctions in terms of the Hermite polynomials given in Topic 12 and then to use their properties. We note that $x=\alpha y$ with $\alpha=(\hbar^2/m_{\mathrm{eff}}k_\mathrm{f})^{1/4}$ (eqn 12.8 of Topic 12). Then we write

$$\int\psi^*_{v_\mathrm{f}}x\psi_{v_\mathrm{i}}\,\mathrm{d}x=N_{v_\mathrm{f}}N_{v_\mathrm{i}}\int_{-\infty}^{\infty}H_{v_\mathrm{f}}xH_{v_\mathrm{i}}\mathrm{e}^{-y^2}\mathrm{d}x$$
$$=\alpha^2N_{v_\mathrm{f}}N_i\int_{-\infty}^{\infty}H_{v_\mathrm{f}}yH_{v_\mathrm{i}}\mathrm{e}^{-y^2}\mathrm{d}y$$

To evaluate the integral we use the 'recursion' relation

$$yH_v=vH_{v-1}+\tfrac{1}{2}H_{v+1}$$

which leads to

$$\int\psi^*_{v_\mathrm{f}}x\psi_{v_\mathrm{i}}\,\mathrm{d}x$$
$$=\alpha^2N_{v_\mathrm{f}}N_{v_\mathrm{i}}\left\{v_\mathrm{i}\int_{-\infty}^{\infty}H_{v_\mathrm{f}}H_{v_\mathrm{i}-1}\mathrm{e}^{-y^2}\mathrm{d}y+\tfrac{1}{2}\int_{-\infty}^{\infty}H_{v_\mathrm{f}}H_{v_\mathrm{i}+1}\mathrm{e}^{-y^2}\mathrm{d}y\right\} \tag{43.12}$$

The first integral is zero unless $v_\mathrm{f}=v_\mathrm{i}-1$, and the second is zero unless $v_\mathrm{f}=v_\mathrm{i}+1$ (Table 12.1). It follows that the transition dipole moment is zero unless $\Delta v=\pm1$.

Transitions for which $\Delta v=+1$ correspond to absorption and those with $\Delta v=-1$ correspond to emission. It follows that the wavenumbers of allowed vibrational transitions, which are denoted $\Delta\tilde{G}_{v+\frac{1}{2}}$ for the transition $v+1\leftarrow v$, are

$$\Delta\tilde{G}_{v+\frac{1}{2}}=\tilde{G}(v+1)-\tilde{G}(v)=\tilde{\nu} \tag{43.13}$$

The wavenumbers of vibrational transitions correspond to those of radiation in the infrared region of the electromagnetic spectrum, so vibrational transitions absorb and generate infrared radiation.

At room temperature $kT/hc\approx200\,\mathrm{cm}^{-1}$, and most vibrational wavenumbers are significantly greater than $200\,\mathrm{cm}^{-1}$. It follows from the Boltzmann distribution (*Foundations*, Topic 2, and Topic 51) that at room temperature almost all the molecules are in their vibrational ground states. Hence, the dominant spectral transition will be the **fundamental transition**, $1\leftarrow0$. As a result, the spectrum is expected to consist of a single absorption line. If the molecules are formed in a vibrationally excited state, such as when vibrationally excited HF molecules are formed in the reaction $H_2+F_2\rightarrow2\,HF^*$, where the star indicates a vibrationally 'hot' molecule, the transitions $5\rightarrow4$, $4\rightarrow3$, … may also appear (in emission). In the harmonic approximation, all these lines lie at the same frequency, and the spectrum is also a single line. However, as we shall now show, the breakdown of the harmonic approximation causes the transitions to lie at slightly different frequencies, so several lines are observed.

43.3 Anharmonicity

The vibrational terms in eqn 43.8 are only approximate because they are based on a parabolic approximation to the actual potential energy curve. A parabola cannot be correct at all extensions because it does not allow a bond to dissociate. At high vibrational excitations the swing of the atoms (more precisely, the spread of the vibrational wavefunction) allows the molecule to explore regions of the potential energy curve where the parabolic approximation is poor and additional terms in the Taylor expansion of V (eqn 43.2) must be retained. The motion then becomes **anharmonic**, in the sense that the restoring force is no longer proportional to the displacement. Because the actual curve is less confining than a parabola, we can anticipate that the energy levels become more closely spaced at high excitations.

One approach to the calculation of the energy levels in the presence of anharmonicity is to use a function that resembles the true potential energy more closely. The **Morse potential energy** is

$$V = hc\tilde{D}_e\{1-e^{-a(R-R_e)}\}^2 \qquad a=\left(\frac{m_{eff}\omega^2}{2hc\tilde{D}_e}\right)^{1/2} \qquad \text{Morse potential energy} \qquad (43.14)$$

where $\tilde{D}_e$ is the depth of the potential minimum (Fig. 43.5). Near the well minimum the variation of V with displacement resembles a parabola (as can be checked by expanding the exponential as far as the first term) but, unlike a parabola, eqn 43.14 allows for dissociation at large displacements. The Schrödinger equation can be solved for the Morse potential and the permitted energy levels are

$$\begin{aligned}\tilde{G}(v) &= \left(v+\tfrac{1}{2}\right)\tilde{\nu} - \left(v+\tfrac{1}{2}\right)^2 x_e\tilde{\nu} \\ x_e &= \frac{a^2\hbar}{2m_{eff}\omega} = \frac{\tilde{\nu}}{4\tilde{D}_e}\end{aligned} \qquad \textit{Morse potential energy} \qquad \text{Vibrational terms} \qquad (43.15)$$

The dimensionless parameter x_e is called the **anharmonicity constant**. The number of vibrational levels of a Morse oscillator is finite, and $v=0, 1, 2, \ldots, v_{max}$, as shown in Fig. 43.6 (see also Problem 43.5). The second term in the expression for $\tilde{G}$ subtracts from the first with increasing effect as v increases, and hence gives rise to the convergence of the levels at high quantum numbers.

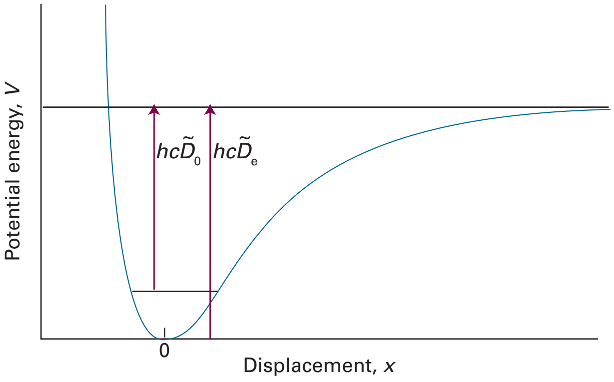

Figure 43.5 The dissociation energy of a molecule, $hc\tilde{D}_0$, differs from the depth of the potential well, $hc\tilde{D}_e$, on account of the zero-point energy of the vibrations of the bond.

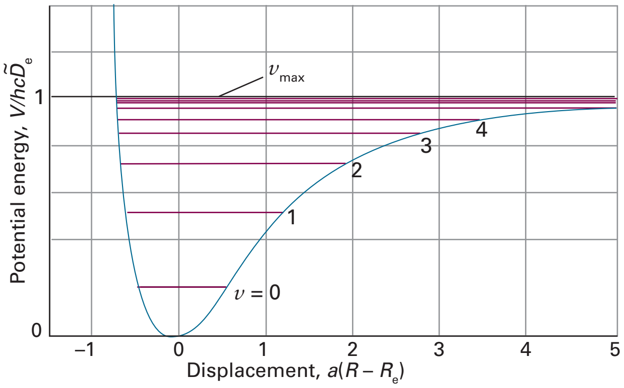

Figure 43.6 The Morse potential energy curve reproduces the general shape of a molecular potential energy curve. The corresponding Schrödinger equation can be solved, and the values of the energies obtained. The number of bound levels is finite.

Example 43.1 Estimating an anharmonicity constant

Estimate the anharmonicity constant x_e for $^1H^{19}F$ from the data in Table 43.1.

Method The anharmonicity constant is evaluated from $\tilde{\nu}$, $\tilde{D}_e$ and eqn 43.15. However, note that Table 43.1 lists values of $\tilde{D}_0 = \tilde{D}_e - \frac{1}{2}\tilde{\nu}$ (Fig. 43.5), so calculate $\tilde{D}_e$ first before using eqn 43.15. A useful conversion factor is $1\ \text{kJ mol}^{-1} = 83.593\ \text{cm}^{-1}$.

Answer The depth of the potential minimum is

$$\begin{aligned}\tilde{D}_e = \tilde{D}_0 + \frac{1}{2}\tilde{\nu} &= \overbrace{(4.718\times10^4\ \text{cm}^{-1})}^{564.4\ \text{kJ mol}^{-1}\times\frac{83.593\ \text{cm}^{-1}}{1\ \text{kJ mol}^{-1}}} + \frac{1}{2}\times(4138.32\ \text{cm}^{-1}) \\ &= \left(4.718\times10^4 + \frac{1}{2}\times4138.32\right)\text{cm}^{-1}\end{aligned}$$

It follows from eqn 43.15 that the anharmonicity constant is

$$x_e = \frac{4138.32\ \text{cm}^{-1}}{4\times\{(4.718\times10^4 + \frac{1}{2}\times4138.32)\ \text{cm}^{-1}\}} = 2.101\times10^{-2}$$

Self-test 43.3 Estimate the anharmonicity constant for $^1H^{81}Br$.

Answer: 2.093×10^{-2}

Table 43.1* Properties of diatomic molecules

	$\tilde{\nu}/\text{cm}^{-1}$	R_e/pm	$\tilde{B}/\text{cm}^{-1}$	$k_f/(\text{N m}^{-1})$	$hc\tilde{D}_o/(\text{kJ mol}^{-1})$
$^1H_2$	4400	74	60.86	575	432
$^1H^{35}Cl$	2991	127	10.59	516	428
$^1H^{127}I$	2308	161	6.51	314	295
$^{35}Cl_2$	560	199	0.244	323	239

* More values are given in the *Resource section.*

Although the Morse oscillator is quite useful theoretically, in practice the more general expression

$$\tilde{G}(v)=\left(v+\frac{1}{2}\right)\tilde{\nu}-\left(v+\frac{1}{2}\right)^2 x_e\tilde{\nu}+\left(v+\frac{1}{2}\right)^3 y_e\tilde{\nu}+\ldots \qquad (43.16)$$

where x_e, y_e, … are empirical dimensionless constants characteristic of the molecule, is used to fit the experimental data and to find the dissociation energy of the molecule. When anharmonicities are present, the wavenumbers of transitions with $\Delta v=+1$ are

$$\Delta\tilde{G}_{v+\frac{1}{2}}=\tilde{G}(v+1)-\tilde{G}(v)=\tilde{\nu}-2(v+1)x_e\tilde{\nu}+\ldots \qquad (43.17)$$

Equation 43.17 shows that, when $x_e>0$, the transitions move to lower wavenumbers as v increases.

Anharmonicity also accounts for the appearance of additional weak absorption lines corresponding to the transitions $2\leftarrow 0$, $3\leftarrow 0$, …, even though these first, second, … **overtones** are forbidden by the selection rule $\Delta v=\pm 1$. The first overtone, for example, gives rise to an absorption at

$$\tilde{G}(v+2)-\tilde{G}(v)=2\tilde{\nu}-2(2v+3)x_e\tilde{\nu}+\ldots \qquad (43.18)$$

The reason for the appearance of overtones is that the selection rule is derived from the properties of harmonic oscillator wavefunctions, which are only approximately valid when anharmonicity is present. Therefore, the selection rule is also only an approximation. For an anharmonic oscillator, all values of Δv are allowed, but transitions with $\Delta v>1$ are allowed only weakly if the anharmonicity is slight.

43.4 Vibration–rotation spectra

Each line of the high-resolution vibrational spectrum of a gas-phase heteronuclear diatomic molecule is found to consist of a large number of closely spaced components (Fig. 43.7). Hence, molecular spectra are often called **band spectra**. The separation between the components is less than 10 cm^{-1}, which suggests that the structure is due to rotational transitions accompanying the vibrational transition. A rotational change should be expected because classically we can think of the vibrational transition as leading to a sudden increase or decrease in the instantaneous bond length. Just as ice-skaters rotate more rapidly when they bring their arms in, and more slowly when they throw them out, so the molecular rotation is either accelerated or retarded by a vibrational transition.

(a) Spectral branches

A detailed analysis of the quantum mechanics of simultaneous vibrational and rotational changes shows that the rotational quantum number J changes by ±1 during the vibrational transition of a diatomic molecule. If the molecule also possesses angular momentum about its axis, as in the case of the electronic orbital angular momentum of the paramagnetic molecule NO, then the selection rules also allow $\Delta J=0$.

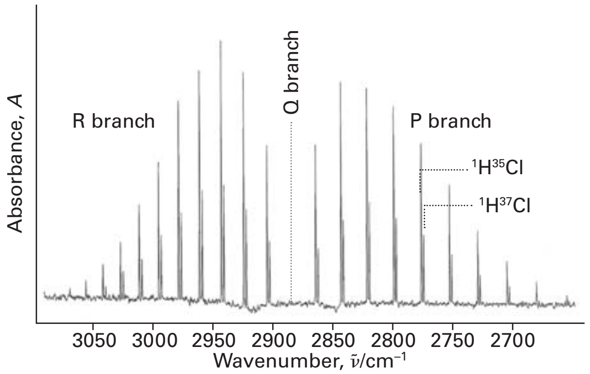

Figure 43.7 A high-resolution vibration–rotation spectrum of HCl. The lines appear in pairs because H^{35}Cl and H^{37}Cl both contribute (their abundance ratio is 3:1). There is no Q branch, because $\Delta J=0$ is forbidden for this molecule.

The appearance of the vibration–rotation spectrum of a diatomic molecule can be discussed in terms of the combined vibration–rotation terms, $\tilde{S}$:

$$\tilde{S}(v,J)=\tilde{G}(v)+\tilde{F}(J) \qquad (43.19)$$

If we ignore anharmonicity and centrifugal distortion we can use eqn 43.8 for the first term on the right and eqn 41.15 for the second, and obtain

$$\tilde{S}(v,J)=\left(v+\frac{1}{2}\right)\tilde{\nu}+\tilde{B}J(J+1) \qquad (43.20)$$

In a more detailed treatment, $\tilde{B}$ is allowed to depend on the vibrational state because, as v increases, the molecule swells slightly and the moment of inertia changes. We shall continue with the simple expression initially.

When the vibrational transition $v+1\leftarrow v$ occurs, J changes by ±1 and in some cases by 0 (when $\Delta J=0$ is allowed). The absorptions then fall into three groups called **branches** of the spectrum. The **P branch** consists of all transitions with $\Delta J=-1$:

$$\tilde{\nu}_P(J)=\tilde{S}(v+1,J-1)-\tilde{S}(v,J)=\tilde{\nu}-2\tilde{B}J \qquad \text{P branch transitions} \qquad (43.21a)$$

This branch consists of lines at $\tilde{\nu}-2\tilde{B}$, $\tilde{\nu}-4\tilde{B}$, … with an intensity distribution reflecting both the populations of the rotational levels and the magnitude of the $J-1\leftarrow J$ transition moment (Fig. 43.8). The **Q branch** consists of all lines with $\Delta J=0$, and its wavenumbers are

$$\tilde{\nu}_Q(J)=\tilde{S}(v+1,J)-\tilde{S}(v,J)=\tilde{\nu} \qquad \text{Q branch transitions} \qquad (43.21b)$$

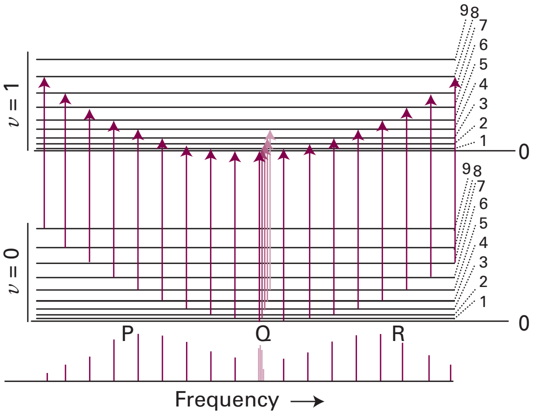

Figure 43.8 The formation of P, Q, and R branches in a vibration–rotation spectrum. The intensities reflect the populations of the initial rotational levels and the magnitudes of the transition moments.

for all values of J. This branch, when it is allowed (as in NO), appears at the vibrational transition wavenumber. In Fig. 43.7 there is a gap at the expected location of the Q branch because it is forbidden in HCl. The **R branch** consists of lines with $\Delta J = +1$:

$$\begin{aligned}\tilde{\nu}_R(J) &= \tilde{S}(v+1, J+1) - \tilde{S}(v, J)\\ &= \tilde{\nu} + 2\tilde{B}(J+1)\end{aligned} \quad \text{R branch transitions} \quad (43.21c)$$

This branch consists of lines displaced from $\tilde{\nu}$ to high wavenumber by $2\tilde{B}$, $4\tilde{B}$, ….

The separation between the lines in the P and R branches of a vibrational transition gives the value of $\tilde{B}$. Therefore, the bond length can be deduced without needing to take a pure rotational microwave spectrum. However, the latter is more precise because microwave frequencies can be measured with greater precision than infrared frequencies.

Brief illustration 43.3 The wavenumber of an R branch transition

Infrared absorption by $^1H^{81}Br$ gives rise to an R branch from $v = 0$. It follows from eqn 43.21c and the data in Table 43.1 that the wavenumber of the line originating from the rotational state with $J = 2$ is

$$\begin{aligned}\tilde{\nu}_R(2) &= \tilde{\nu} + 6\tilde{B} = (2648.98\,\text{cm}^{-1}) + 6\times(8.465\,\text{cm}^{-1})\\ &= 2699.77\,\text{cm}^{-1}\end{aligned}$$

Self-test 43.4 Infrared absorption by $^1H^{127}I$ gives rise to an R branch from $v = 0$. What is the wavenumber of the line originating from the rotational state with $J = 2$?

Answer: $2347.16\,\text{cm}^{-1}$

(b) Combination differences

The rotational constant of the vibrationally excited state, $\tilde{B}_1$ (in general, $\tilde{B}_v$), is different from that of the ground vibrational state, $\tilde{B}_0$. One contribution to the difference is the anharmonicity of the vibration, which results in a slightly extended bond in the upper state. However, even in the absence of anharmonicity, the average value of $1/R^2$ ($\langle 1/R^2 \rangle$) varies with the vibrational state (see Problems 43.10 and 43.11). As a result, the Q branch (if it exists) consists of a series of closely spaced lines. The lines of the R branch converge slightly as J increases; and those of the P branch diverge:

$$\begin{aligned}\tilde{\nu}_P(J) &= \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2\\ \tilde{\nu}_Q(J) &= \tilde{\nu} + (\tilde{B}_1 - \tilde{B}_0)J(J+1)\\ \tilde{\nu}_R(J) &= \tilde{\nu} + (\tilde{B}_1 + \tilde{B}_0)(J+1) + (\tilde{B}_1 - \tilde{B}_0)(J+1)^2\end{aligned} \quad (43.22)$$

To determine the two rotational constants individually, we use the method of **combination differences**. This procedure is used widely in spectroscopy to extract information about a particular state. It involves setting up expressions for the difference in the wavenumbers of transitions to a common state; the resulting expression then depends solely on properties of the other state.

As can be seen from Fig. 43.9, the transitions $\tilde{\nu}_R(J-1)$ and $\tilde{\nu}_P(J+1)$ have a common upper state, and hence can be anticipated to depend on $\tilde{B}_0$. Indeed, from eqn 43.22 it follows that

$$\tilde{\nu}_R(J-1) - \tilde{\nu}_P(J+1) = 4\tilde{B}_0(J+\tfrac{1}{2}) \quad (43.23a)$$

Therefore, a plot of the combination difference against $J+\frac{1}{2}$ should be a straight line of slope $4\tilde{B}_0$, so the rotational constant of the molecule in the state $v = 0$ can be determined. (Any deviation from a straight line is a consequence of centrifugal distortion, so that effect can be investigated too.) Similarly, $\tilde{\nu}_R(J)$ and $\tilde{\nu}_P(J)$ have a common lower state, and hence their combination difference gives information about the upper state:

$$\tilde{\nu}_R(J) - \tilde{\nu}_P(J) = 4\tilde{B}_1(J+\tfrac{1}{2}) \quad (43.23b)$$

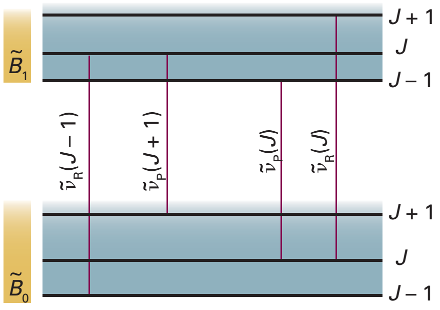

Figure 43.9 The method of combination differences makes use of the fact that some transitions share a common level.

Brief illustration 43.4 Combination differences

To develop a sense of the relative values of the rotational constants, we can estimate the rotational constants of $\tilde{B}_0$ and $\tilde{B}_1$ from a quick calculation involving only a few transitions. For $^1H^{35}Cl$, $\tilde{\nu}_R(0)-\tilde{\nu}_P(2)=62.6\,\text{cm}^{-1}$, and it follows from eqn 43.23a, with $J=1$, that $\tilde{B}_0=62.6/\{4\times(1+\frac{1}{2})\}\,\text{cm}^{-1}=10.4\,\text{cm}^{-1}$. Similarly, $\tilde{\nu}_R(1)-\tilde{\nu}_P(1)=60.8\,\text{cm}^{-1}$, and it follows from eqn 43.23b, again with $J=1$, that $\tilde{B}_1=60.8/\{4\times(1+\frac{1}{2})\}\,\text{cm}^{-1}=10.1\,\text{cm}^{-1}$. The linear least-squares procedure applied to a larger data set gives $\tilde{B}_0=10.440\,\text{cm}^{-1}$ and $\tilde{B}_1=10.136\,\text{cm}^{-1}$.

Self-test 43.5 For $^{12}C^{16}O$, $\tilde{\nu}_R(0)=2147.084\,\text{cm}^{-1}$, $\tilde{\nu}_R(1)=2150.858\,\text{cm}^{-1}$, $\tilde{\nu}_P(1)=2139.427\,\text{cm}^{-1}$, and $\tilde{\nu}_P(2)=2135.548\,\text{cm}^{-1}$. Estimate the values of $\tilde{B}_0$ and $\tilde{B}_1$.

Answer: $\tilde{B}_0=1.923\,\text{cm}^{-1}$, $\tilde{B}_1=1.905\,\text{cm}^{-1}$

43.5 Vibrational Raman spectra of diatomic molecules

The gross selection rule for vibrational Raman transitions (see the following *Justification*) is that *the polarizability should change as the molecule vibrates*. The polarizability plays a role in vibrational Raman spectroscopy because the molecule must be squeezed and stretched by the incident radiation in order that a vibrational excitation may occur during the photon–molecule collision.

Brief illustration 43.5 The gross selection rule for vibrational Raman spectra

Both homonuclear and heteronuclear diatomic molecules swell and contract during a vibration, the control of the nuclei over the electrons varies, and hence the molecular polarizability changes. Both types of diatomic molecule are therefore vibrationally Raman active.

Self-test 43.6 Can a linear, nonpolar molecule like CO_2 have a Raman spectrum?

Answer: Yes

The specific selection rule for vibrational Raman transitions in the harmonic approximation is $\Delta v=\pm 1$. The formal basis for the gross and specific selection rules is given in the following *Justification*.

Justification 43.2 Gross and specific selection rules for vibrational Raman spectra

For simplicity, we consider a one-dimensional harmonic oscillator (like a diatomic molecule). First, we note that the oscillating electric field, $\mathcal{E}(t)$, of the incident electromagnetic radiation can induce a dipole moment that is proportional to the strength of the field. We write $\mu=\alpha(x)\mathcal{E}(t)$, where $\alpha(x)$ is the polarizability of the molecule, a measure of its responsiveness to the field. The transition dipole moment is then

$$\mu_{\text{fi}}=\int\psi^*_{v_\text{f}}\alpha(x)\mathcal{E}(t)\psi_{v_\text{i}}\,\text{d}x=\mathcal{E}(t)\int\psi^*_{v_\text{f}}\alpha(x)\psi_{v_\text{i}}\,\text{d}x \qquad (43.24)$$

(where the polarizability operator is represented by multiplication by $\alpha(x)$ because it depends only on coordinates). The polarizability varies with the length of the bond because the control of the nuclei over the electrons varies as their position changes, so $\alpha(x)=\alpha_0+(\text{d}\alpha/\text{d}x)_0x+\ldots$. Now the calculation proceeds as in *Justification* 43.1, but $(\text{d}\mu/\text{d}x)_0$ is replaced by $\mathcal{E}(t)(\text{d}\alpha/\text{d}x)_0$ in eqn 43.11. For $\text{f}\neq\text{i}$,

$$\mu_{\text{fi}}=\mathcal{E}(t)\left(\frac{\text{d}\alpha}{\text{d}x}\right)_0\int\psi^*_{v_\text{f}}x\psi_{v_\text{i}}\,\text{d}x \qquad (43.25)$$

Therefore, the vibration is Raman active only if $(\text{d}\alpha/\text{d}x)_0\neq 0$ (that is, the polarizability varies with displacement) and, as we saw in *Justification* 43.1, if $v_\text{f}-v_\text{i}=\pm 1$.

The lines to high frequency of the incident radiation, in the language introduced in Topic 40, the 'anti-Stokes lines', are those for which $\Delta v=-1$. The lines to low frequency, the 'Stokes lines', correspond to $\Delta v=+1$. The intensities of the anti-Stokes and Stokes lines are governed largely by the Boltzmann populations of the vibrational states involved in the transition. It follows that anti-Stokes lines are usually weak because very few molecules are in an excited vibrational state initially.

In gas-phase spectra, the Stokes and anti-Stokes lines have a branch structure arising from the simultaneous rotational transitions that accompany the vibrational excitation (Fig. 43.10). The selection rules are $\Delta J=0, \pm 2$ (as in pure rotational Raman spectroscopy), and give rise to the **O branch** ($\Delta J=-2$), the **Q branch** ($\Delta J=0$), and the **S branch** ($\Delta J=+2$):

$$\begin{aligned}\tilde{\nu}_\text{O}(J)&=\tilde{\nu}_\text{i}-\tilde{\nu}-2\tilde{B}+4\tilde{B}J && \text{O branch transitions}\\ \tilde{\nu}_\text{Q}(J)&=\tilde{\nu}_\text{i}-\tilde{\nu} && \text{Q branch transitions}\\ \tilde{\nu}_\text{S}(J)&=\tilde{\nu}_\text{i}-\tilde{\nu}-6\tilde{B}-4\tilde{B}J && \text{S branch transitions}\end{aligned} \qquad (43.26)$$

where $\tilde{\nu}_\text{i}$ is the wavenumber of the incident radiation. Note that, unlike in infrared spectroscopy, a Q branch is obtained for all linear molecules. The spectrum of CO, for instance, is shown in Fig. 43.11: the structure of the Q branch arises from the differences in rotational constants of the upper and lower vibrational states.

The information available from vibrational Raman spectra adds to that from infrared spectroscopy because homonuclear diatomics can also be studied. The spectra can be interpreted in terms of the force constants, dissociation energies, and bond lengths, and some of the information obtained is included in Table 43.1.

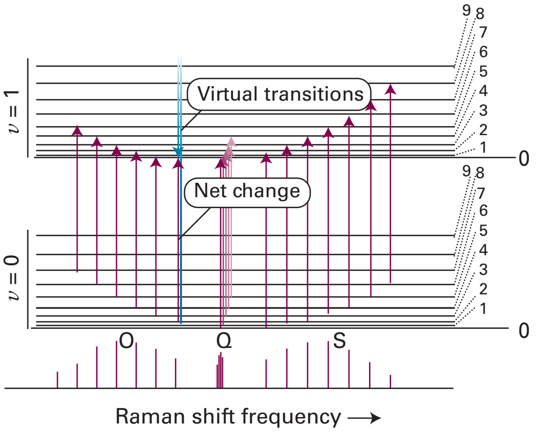

Figure 43.10 The formation of O, Q, and S branches in a vibration–rotation Raman spectrum of a linear rotor. Note that the frequency scale runs in the opposite direction to that in Fig. 43.8, because the higher-energy transitions (on the right) extract more energy from the incident beam and leave it at lower frequency.

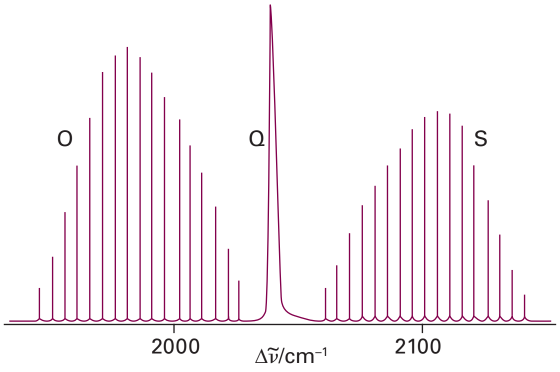

Figure 43.11 The structure of a vibrational line in the vibrational Raman spectrum of carbon monoxide, showing the O, Q, and S branches. The horizontal axis represents the wavenumber difference between the incident and scattered radiation.

Checklist of concepts

☐ 1. The vibrational energy levels of a diatomic molecule modelled as a harmonic oscillator depend on a **force constant** k_f (a measure of the bond's stiffness) and the **effective mass** of the vibration.

☐ 2. The gross selection rule for infrared spectra is that the electric dipole moment of the molecule must change when the atoms are displaced relative to one another.

☐ 3. The specific selection rule for infrared spectra (within the harmonic approximation) is $\Delta v = \pm 1$.

☐ 4. The **Morse potential energy function** can be used to describe anharmonic motion.

☐ 5. The strongest infrared transitions are the **fundamental transitions** ($v = 1 \leftarrow v = 0$).

☐ 6. Anharmonicity gives rise to weaker **overtone transitions** ($v = 2 \leftarrow v = 0$, $v = 3 \leftarrow v = 0$, etc.).

☐ 7. In the gas phase, vibrational transitions have a **P, Q, R branch structure** due to simultaneous rotational transitions.

☐ 8. For a vibration to be **Raman active**, the polarizability must change as the molecule vibrates.

☐ 9. The specific selection rule for vibrational Raman spectra (within the harmonic approximation) is $\Delta v = \pm 1$.

☐ 10. In gas-phase spectra, the Stokes and anti-Stokes lines in a Raman spectrum have an **O, Q, S branch structure.**

Checklist of equations

Property	Equation	Comment	Equation number
Vibrational terms (diatomic molecules)	$\tilde{G}(v) = \left(v + \frac{1}{2}\right)\tilde{\nu}$, $\tilde{\nu} = (1/2\pi c)(k_f/m_{\text{eff}})^{1/2}$	Simple harmonic oscillator	43.8
Infrared spectra (vibrational)	$\Delta\tilde{G}_{v+\frac{1}{2}} = \tilde{\nu}$	Simple harmonic oscillator	43.13

Property	Equation	Comment	Equation number
Morse potential energy	$V=hc\tilde{D}_e\{1-e^{-a(R-R_e)}\}^2$, $a=(m_{\text{eff}}\omega^2/2hc\tilde{D}_e)^{1/2}$, $m_{\text{eff}}=m_1m_2/(m_1+m_2)$		43.14
Vibrational terms (Morse potential energy)	$\tilde{G}(v)=\left(v+\frac{1}{2}\right)\tilde{\nu}-\left(v+\frac{1}{2}\right)^2x_e\tilde{\nu}$, $x_e=\tilde{\nu}/4\tilde{D}_e$		43.15
Infrared spectra (vibration)	$\Delta\tilde{G}_{v+\frac{1}{2}}=\tilde{\nu}-2(v+1)x_e\tilde{\nu}+\cdots$	Anharmonic oscillator	43.17
	$\tilde{G}(v+2)-\tilde{G}(v)$ $=2\tilde{\nu}-2(2v+3)x_e\tilde{\nu}+\cdots$	Overtones	43.18
Infrared spectra (vibration–rotation)	$\tilde{S}(v,J)=\left(v+\frac{1}{2}\right)\tilde{\nu}+\tilde{B}J(J+1)$	Rotation coupled to vibration	43.20
	$\tilde{\nu}_P(J)=\tilde{S}(v+1,J-1)-\tilde{S}(v,J)$ $=\tilde{\nu}-2\tilde{B}J$	P branch ($\Delta J=-1$)	43.21a
	$\tilde{\nu}_Q(J)=\tilde{S}(v+1,J)-\tilde{S}(v,J)=\tilde{\nu}$	Q branch ($\Delta J=0$)	43.21b
	$\tilde{\nu}_R(J)=\tilde{S}(v+1,J+1)-\tilde{S}(v,J)=\tilde{\nu}+2\tilde{B}(J+1)$	R branch ($\Delta J=+1$)	43.21c
	$\tilde{\nu}_R(J-1)-\tilde{\nu}_P(J+1)=4\tilde{B}_0\left(J+\frac{1}{2}\right)$ $\tilde{\nu}_R(J)-\tilde{\nu}_P(J)=4\tilde{B}_1\left(J+\frac{1}{2}\right)$	Combination differences	43.23a,b
Raman spectra (vibration–rotation)	$\tilde{\nu}_O(J)=\tilde{\nu}_i-\tilde{\nu}-2\tilde{B}+4\tilde{B}J$	O branch ($\Delta J=-2$)	43.26
	$\tilde{\nu}_Q(J)=\tilde{\nu}_i-\tilde{\nu}$	Q branch ($\Delta J=0$)	
	$\tilde{\nu}_S(J)=\tilde{\nu}_i-\tilde{\nu}-6\tilde{B}-4\tilde{B}J$	S branch ($\Delta J=+2$)	

TOPIC 44

Vibrational spectroscopy: polyatomic molecules

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➤ Why do you need to know this material?

The analysis of vibrational spectra provides information about the identity, conformation, and rigidity of polyatomic molecules in the gas and condensed phases. Even complex systems, such as synthetic materials and biological cells, can be studied.

➤ What is the key idea?

The vibrational spectrum of a polyatomic molecule can be interpreted in terms of the coupled harmonic motion of atoms.

➤ What do you need to know already?

You need to be familiar with the harmonic oscillator model (Topic 12) of molecular motion, general principles of spectroscopy (Topic 40), and the selection rules for infrared and Raman spectroscopy (Topic 43). The treatment of the symmetry aspects of infrared and Raman active vibrations requires concepts from Topics 31–33.

There is only one mode of vibration for a diatomic molecule: bond stretch. In polyatomic molecules there are several modes, sometimes hundreds of modes, of vibration because all the bond lengths and angles may change and the vibrational spectra are very complex. Nonetheless, infrared and Raman spectroscopy can be used to obtain information about the structure of systems as large as animal and plant tissues. Raman spectroscopy is particularly useful for characterizing nanomaterials, especially carbon nanotubes.

44.1 Normal modes

We begin by calculating the total number of vibrational modes of a polyatomic molecule. We then see that we can choose combinations of these atomic displacements that give the simplest description of the vibrations.

As shown in the following *Justification*, the number of independent modes of motion of an N-atom molecule depends on whether it is linear or nonlinear:

Linear molecule: $3N-5$

Nonlinear molecule: $3N-6$

Brief illustration 44.1 The numbers of normal modes

Water, H_2O, is a nonlinear triatomic molecule, $N=3$, and has $3N-6=3$ modes of vibration (and three modes of rotation); CO_2 is a linear triatomic molecule, and has $3N-5=4$ modes of vibration (and only two modes of rotation). A biological macromolecule with $N\approx 500$ atoms can vibrate in nearly 1500 different independent ways.

Self-test 44.1 How many normal modes does naphthalene ($C_{10}H_8$) have?

Answer: 48

Justification 44.1 The number of vibrational modes

The location of one atom is specified by its three coordinates. The total number of coordinates needed to specify the locations of N atoms is $3N$. Each atom may change its location by varying one of its three coordinates (x, y, and z), so the total number of displacements available is $3N$. These displacements can be grouped together in a physically sensible way. For example, three coordinates are needed to specify the location of the centre of mass of the molecule, so three of the $3N$ displacements correspond to the translational motion of the molecule as a whole. The remaining $3N-3$ are non-translational 'internal' modes of the molecule that leave its centre of mass unchanged.

Two angles are needed to specify the orientation of a linear molecule in space: in effect, we need to give only the latitude and longitude of the direction in which the molecular axis is pointing (Fig. 44.1a). However, three angles are needed for a nonlinear molecule because we also need to specify the orientation of the molecule around the direction defined by the latitude and longitude (Fig. 44.1b). Therefore, two (linear) or three (nonlinear) of the $3N-3$ internal displacements are rotational. This leaves $3N-5$ (linear) or $3N-6$ (nonlinear) displacements of the atoms relative to one another: these are the vibrational modes. It follows that the number of modes of vibration N_{vib} is $3N-5$ for linear molecules and $3N-6$ for nonlinear molecules.

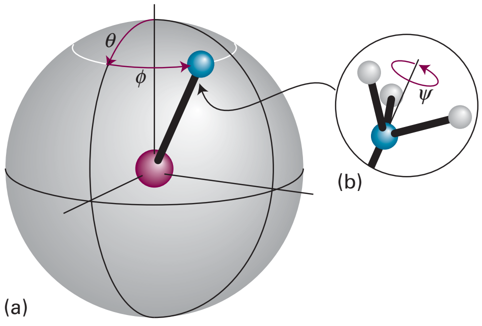

Figure 44.1 (a) The orientation of a linear molecule requires the specification of two angles. (b) The orientation of a nonlinear molecule requires the specification of three angles.

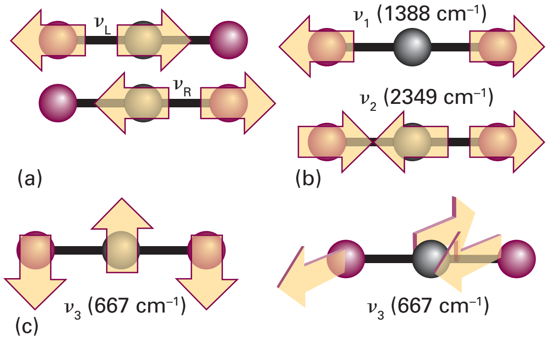

Figure 44.2 Alternative descriptions of the vibrations of CO_2. (a) The stretching modes are not independent, and if one C–O group is excited the other begins to vibrate. They are not normal modes of vibration of the molecule. (b) The symmetric and antisymmetric stretches are independent, and one can be excited without affecting the other: they are normal modes. (c) The two perpendicular bending motions are also normal modes.

The next step is to find the best description of the modes. One choice for the four modes of CO_2, for example, might be the ones in Fig. 44.2a and 44.2c. This illustration shows the stretching of one bond (the mode ν_L), the stretching of the other (ν_R), and the two perpendicular bending modes (ν_3). The description, while permissible, has a disadvantage: when one CO bond vibration is excited, the motion of the C atom sets the other CO bond in motion, so energy flows backwards and forwards between ν_L and ν_R. Moreover, the position of the centre of mass of the molecule varies in the course of either vibration.

The description of the vibrational motion is much simpler if linear combinations of ν_L and ν_R are taken. For example, one combination is ν_1 in Fig. 44.2b: this mode is the **symmetric stretch**. In this mode, the C atom is buffeted simultaneously from each side and the motion continues indefinitely. Another mode is ν_2, the **antisymmetric stretch**, in which the two O atoms always move in the same direction as each other and opposite to that of the C atom. Both modes are independent in the sense that, if one is excited, then it does not excite the other. They are two of the 'normal modes' of the molecule, its independent, collective vibrational displacements. The two other normal modes (Fig. 44.2c) are the bending modes ν_3. In general, a **normal mode** is an independent, synchronous motion of atoms or groups of atoms that may be excited without leading to the excitation of any other normal mode and without involving translation or rotation of the molecule as a whole.

The four normal modes of CO_2, and the N_{vib} normal modes of polyatomics in general, are the key to the description of molecular vibrations. Each normal mode, q, behaves like an independent harmonic oscillator (if anharmonicities are neglected), so each has a series of terms

$$\tilde{G}_q(\upsilon)=\left(\upsilon+\frac{1}{2}\right)\tilde{\nu}_q \qquad \tilde{\nu}_q=\frac{1}{2\pi c}\left(\frac{k_{\text{f},q}}{m_q}\right)^{1/2} \qquad (44.1)$$

Vibrational terms of normal modes

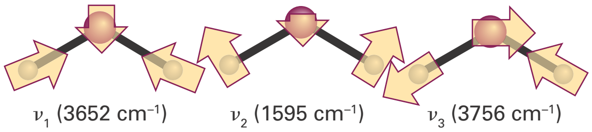

Figure 44.3 The three normal modes of H_2O. The mode ν_2 is predominantly bending, and occurs at lower wavenumber than the other two.

where $\tilde{\nu}_q$ is the wavenumber of mode q and depends on the force constant $k_{f,q}$ for the mode and on the effective mass m_q of the mode. The effective mass of the mode is a measure of the mass that is swung about by the vibration and in general is a complicated function of the masses of the atoms. For example, in the symmetric stretch of CO_2, the C atom is stationary, and the effective mass depends on the masses of only the O atoms. In the antisymmetric stretch and in the bends, all three atoms move, so all contribute to the effective mass. The three normal modes of H_2O are shown in Fig. 44.3: note that the predominantly bending mode (ν_2) has a lower frequency than the others, which are predominantly stretching modes. It is generally the case that the frequencies of bending motions are lower than those of stretching modes. One point that must be appreciated is that only in special cases (such as the CO_2 molecule) are the normal modes purely stretches or purely bends. In general, a normal mode is a composite motion of simultaneous stretching and bending of bonds. Another point in this connection is that heavy atoms generally move less than light atoms in normal modes.

The vibrational state of a polyatomic molecule is specified by the vibrational quantum number v for each of the normal modes. For example, for the water molecule with three normal modes, the vibrational state is designated as (v_1,v_2,v_3), where v_i is the number of vibrational quanta in normal mode i. The vibrational ground state of an H_2O molecule is therefore (0,0,0).

44.2 Infrared absorption spectra of polyatomic molecules

The gross selection rule for infrared activity is that *the motion corresponding to a normal mode should be accompanied by a change of dipole moment*. Simple inspection of atomic motions is sometimes all that is needed in order to assess whether a normal mode is infrared active. For example, the symmetric stretch of CO_2 leaves the dipole moment unchanged (at zero, see Fig. 44.2), so this mode is infrared inactive. The antisymmetric stretch, however, changes the dipole moment because the molecule becomes unsymmetrical as it vibrates, so this mode is infrared active. Because the dipole moment change is parallel to the principal axis, the transitions arising from this mode are classified as **parallel bands** in the spectrum. Both bending modes are infrared active: they are accompanied by a changing dipole perpendicular to the principal axis, so transitions involving them lead to a **perpendicular band** in the spectrum.

Example 44.1 Using the gross selection rule for infrared spectroscopy

State which of the following molecules are infrared active: N_2O, OCS, H_2O, $CH_2{=}CH_2$.

Method Molecules that are infrared active have dipole moments that change during the course of a vibration. Therefore, judge whether a distortion of the molecule can change its dipole moment (including changing it from zero).

Answer All the molecules possess at least one normal mode that results in a change of dipole moment, so all are infrared active. Again note that not all the modes of complicated molecules are infrared active. For example, a vibration of $CH_2{=}CH_2$ in which the C=C bond stretches and contracts (while the C—H bonds either do not vibrate or stretch and contract synchronously) is inactive because it leaves the dipole moment unchanged (at zero) (Fig. 44.4).

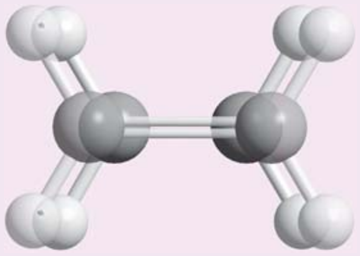

Figure 44.4 A normal mode of $CH_2{=}CH_2$ (ethene) that is not infrared active.

Self-test 44.2 Identify a normal mode of C_6H_6 that is not infrared active.

Answer: A 'breathing' mode in which all the carbon–carbon bonds contract and stretch synchronously, while the C—H bonds either do not vibrate or stretch and contract synchronously (see Fig. 44.5)

Figure 44.5 A normal mode of C_6H_6 (benzene) that is not infrared active.

The active modes are subject to the specific selection rule $\Delta v_q = \pm 1$ in the harmonic approximation, so the wavenumber of the fundamental transition (the 'first harmonic') of each active mode is $\tilde{\nu}_q$. A polyatomic molecule has several fundamental transitions. For example, the spectrum of a molecule with three infrared active normal modes features three fundamental transitions: $(1,0,0) \leftarrow (0,0,0)$, $(0,1,0) \leftarrow (0,0,0)$, and $(0,0,1) \leftarrow (0,0,0)$. Also possible are **combination bands** corresponding to the excitation of more than one normal mode in the transition, as in $(1,1,0) \leftarrow (0,0,0)$. Moreover, overtone transitions, such as $(2,0,0) \leftarrow (0,0,0)$, can appear in the spectrum when anharmonicity is important (Topic 43).

From the analysis of the spectrum, a picture may be constructed of the stiffness of various parts of the molecule; that is, we can establish its **force field**, the set of force constants corresponding to all the displacements of the atoms. The force field may also be estimated by using the semi-empirical, *ab initio*, and density functional theory computational techniques described in Topics 28–30. Superimposed on the simple force field scheme are the complications arising from anharmonicities and the effects of molecular rotation. In the gas phase, rotational transitions affect the spectrum in a way similar to their effect on diatomic molecules (Topic 43), but as polyatomic molecules are typically asymmetric rotors, the resulting band structure is very complex.

In a liquid or a solid, the molecules are unable to rotate freely. In a liquid, for example, a molecule may be able to rotate through only a few degrees before it is struck by another, so it changes its rotational state frequently. This random changing of orientation is called **tumbling**. As a result of this intermolecular buffeting, the lifetimes of rotational states in liquids are very short, so in most cases the rotational energies are ill-defined. Collisions occur at a rate of about $10^{13}\,\mathrm{s}^{-1}$ and, even allowing for only a 10 per cent success rate in knocking the molecule into another rotational state, a lifetime broadening (eqn 40.14, in the form $\delta\tilde{\nu} \approx 1/2\pi c\tau$) of more than $1\,\mathrm{cm}^{-1}$ can easily result. The rotational structure of the vibrational spectrum is blurred by this effect, so the infrared spectra of molecules in condensed phases usually consist of broad lines spanning the entire range of the resolved gas-phase spectrum, and showing no branch structure.

One very important application of infrared spectroscopy to condensed-phase samples, and for which the blurring of the rotational structure by random collisions is a welcome simplification, is to chemical analysis. The vibrational spectra of different groups in a molecule give rise to absorptions at characteristic frequencies because a normal mode of even a very large molecule is often dominated by the motion of a small group of atoms. The intensities of the vibrational bands that can be identified with the motions of small groups are also transferable between molecules. Consequently, the molecules in a sample can often be identified by examining its infrared spectrum and referring to a table of characteristic frequencies and intensities (Table 44.1).

Table 44.1* Typical vibrational wavenumbers

Vibration type	$\tilde{\nu}/\mathrm{cm}^{-1}$
C—H stretch	2850–2960
C—H bend	1340–1465
C—C stretch, bend	700–1250
C═C stretch	1620–1680

* More values are given in the *Resource section*.

Example 44.2 Interpreting an infrared spectrum

The infrared spectrum of an organic compound is shown in Fig. 44.6. Suggest an identification.

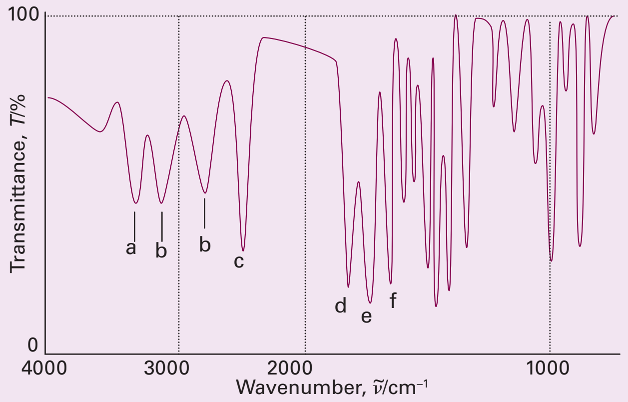

Figure 44.6 A typical infrared absorption spectrum taken by forming a sample into a disk with potassium bromide. As explained in the example, the substance can be identified as $O_2NC_6H_4{-}C{\equiv}C{-}COOH$.

Method Some of the features at wavenumbers above $1500\,\mathrm{cm}^{-1}$ can be identified by comparison with the data in Table 44.1.

Answer (a) C—H stretch of a benzene ring, indicating a substituted benzene; (b) carboxylic acid O—H stretch, indicating a carboxylic acid; (c) the strong absorption of a conjugated C≡C group, indicating a substituted alkyne; (d) this strong absorption is also characteristic of a carboxylic acid that is conjugated to a carbon–carbon multiple bond; (e) a characteristic vibration of a benzene ring, confirming the deduction drawn from (a); (f) a characteristic absorption of a nitro group ($-NO_2$) connected to a multiply bonded carbon–carbon system, suggesting a nitro-substituted benzene. The molecule contains as components a benzene ring, an aromatic carbon–carbon bond, a –COOH group, and a $-NO_2$ group. The molecule is in fact $O_2N{-}C_6H_4{-}C{\equiv}C{-}COOH$. A more detailed analysis and comparison of the fingerprint region shows it to be the 1,4-isomer.

Self-test 44.3 Suggest an identification of the organic compound responsible for the spectrum shown in Fig. 44.7. *Hint*: The molecular formula of the compound is C_3H_5ClO.

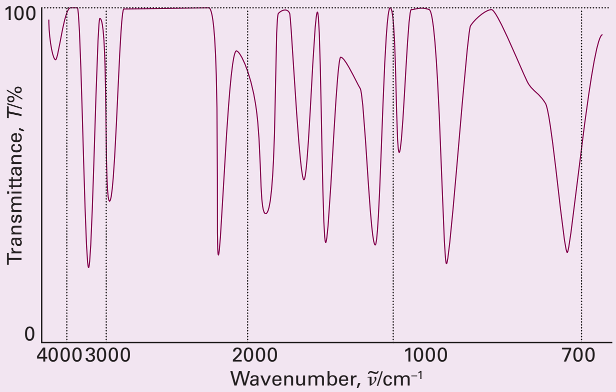

Figure 44.7 The spectrum considered in Self-test 44.3.

Answer: $CH_2{=}CClCH_2OH$

44.3 Vibrational Raman spectra of polyatomic molecules

The normal modes of vibration of molecules are Raman active if they are accompanied by a changing polarizability. A closer analysis of infrared and Raman activity of normal modes based on considerations of symmetry leads to the **exclusion rule**:

> If the molecule has a centre of symmetry
> then no modes can be both infrared and Raman active.

Exclusion rule

(A mode may be inactive in both.) Because it is often possible to judge intuitively if a mode changes the molecular dipole moment, we can use this rule to identify modes that are not Raman active.

Brief illustration 44.2 Raman active modes of polyatomic molecules

The symmetric stretch of CO_2 alternately swells and contracts the molecule: this motion changes the polarizability of the molecule, so the mode is Raman active. The other modes of CO_2 leave the polarizability unchanged, so they are Raman inactive. Furthermore, the exclusion rule applies to CO_2 because it has a centre of symmetry.

Self-test 44.4 Does the exclusion rule apply to H_2O or CH_4?

Answer: No; neither molecule has a centre of symmetry

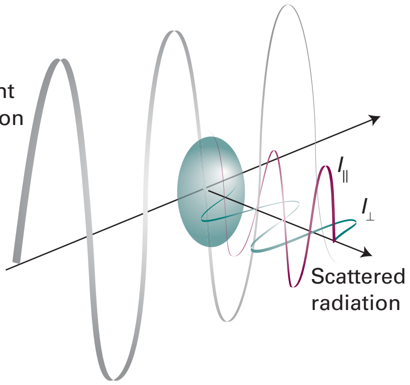

Figure 44.8 The definition of the planes used for the specification of the depolarization ratio, ρ, in Raman scattering.

The assignment of Raman lines to particular vibrational modes is aided by noting the state of polarization of the scattered light. The **depolarization ratio**, ρ, of a line is the ratio of the intensities, I, of the scattered light with polarizations perpendicular and parallel to the plane of polarization of the incident radiation:

$$\rho = \frac{I_\perp}{I_\parallel} \qquad \textit{Definition} \quad \text{Depolarization ratio} \qquad (44.2)$$

To determine ρ, the intensity of a Raman line is measured with a polarizing filter (a 'half-wave plate') first parallel and then perpendicular to the polarization of the incident beam. If the emergent light is not polarized, then both intensities are the same and ρ is close to 1; if the light retains its initial polarization, then $I_\perp = 0$, so $\rho = 0$ (Fig. 44.8). A line is classified as **depolarized** if it has ρ close to or greater than 0.75 and as **polarized** if $\rho < 0.75$. Only totally symmetrical vibrations give rise to polarized lines in which the incident polarization is largely preserved. Vibrations that are not totally symmetrical give rise to depolarized lines because the incident radiation can give rise to radiation in the perpendicular direction too.

44.4 Symmetry aspects of molecular vibrations

One of the most powerful ways of dealing with normal modes, especially of complex molecules, is to classify them according to their symmetries. Each normal mode must belong to one of the symmetry species of the molecular point group, as discussed in Topics 31–33.

Example 44.3 Identifying the symmetry species of a normal mode

Establish the symmetry species of the normal mode vibrations of CH_4, which belongs to the group T_d.

Method The first step in the procedure is to identify the symmetry species of the irreducible representations spanned by all the $3N$ displacements of the atoms, using the characters of the molecular point group. Find these characters by counting 1 if the displacement is unchanged under a symmetry operation, −1 if it changes sign, and 0 if it is changed into some other displacement. Next, subtract the symmetry species of the translations. Translational displacements span the same symmetry species as x, y, and z, so they can be obtained from the right-most column of the character table. Finally, subtract the symmetry species of the rotations, which are also given in the character table (and denoted there by R_x, R_y, or R_z).

Answer There are $3\times5=15$ degrees of freedom, of which $(3\times5)-6=9$ are vibrations. Refer to Fig. 44.9. Under E, no displacement coordinates are changed, so the character is 15. Under C_3, no displacements are left unchanged, so the character is 0. Under the C_2 indicated, the z-displacement of the central atom is left unchanged, whereas its x- and y-components both change sign. Therefore $\chi(C_2)=1-1-1+0+0+\ldots=-1$. Under the S_4 indicated, the z-displacement of the central atom is reversed, so $\chi(S_4)=-1$. Under σ_d, the x- and z-displacements of C, H_3, and H_4 are left unchanged and the y-displacements are reversed; hence $\chi(\sigma_d)=3+3-3=3$. The characters are therefore 15, 0, −1, −1, 3. By decomposing the direct product (Topic 33), we find that this representation spans $A_1+E+T_1+3T_2$. The translations span T_2; the rotations span T_1. Hence, the nine vibrations span A_1+E+2T_2. The modes are shown in Fig. 44.10. We shall see in the next subsection that symmetry analysis gives a quick way of deciding which modes are active.

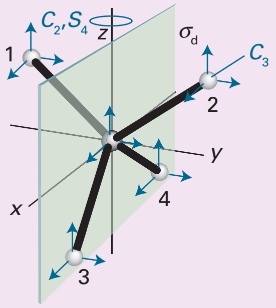

Figure 44.9 The atomic displacements of CH_4 and the symmetry elements used to calculate the characters.

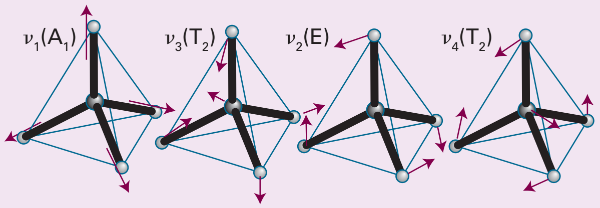

Figure 44.10 Typical normal modes of vibration of a tetrahedral molecule. There are in fact two modes of symmetry species E and three modes of each T_2 symmetry species.

Self-test 44.5 Establish the symmetry species of the normal modes of H_2O.

Answer: $2A_1+B_2$

(a) Infrared activity of normal modes

It is best to use group theory to judge the activities of more complex modes of vibration. This is easily done by checking the character table of the molecular point group for the symmetry species of the irreducible representations spanned by x, y, and z, for their species are also the symmetry species of the components of the electric dipole moment. Then apply the following rule, which is developed in the following *Justification*:

> If the symmetry species of a normal mode is the same as any of the symmetry species of x, y, or z, then the mode is infrared active.

Symmetry test for IR activity

Brief illustration 44.3 Infrared activity of modes

To decide which modes of CH_4 are IR active, we note that we found in Example 44.3 that the symmetry species of the normal modes are A_1+E+2T_2. Therefore, because x, y, and z span T_2 in the group T_d, only the T_2 modes are infrared active. The distortions accompanying these modes lead to a changing dipole moment. The A_1 mode, which is inactive, is the symmetrical 'breathing' mode of the molecule.

Self-test 44.6 Which of the normal modes of H_2O are infrared active?

Answer: All three

Justification 44.2 The infrared activity of normal modes

The rule hinges on the form of the transition dipole moment (Topic 16): $\mu_{\mathrm{fi},x}\propto\int\psi_{v_\mathrm{f}}^{*}x\psi_{v_\mathrm{i}}\,\mathrm{d}x$ in the x-direction, with similar expressions for the two other components of the transition moment. Consider a harmonic oscillator in the x-direction undergoing a transition from the ground vibrational state ($v_i=0$) to the first excited state ($v_f=1$). Because $\psi_0 \propto e^{-x^2}$ and $\psi_1 \propto xe^{-x^2}$ (Topic 12), the components of the transition dipole moment take the following forms:

- $\int_{-\infty}^{+\infty} \overbrace{xe^{-x^2}}^{\text{form of }\psi_1} \overbrace{x}^{\text{form of }\mu_x} \overbrace{e^{-x^2}}^{\text{form of }\psi_0} dx = \int_{-\infty}^{+\infty} x^2 e^{-2x^2} dx$ in the x-direction. As can be verified by direct calculation, this integral does not vanish.
- $\int_{-\infty}^{+\infty} xye^{-2x^2} dx$ and $\int_{-\infty}^{+\infty} xze^{-2x^2} dx$ in the y- and z-directions, respectively. A direct calculation shows that both integrals vanish.

Consequently, the excited state wavefunction must have the same symmetry as the displacement x.

(b) Raman activity of normal modes

Group theory provides an explicit recipe for judging the Raman activity of a normal mode. First, we need to know that the polarizability transforms in the same way as the quadratic forms (x^2, xy, etc.) listed in character tables. The justification of this observation is that the polarizability α of a molecule is calculated from second-order perturbation theory (Topic 15), with the perturbation $-\boldsymbol{\mu}\cdot\boldsymbol{\mathcal{E}}$. Products of integrals of the form $\int\psi_0^*\boldsymbol{\mu}\psi_n d\tau$ and $\int\psi_n^*\boldsymbol{\mu}\psi_0 d\tau$ occur in the numerator of the expression for α, and hence terms proportional to components of $\boldsymbol{rr}$, such as x^2 and xy then occur. Then we use the following rule:

> If the symmetry species of a normal mode is the same as the symmetry species of a quadratic form, then the mode is Raman active.

Symmetry test for Raman activity

Brief illustration 44.4 Raman activity of modes

To decide which of the vibrations of CH_4 are Raman active, refer to the T_d character table. It was established in Example 44.3 that the symmetry species of the normal modes are A_1+E+2T_2. Because the quadratic forms span A_1+E+T_2, all the normal modes are Raman active. By combining this information with that in *Brief illustration* 44.3, we see how the infrared and Raman spectra of CH_4 are assigned. The assignment of spectral features to the T_2 modes is straightforward because these are the only modes that are both infrared and Raman active. This leaves the A_1 and E modes to be assigned in the Raman spectrum. Measurement of the depolarization ratio distinguishes between these modes because the A_1 mode, being totally symmetric, is polarized and the E mode is depolarized.

Self-test 44.7 Which of the vibrational modes of H_2O are Raman active?

Answer: All three

Checklist of concepts

☐ **1.** A **normal mode** is an independent, synchronous motion of atoms or groups of atoms that may be excited without leading to the excitation of any other normal mode.

☐ **2.** The number of normal modes is $3N-6$ (for nonlinear molecules) or $3N-5$ (linear molecules).

☐ **3.** A normal mode is infrared active if it is accompanied by a change of dipole moment. The specific selection rule is $\Delta v_q=\pm1$.

☐ **4.** The **exclusion rule** states that, if the molecule has a centre of symmetry, then no modes can be both infrared and Raman active.

☐ **5.** Totally symmetrical vibrations give rise to polarized lines.

☐ **6.** A normal mode is infrared active if its symmetry species is the same as any of the symmetry species of x, y, or z.

☐ **7.** A normal mode is Raman active if its symmetry species is the same as the symmetry species of a quadratic form.

Checklist of equations

Property	Equation	Comment	Equation number
Vibrational terms of normal modes	$\tilde{G}_q(v)=\left(v+\frac{1}{2}\right)\tilde{\nu}_q$, $\tilde{\nu}_q=(1/2\pi c)(k_{f,q}/m_q)^{1/2}$		44.1
Depolarization ratio	$\rho=I_{\perp}/I_{\parallel}$	Depolarized lines: ρ close to or greater than 0.75 Polarized lines: $\rho<0.75$	44.2

TOPIC 45

Electronic spectroscopy

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➤ Why do you need to know this material?

Many of the colours of the objects in the world around us stem from transitions in which an electron is promoted from one orbital of a molecule or ion into another. In some cases the relocation of an electron may be so extensive that it results in the breaking of a bond and the initiation of a chemical reaction. To understand these physical and chemical phenomena, you need to explore the origins of electronic transitions in molecules.

➤ What is the key idea?

Electronic transitions occur within a stationary nuclear framework.

➤ What do you need to know already?

You need to be familiar with the general features of spectroscopy (Topic 40), the quantum mechanical origins of selection rules (Topic 16), and vibration–rotation spectra (Topic 43); it would be helpful to be aware of atomic term symbols (Topic 21).

Unlike for the rotational and vibrational modes of motion treated in Topics 41–44, simple analytical expressions for the electronic energy levels of molecules cannot be given. Therefore we concentrate on the qualitative features of electronic transitions.

To set the scene, consider a molecule in the lowest vibrational state of its ground electronic state. The nuclei are (in a classical sense) at their equilibrium locations and experience no net force from the electrons and other nuclei in the molecule. The electron distribution is changed when an electronic transition occurs and the nuclei become subjected to different forces. In response, they start to vibrate around their new equilibrium locations. The resulting vibrational transitions that accompany the electronic transition give rise to the **vibrational structure** of the electronic transition. This structure can be resolved for gaseous samples, but in a liquid or solid the lines usually merge together and result in a broad, almost featureless band (Fig. 45.1).

The energies needed to change the electron distributions of molecules are of the order of several electronvolts (1 eV is equivalent to about 8000 cm^{-1} or 100 kJ mol^{-1}). Consequently, the photons emitted or absorbed when such changes occur lie in the visible and ultraviolet regions of the spectrum (Table 45.1). What follows is a discussion of absorption processes. Emission processes are discussed in Topic 46.

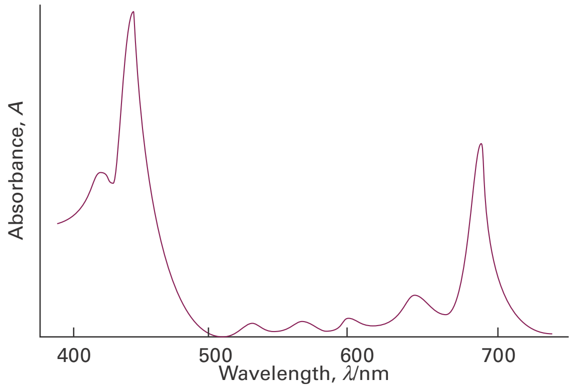


Figure 45.1 The absorption spectrum of chlorophyll in the visible region. Note that it absorbs in the red and blue regions, and that green light is not absorbed.

Table 45.1* Colour, wavelength, frequency, and energy of light

Colour	λ/nm	$\nu/(10^{14}\ \mathrm{Hz})$	$E/(\mathrm{kJ\ mol^{-1}})$
Infrared	>1000	<3.0	<120
Red	700	4.3	170
Yellow	580	5.2	210
Blue	470	6.4	250
Ultraviolet	<400	>7.5	>300

* More values are given in the *Resource section*.

45.1 The electronic spectra of diatomic molecules

Topic 21 explains how the states of atoms are expressed by using term symbols and how the selection rules for electronic transitions can be expressed in terms of these term symbols. Much the same is true of diatomic molecules, one principal difference being the replacement of full spherical symmetry of atoms by the cylindrical symmetry defined by the axis of the molecule. The second principal difference is the fact that a diatomic molecule can vibrate and rotate.

(a) Term symbols

The term symbols of linear molecules (the analogues of the symbols ^{2}P, etc. for atoms) are constructed in a similar way to those for atoms, with the Roman uppercase letter (the P in this instance) representing the total orbital angular momentum of the electrons around the nucleus. In a linear molecule, and specifically a diatomic molecule, a Greek uppercase letter represents the total orbital angular momentum of the electrons around the internuclear axis. If this component of orbital angular momentum is $\Lambda\hbar$ with $\Lambda=0, \pm1, \pm2, \ldots$, we use the following designation:

$\lvert\Lambda\rvert$	0	1	2	…
	Σ	Π	Δ	…

These labels are the analogues of S, P, D, … for atoms for states with $L=0, 1, 2, \ldots$. To decide on the value of L for atoms we have to use the Clebsch–Gordan series (Topic 21) to couple the individual angular momenta. The procedure to determine Λ is much simpler in a diatomic molecule because we simply add the values of the individual components of each electron, $\lambda\hbar$:

$$\Lambda=\lambda_1+\lambda_2+\ldots \tag{45.1}$$

We note the following:

- A single electron in a σ orbital has $\lambda=0$.

The orbital is cylindrically symmetrical and has no angular nodes when viewed along the internuclear axis. Therefore, if that is the only type of electron present, $\Lambda=0$. The term symbol for the ground state of H_2^+ with electron configuration $1\sigma_g^2$ is therefore Σ.

- A π electron in a diatomic molecule has one unit of orbital angular momentum about the internuclear axis ($\lambda=\pm1$).

If it is the only electron outside a closed shell, it gives rise to a Π term. If there are two π electrons (as in the ground state of O_2, with configuration [closed shell] $1\pi_g^2$), there are two possible outcomes. If the electrons are travelling in opposite directions, then $\lambda_1=+1$ and $\lambda_2=-1$ (or vice versa) and $\Lambda=0$, corresponding to a Σ term. Alternatively, the electrons might occupy the same π orbital and $\lambda_1=\lambda_2=+1$ (or -1), and $\Lambda=\pm2$, corresponding to a Δ term. In O_2 it is energetically favourable for the electrons to occupy different orbitals, so the ground term is Σ.

As in atoms, we use a left superscript with the value of $2S+1$ to denote the multiplicity of the term, where S is the total spin quantum number of the electrons.

Brief illustration 45.1 Multiplicity of a term

It follows from the procedure for assigning multiplicity of terms that for H_2^+, because there is only one electron, $S=s=\frac{1}{2}$ and the term symbol is $^2\Sigma$, a doublet term. In O_2, because in the ground state the two π electrons occupy different orbitals (as we saw above), they may have either parallel or antiparallel spins; the lower energy is obtained (as in atoms) if the spins are parallel, so $S=1$ and the ground state is $^3\Sigma$.

Self-test 45.1 What are S and the term for H_2?

Answer: $S=0$, $^1\Sigma$

The overall parity of the state (its symmetry under inversion through the centre of the molecule, if it has one) is added as a right subscript to the term symbol. For H_2^+ in its ground state, the parity of the only occupied orbital ($1\sigma_g$) is g (gerade, even), so the term itself is also g, and in full dress is ${}^2\Sigma_g$. If there are several electrons, the overall parity is calculated by noting the parity of each occupied orbital and using

$$g \times g = g \quad u \times u = g \quad u \times g = u \tag{45.2}$$

These rules are generated by interpreting g as +1 and u as −1. As a consequence:

- The term symbol for the ground state of any closed-shell homonuclear diatomic molecule is ${}^1\Sigma_g$ because the spin is zero (a singlet term in which all electrons paired), there is no orbital angular momentum from a closed shell, and the overall parity is g.
- If the molecule is heteronuclear, parity is irrelevant and the ground state of a closed-shell species, such as CO, is ${}^1\Sigma$.

Brief illustration 45.2 Term symbol of O_2 1

The parity of the ground state of O_2, with configuration [closed shell]$1\pi_g^2$, is $g \times g = g$, so it is denoted ${}^3\Sigma_g$. An excited configuration of O_2 is [closed shell]$1\pi_g^2$, with both π electrons in the same orbital. As we have seen, $|\Lambda| = 2$, represented by Δ. The two electrons must be paired if they occupy the same orbital, so $S = 0$. The overall parity is $g \times g = g$. Therefore, the term symbol is ${}^1\Delta_g$.

Self-test 45.2 The term symbol for one of the excited states of H_2 is ${}^3\Pi_u$. To which excited-state configuration does this term symbol correspond?

Answer: $1\sigma_g^1 1\pi_u^1$

It is shown in Topic 21 that electronic angular momentum is an aspect of the symmetry of states. That remains true for linear molecules provided we confine our attention to motion around the internuclear axis, and the term symbols denote various aspects of the rotational symmetry of the electronic wavefunction of the molecule. With that in mind, there is an additional symmetry operation that distinguishes different types of Σ term: reflection in a plane containing the internuclear axis. A + superscript on Σ is used to denote a wavefunction that does not change sign under this reflection and a – sign is used if the wavefunction changes sign (Fig. 45.2).

Brief illustration 45.3 Term symbol of O_2 2

If we think of O_2 in its ground state as having one electron in $1\pi_{g,x}$, which changes sign under reflection in the *yz*-plane, and the other electron in $1\pi_{g,y}$, which does not change sign under reflection in the same plane, then the overall reflection symmetry is (closed shell) × (+) × (−) = (−), and the full term symbol of the ground electronic state of O_2 is ${}^3\Sigma_g^-$.

Self-test 45.3 What is the full term symbol of the ground electronic state of Li_2^+?

Answer: ${}^2\Sigma_g^+$

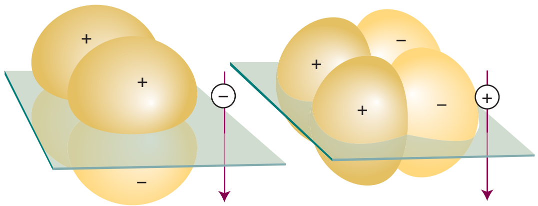


Figure 45.2 The + or – on a term symbol refers to the overall symmetry of a configuration under reflection in a plane containing the two nuclei.

As for atoms, sometimes it is necessary to denote the total angular momentum. In atoms we use the quantum number *J*, which appears as a right subscript in the term symbol, as in ${}^2P_{1/2}$, with different values of *J* corresponding to different *levels* of a term. In a linear molecule, only the angular momentum about the internuclear axis is well defined, and has the value $\Omega\hbar$. For light molecules, where the spin–orbit coupling is weak, Ω is obtained by adding together the components of orbital angular momentum around the axis (the value of Λ) and the component of the electron spin on that axis (Fig. 45.3). The latter is denoted Σ, where $\Sigma = S, S-1, S-2, \ldots, -S$. (It is important to distinguish between the upright term symbol Σ and the sloping quantum number Σ.) Then

$$\Omega = \Lambda + \Sigma \tag{45.3}$$

The value of $|\Omega|$ may then be attached to the term symbol as a right subscript (just like *J* is used in atoms) to denote the different levels. These levels differ in energy, as in atoms, as a result of spin–orbit coupling.

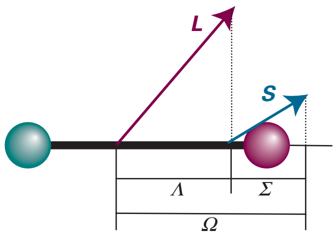


Figure 45.3 The coupling of spin and orbital angular momenta in a linear molecule: only the components along the internuclear axis are conserved.

Brief illustration 45.4 Term symbol of NO

The ground state configuration of NO is … π_g^1, so it is a $^2\Pi$ term with $\Lambda = \pm 1$ and $\Sigma = \pm\frac{1}{2}$. Therefore, there are two levels of the term, one with $\Omega = \pm\frac{1}{2}$ and the other with $\pm\frac{3}{2}$, denoted $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, respectively. Each level is doubly degenerate (corresponding to the opposite signs of Ω). In NO, $^2\Pi_{1/2}$ lies slightly lower than $^2\Pi_{3/2}$.

Self-test 45.4 What are the levels of the term for the ground electronic state of O_2^-?

Answer: $^2\Pi_{1/2}$, $^2\Pi_{3/2}$

(b) Selection rules

A number of selection rules govern which transitions will be observed in the electronic spectrum of a molecule. The selection rules concerned with changes in angular momentum are

$$\Delta\Lambda = 0, \pm 1 \quad \Delta S = 0 \qquad \Delta\Sigma = 0 \quad \Delta\Omega = 0, \pm 1 \qquad (45.4)$$

Linear molecules Selection rules for electronic spectra

As in atoms (Topic 21), the origins of these rules are conservation of angular momentum during a transition and the fact that a photon has a spin of 1.

There are two selection rules concerned with changes in symmetry. First, as we show in the following *Justification*,

For Σ terms, only $\Sigma^+ \leftrightarrow \Sigma^+$ and $\Sigma^- \leftrightarrow \Sigma^-$ are allowed.

Second, the **Laporte selection rule** for centrosymmetric molecules (those with a centre of inversion) states that *the only allowed transitions are transitions that are accompanied by a change of parity*. That is,

For centrosymmetric molecules, only $u \rightarrow g$ and $g \rightarrow u$ are allowed.

Laporte selection rule

Justification 45.1 Symmetry-based selection rules

The last two selection rules result from the fact that the electric-dipole transition moment introduced in Topic 16, $\boldsymbol{\mu}_{fi} = \int \psi_f^* \boldsymbol{\mu} \psi_i d\tau$, vanishes unless the integrand is invariant under all symmetry operations of the molecule.

The z-component of the dipole moment operator is the component of $\boldsymbol{\mu}$ responsible for $\Sigma \leftrightarrow \Sigma$ transitions (the other components have Π symmetry and cannot make a contribution). The z-component of $\boldsymbol{\mu}$ has (+) symmetry with respect to reflection in a plane containing the internuclear axis. Therefore, for a $(+) \leftrightarrow (-)$ transition, the overall symmetry of the transition dipole moment is $(+) \times (+) \times (-) = (-)$, so it must be zero and hence $\Sigma^+ \leftrightarrow \Sigma^-$ transitions are not allowed. The integrals for $\Sigma^+ \leftrightarrow \Sigma^+$ and $\Sigma^- \leftrightarrow \Sigma^-$ transform as $(+) \times (+) \times (+) = (+)$ and $(-) \times (+) \times (-) = (+)$, respectively, and so both transitions are allowed.

The three components of $\boldsymbol{\mu}$ transform like x, y, and z, and in a centrosymmetric molecule are all u (ungerade, odd). Therefore, for a $g \rightarrow g$ transition, the overall parity of the transition dipole moment is $g \times u \times g = u$, so it must be zero. Likewise, for a $u \rightarrow u$ transition, the overall parity is $u \times u \times u = u$, so the transition dipole moment must also vanish. Hence, transitions without a change of parity are forbidden. For a $g \leftrightarrow u$ transition the integral transforms as $g \times u \times u = g$, and is allowed.

A forbidden $g \rightarrow g$ transition can become allowed if the centre of symmetry is eliminated by an asymmetrical vibration, such as the one shown in Fig. 45.4. When the centre of symmetry is lost, $g \rightarrow g$ and $u \rightarrow u$ transitions are no longer parity-forbidden and become weakly allowed. A transition that derives its intensity from an asymmetrical vibration of a molecule is called a **vibronic transition**.

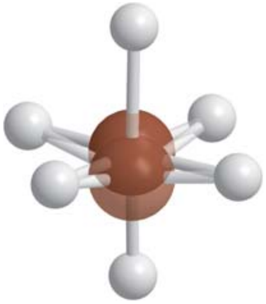


Figure 45.4 A d–d transition is parity-forbidden because it corresponds to a g–g transition. However, a vibration of the molecule can destroy the inversion symmetry of the molecule and the g,u classification no longer applies. The removal of the centre of symmetry gives rise to a vibronically allowed transition.

Brief illustration 45.5 Allowed transitions of O_2

If we were presented with the following possible transitions in the electronic spectrum of O_2, namely $^3\Sigma_g^- \leftarrow {}^3\Sigma_u^-$, $^3\Sigma_g^- \leftarrow {}^1\Delta_g$, $^3\Sigma_g^- \leftarrow {}^3\Sigma_u^+$, we could decide which are allowed by constructing the following table and referring to the rules. Forbidden values are in red.

	ΔS	$\Delta\Lambda$	$\Sigma^\pm \leftarrow \Sigma^\pm$	**Change of parity**	
$^3\Sigma_g^- \leftarrow {}^3\Sigma_u^-$	0	0	$\Sigma^- \leftarrow \Sigma^-$	$g \leftarrow u$	Allowed
$^3\Sigma_g^- \leftarrow {}^1\Delta_g$	+1	−2	Not applicable	$g \leftarrow g$	Forbidden
$^3\Sigma_g^- \leftarrow {}^3\Sigma_u^+$	0	0	$\Sigma^- \leftarrow \Sigma^+$	$g \leftarrow u$	Forbidden

Self-test 45.5 Which of the following electronic transitions are allowed in O_2: $^3\Sigma_g^- \leftrightarrow {}^1\Sigma_g^+$ and $^3\Sigma_g^- \leftrightarrow {}^3\Delta_u$?

Answer: None

The large number of photons in an incident beam generated by a laser gives rise to a qualitatively different branch of spectroscopy, for the photon density is so great that more than one photon may be absorbed by a single molecule and give rise to **multiphoton processes**. One application of multiphoton processes is that states inaccessible by conventional one-photon spectroscopy become observable because the overall transition occurs with no change of parity. For example, in one-photon spectroscopy, only g↔u transitions are observable; in two-photon spectroscopy, however, the overall outcome of absorbing two photons is a g←g or a u←u transition.

(c) Vibrational structure

To account for the vibrational structure in electronic spectra of molecules (Fig. 45.5), we apply the **Franck–Condon principle**:

> Because the nuclei are so much more massive than the electrons, an electronic transition takes place very much faster than the nuclei can respond.

Franck–Condon principle

As a result of the transition, electron density is rapidly built up in new regions of the molecule and removed from others. In classical terms, the initially stationary nuclei suddenly experience a new force field, to which they respond by beginning to vibrate and (in classical terms) swing backwards and forwards from their original separation (which was maintained during the rapid electronic excitation). The stationary equilibrium separation of the nuclei in the initial electronic state therefore becomes a turning point in the final electronic state (Fig. 45.6). We can imagine the transition as taking place up the vertical line in Fig. 45.6. This interpretation is the origin of the expression **vertical transition**, which denotes an electronic transition that occurs without change of nuclear geometry.

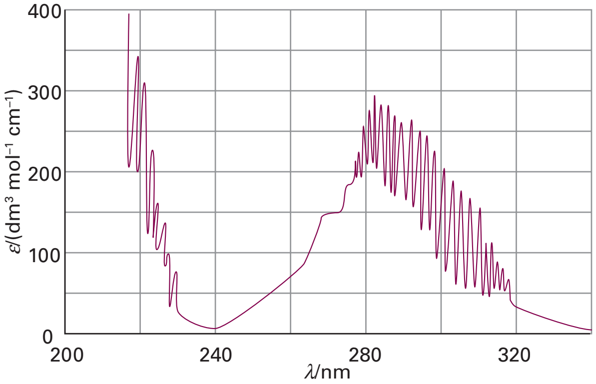


Figure 45.5 The electronic spectra of some molecules show significant vibrational structure. Shown here is the ultraviolet spectrum of gaseous SO_2 at 298 K. As explained in the text, the sharp lines in this spectrum are due to transitions from a lower electronic state to different vibrational levels of a higher electronic state. Vibrational structure due to transitions to two different excited electronic states is apparent.

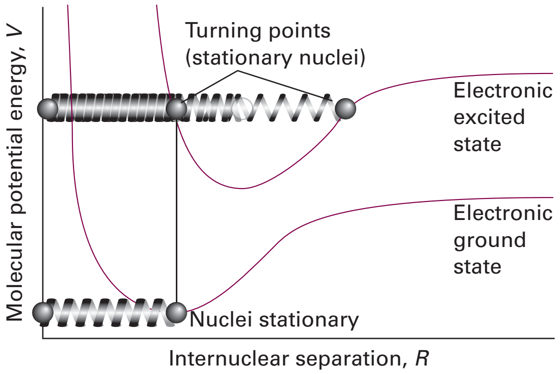


Figure 45.6 According to the Franck–Condon principle, the most intense vibronic transition is from the ground vibrational state to the vibrational state lying vertically above it. As a result of the vertical transition, the nuclei suddenly experience a new force field, to which they respond through their vibrational motion. The equilibrium separation of the nuclei in the initial electronic state therefore becomes a turning point in the final electronic state. Transitions to other vibrational levels also occur, but with lower intensity.

The vibrational structure of the spectrum depends on the relative horizontal position of the two potential energy curves, and a long **vibrational progression**, a lot of vibrational structure, is stimulated if the upper potential energy curve is appreciably displaced horizontally from the lower. The upper curve is usually displaced to greater equilibrium bond lengths because electronically excited states usually have more antibonding character than electronic ground states. The separation of the vibrational lines depends on the vibrational energies of the *upper* electronic state.

The quantum mechanical version of the Franck–Condon principle refines this picture. Instead of saying that the nuclei stay at the same locations and are stationary during the transition, we say that *they retain their initial dynamical state*. In quantum mechanics, the dynamical state is expressed by the wavefunction, so an equivalent statement is that the nuclear wavefunction does not change during the electronic transition. Initially the molecule is in the lowest vibrational state of its ground electronic state with a bell-shaped wavefunction centred on the equilibrium bond length (Fig. 45.7). To find the nuclear state to which the transition takes place, we look for the vibrational wavefunction that most closely resembles this initial wavefunction, for that corresponds to the nuclear dynamical state that is least changed in the transition. Intuitively, we can see that the final wavefunction is the one with a large peak close to the position of the initial bell-shaped function. As explained in Topic 12, provided the vibrational quantum number is not zero, the biggest peaks of vibrational wavefunctions occur close to the edges of the confining potential, so we

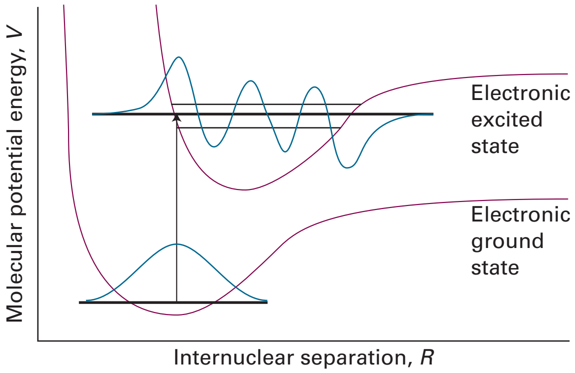


Figure 45.7 In the quantum mechanical version of the Franck–Condon principle, the molecule undergoes a transition to the upper vibrational state that most closely resembles the vibrational wavefunction of the vibrational ground state of the lower electronic state. The two wavefunctions shown here have the greatest overlap integral of all the vibrational states of the upper electronic state and hence are most closely similar.

can expect the transition to occur to those vibrational states, in accord with the classical description. However, several vibrational states have their major peaks in similar positions, so we should expect transitions to occur to a range of vibrational states, as is observed.

The quantitative form of the Franck–Condon principle and the justification of the preceding description is derived from the expression for the transition dipole moment (as in *Justification* 45.1). The dipole moment (and the corresponding operator) is a sum over all nuclei and electrons in the molecule:

$$\boldsymbol{\mu}=-e\sum_i \boldsymbol{r}_i+e\sum_I Z_I\boldsymbol{R}_I \qquad (45.5)$$

where the vectors are the distances from the centre of charge of the molecule. The intensity of the transition is proportional to the square modulus, $|\boldsymbol{\mu}_{\mathrm{fi}}|^2$, of the magnitude of the transition dipole moment, and we show in the following *Justification* that this intensity is proportional to the square modulus of the overlap integral, $S(\upsilon_{\mathrm{f}},\upsilon_{\mathrm{i}})$, between the vibrational states of the initial and final electronic states. This overlap integral is a measure of the match between the vibrational wavefunctions in the upper and lower electronic states: $S=1$ for a perfect match and $S=0$ when there is no similarity.

Justification 45.2 The Franck–Condon approximation

The overall state of the molecule consists of an electronic part, labelled with ε, and a vibrational part, labelled with υ. Therefore, within the Born–Oppenheimer approximation, the transition dipole moment factorizes as follows:

$$\begin{aligned}\boldsymbol{\mu}_{\mathrm{fi}}&=\int\psi^*_{\varepsilon,\mathrm{f}}\psi^*_{\upsilon,\mathrm{f}}\left\{-e\sum_i\boldsymbol{r}_i+e\sum_I Z_I\boldsymbol{R}_I\right\}\psi_{\varepsilon,\mathrm{i}}\psi_{\upsilon,\mathrm{i}}\,\mathrm{d}\tau\\&=-e\sum_i\int\psi^*_{\varepsilon,\mathrm{f}}\boldsymbol{r}_i\psi_{\varepsilon,\mathrm{i}}\,\mathrm{d}\tau_{\mathrm{e}}\int\psi^*_{\upsilon,\mathrm{f}}\psi_{\upsilon,\mathrm{i}}\,\mathrm{d}\tau_{\mathrm{n}}\\&\quad+e\sum_I Z_I\overbrace{\int\psi^*_{\varepsilon,\mathrm{f}}\psi_{\varepsilon,\mathrm{i}}\,\mathrm{d}\tau_e}^{0}\int\psi^*_{\upsilon,\mathrm{f}}\boldsymbol{R}_I\psi_{\upsilon,\mathrm{i}}\,\mathrm{d}\tau_{\mathrm{n}}\end{aligned}$$

The term in blue is zero, because two different electronic states are orthogonal. Therefore,

$$\boldsymbol{\mu}_{\mathrm{fi}}=\overbrace{-e\sum_i\int\psi^*_{\varepsilon,\mathrm{f}}\boldsymbol{r}_i\psi_{\varepsilon,\mathrm{i}}\,\mathrm{d}\tau_{\mathrm{e}}}^{\mu_{\varepsilon,\mathrm{fi}}}\overbrace{\int\psi^*_{\upsilon,\mathrm{f}}\psi_{\upsilon,\mathrm{i}}\,\mathrm{d}\tau_{\mathrm{n}}}^{S(\upsilon_{\mathrm{f}},\upsilon_{\mathrm{i}})}=\boldsymbol{\mu}_{\varepsilon,\mathrm{fi}}S(\upsilon_{\mathrm{f}},\upsilon_{\mathrm{i}})$$

The quantity $\boldsymbol{\mu}_{\varepsilon,\mathrm{fi}}$ is the electric-dipole transition moment arising from the redistribution of electrons (and a measure of the 'kick' this redistribution gives to the electromagnetic field, and vice versa for absorption). The factor $S(\upsilon_{\mathrm{f}},\upsilon_{\mathrm{i}})$, is the overlap integral between the vibrational state with quantum number υ_{i} in the initial electronic state of the molecule, and the vibrational state with quantum number υ_{f} in the final electronic state of the molecule.

Because the transition intensity is proportional to the square of the magnitude of the transition dipole moment, the intensity of an absorption is proportional to $|S(\upsilon_{\mathrm{f}},\upsilon_{\mathrm{i}})|^2$, which is known as the **Franck–Condon factor** for the transition:

$$|S(\upsilon_{\mathrm{f}},\upsilon_{\mathrm{i}})|^2=\left(\int\psi^*_{\upsilon,\mathrm{f}}\psi_{\upsilon,\mathrm{i}}\,\mathrm{d}\tau_{\mathrm{n}}\right)^2 \qquad \text{Franck–Condon factor} \qquad (45.6)$$

It follows that the greater the overlap of the vibrational state wavefunction in the upper electronic state with the vibrational wavefunction in the lower electronic state, the greater the absorption intensity of that particular simultaneous electronic and vibrational transition.

Example 45.1 Calculating a Franck–Condon factor

Consider the transition from one electronic state to another, their bond lengths being R_{e} and R'_{e} and their force constants equal. Calculate the Franck–Condon factor for the 0–0 transition and show that the transition is most intense when the bond lengths are equal.

Method We need to calculate $S(0,0)$, the overlap integral of the two ground-state vibrational wavefunctions, and then take its square. The difference between harmonic and anharmonic vibrational wavefunctions is negligible for $\upsilon=0$, so harmonic oscillator wavefunctions can be used (Table 12.1).

Answer We use the (real) wavefunctions

$$\psi_0=\left(\frac{1}{\alpha\pi^{1/2}}\right)^{1/2}\mathrm{e}^{-x^2/2\alpha^2}\qquad \psi_0'=\left(\frac{1}{\alpha\pi^{1/2}}\right)^{1/2}\mathrm{e}^{-x'^2/2\alpha^2}$$

where $x=R-R_\mathrm{e}$ and $x'=R-R_\mathrm{e}'$ with $\alpha=(\hbar^2/mk_\mathrm{f})^{1/4}$ (Topic 12). The overlap integral is

$$S(0,0)=\int_{-\infty}^{\infty}\psi_0'\psi_0\,\mathrm{d}R=\frac{1}{\alpha\pi^{1/2}}\int_{-\infty}^{\infty}\mathrm{e}^{-(x^2+x'^2)/2\alpha^2}\,\mathrm{d}x$$

We now write $\alpha z=R-\frac{1}{2}(R_\mathrm{e}+R_\mathrm{e}')$ and manipulate this expression into

$$S(0,0)=\frac{1}{\pi^{1/2}}\mathrm{e}^{-(R_\mathrm{e}-R_\mathrm{e}')^2/4\alpha^2}\overbrace{\int_{-\infty}^{\infty}\mathrm{e}^{-z^2}\,\mathrm{d}z}^{\pi^{1/2}\ (\text{Integral G.1})}=\mathrm{e}^{-(R_\mathrm{e}-R_\mathrm{e}')^2/4\alpha^2}$$

and the Franck–Condon factor is

$$S(0,0)^2=\mathrm{e}^{-(R_\mathrm{e}-R_\mathrm{e}')^2/2\alpha^2}$$

This factor is equal to 1 when $R_\mathrm{e}'=R_\mathrm{e}$ and decreases as the equilibrium bond lengths diverge from each other (Fig. 45.8).

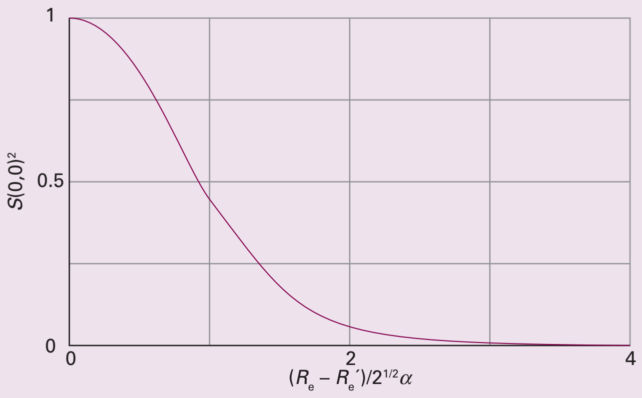


Figure 45.8 The Franck–Condon factor for the arrangement discussed in Example 45.1.

For Br_2, $R_\mathrm{e}=228$ pm and there is an upper state with $R_\mathrm{e}'=266$ pm. Taking the vibrational wavenumber as 250 cm^{-1} gives $S(0,0)^2=5.1\times10^{-10}$, so the intensity of the 0–0 transition is only 5.1×10^{-10} what it would have been if the potential curves had been directly above each other.

Self-test 45.6 Suppose the vibrational wavefunctions can be approximated by rectangular functions of width W and W', centred on the equilibrium bond lengths (Fig. 45.9). Find the corresponding Franck–Condon factors when the centres are coincident and $W'<W$.

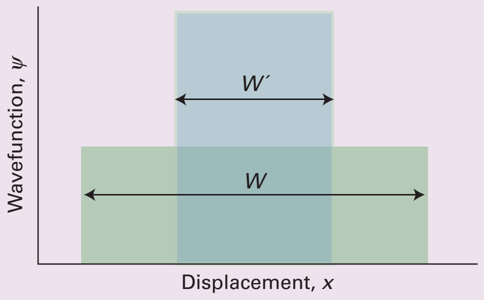


Figure 45.9 The model wavefunctions used in Self-test 45.6.

Answer: $S^2=W'/W$

(d) Rotational structure

Just as in vibrational spectroscopy, where a vibrational transition is accompanied by rotational excitation, so rotational transitions accompany the excitation of the vibrational excitation that accompanies electronic excitation. We therefore see P, Q, and R branches for each vibrational transition, and the electronic transition has a very rich structure. However, the principal difference is that electronic excitation can result in much larger changes in bond length than vibrational excitation causes alone, and the rotational branches have a more complex structure than in vibration–rotation spectra.

We suppose that the rotational constants of the electronic ground and excited states are $\tilde{B}$ and $\tilde{B}'$, respectively. The rotational energy levels of the initial and final states are

$$E(J)=hc\tilde{B}J(J+1)\qquad E(J')=hc\tilde{B}'J'(J'+1)\qquad(45.7)$$

When a transition occurs with $\Delta J=-1$ the wavenumber of the vibrational component of the electronic transition is shifted from $\tilde{\nu}$ to

$$\tilde{\nu}+\tilde{B}'(J-1)J-\tilde{B}J(J+1)=\tilde{\nu}-(\tilde{B}'+\tilde{B})J+(\tilde{B}'-\tilde{B})J^2$$

This transition is a contribution to the P branch (just as in Topic 43). There are corresponding transitions for the Q and R branches with wavenumbers that may be calculated in a similar way. All three branches are:

P branch($\Delta J=-1$):

$$\tilde{\nu}_\mathrm{P}(J)=\tilde{\nu}-(\tilde{B}'+\tilde{B})J+(\tilde{B}'-\tilde{B})J^2\qquad(45.8\mathrm{a})$$

Branch structure

Q branch($\Delta J=0$):

$$\tilde{\nu}_\mathrm{Q}(J)=\tilde{\nu}+(\tilde{B}'-\tilde{B})J(J+1)\qquad(45.8\mathrm{b})$$

R branch($\Delta J=+1$):

$$\tilde{\nu}_\mathrm{R}(J)=\tilde{\nu}+(\tilde{B}'+\tilde{B})(J+1)+(\tilde{B}'-\tilde{B})(J+1)^2\qquad(45.8\mathrm{c})$$

These expressions are the analogues of eqn 43.21.

Example 45.2 Estimating rotational constants from electronic spectra

The following rotational transitions were observed in the 0–0 band of the ${}^1\Sigma^+ \leftarrow {}^1\Sigma^+$ electronic transition of ${}^{63}\mathrm{Cu}^2\mathrm{H}$: $\tilde{\nu}_\mathrm{R}(3) = 23347.69\,\mathrm{cm}^{-1}$, $\tilde{\nu}_\mathrm{P}(3) = 23298.85\,\mathrm{cm}^{-1}$, and $\tilde{\nu}_\mathrm{P}(5) = 23275.77\,\mathrm{cm}^{-1}$. Estimate the values of $\tilde{B}'$ and $\tilde{B}$.

Method Use the method of combination differences introduced in Topic 43: form the differences $\tilde{\nu}_\mathrm{R}(J) - \tilde{\nu}_\mathrm{P}(J)$ and $\tilde{\nu}_\mathrm{R}(J-1) - \tilde{\nu}_\mathrm{P}(J+1)$ from eqns 45.8a and 45.8b, then use the resulting expressions to calculate the rotational constants $\tilde{B}'$ and $\tilde{B}$ from the wavenumbers provided.

Answer From eqns 45.8a and 45.8b it follows that

$$\begin{aligned}&\tilde{\nu}_\mathrm{R}(J) - \tilde{\nu}_\mathrm{P}(J)\\&= (\tilde{B}'+\tilde{B})(J+1) + (\tilde{B}'-\tilde{B})(J+1)^2 - \left\{-\left(\tilde{B}'+\tilde{B}\right)J + \left(\tilde{B}'-\tilde{B}\right)J^2\right\}\\&= 4\tilde{B}'\left(J+\tfrac{1}{2}\right)\tilde{\nu}_\mathrm{R}(J-1) - \tilde{\nu}_\mathrm{P}(J+1)\\&= \left(\tilde{B}'+\tilde{B}\right)J + \left(\tilde{B}'-\tilde{B}\right)J^2 - \left\{-(\tilde{B}'+\tilde{B})(J+1) + (\tilde{B}'-\tilde{B})(J+1)^2\right\}\\&= 4\tilde{B}\left(J+\tfrac{1}{2}\right)\end{aligned}$$

(These equations are analogous to eqns 43.23a and 43.23b.) After using the data provided, we obtain

$$\text{For } J=3\text{:}\quad \tilde{\nu}_\mathrm{R}(3) - \tilde{\nu}_\mathrm{P}(3) = \overbrace{48.84}^{23347.69\,-\,23298.85}\ \mathrm{cm}^{-1} = 14\tilde{B}'$$

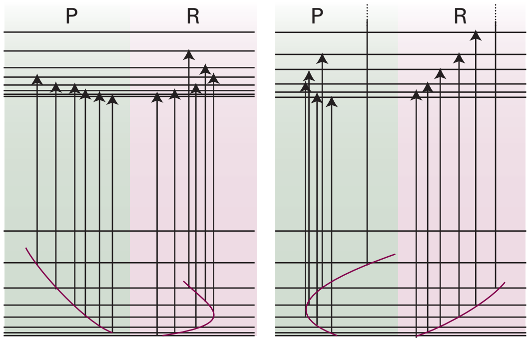
$$\text{For } J=4\text{:}\quad \tilde{\nu}_\mathrm{R}(3) - \tilde{\nu}_\mathrm{P}(5) = \overbrace{71.92}^{23347.69\,-\,23275.77}\ \mathrm{cm}^{-1} = 18\tilde{B}$$

and calculate $\tilde{B}' = 3.489\,\mathrm{cm}^{-1}$ and $\tilde{B} = 3.996\,\mathrm{cm}^{-1}$.

Self-test 45.7 The following rotational transitions were observed in the ${}^1\Sigma^+ \leftarrow {}^1\Sigma^+$ electronic transition of RhN: $\tilde{\nu}_\mathrm{R}(5) = 22\,387.06\,\mathrm{cm}^{-1}$, $\tilde{\nu}_\mathrm{P}(5) = 22\,376.87\,\mathrm{cm}^{-1}$, and $\tilde{\nu}_\mathrm{P}(7) = 22\,373.95\,\mathrm{cm}^{-1}$. Estimate the values of $\tilde{B}'$ and $\tilde{B}$.

Answer: $\tilde{B}' = 0.4632\,\mathrm{cm}^{-1}, \tilde{B} = 0.5042\,\mathrm{cm}^{-1}$

Suppose that the bond length in the electronically excited state is greater than that in the ground state; then $\tilde{B}' < \tilde{B}$ and $\tilde{B}' - \tilde{B}$ is negative. In this case the lines of the R branch converge with increasing J and when J is such that $|\tilde{B}' - \tilde{B}|(J+1) > \tilde{B}' + \tilde{B}$ the lines start to appear at successively decreasing wavenumbers. That is, the R branch has a **band head** (Fig. 45.10a). When the bond is shorter in the excited state than in the ground state, $\tilde{B}' > \tilde{B}$ and $\tilde{B}' - \tilde{B}$ is positive. In this case, the lines of the P branch begin to converge and go through a head when J is such that $|\tilde{B}' - \tilde{B}|J > \tilde{B}' + \tilde{B}$ (Fig. 45.10b).



(a) $\tilde{B}' < \tilde{B}$ (b) $\tilde{B}' > \tilde{B}$

Figure 45.10 When the rotational constants of a diatomic molecule differ significantly in the initial and final states of an electronic transition, the P and R branches show a head. (a) The formation of a head in the R branch when $\tilde{B}' < \tilde{B}$; (b) the formation of a head in the P branch when $\tilde{B}' > \tilde{B}$.

45.2 The electronic spectra of polyatomic molecules

The absorption of a photon can often be traced to the excitation of specific types of electrons or to electrons that belong to a small group of atoms in a polyatomic molecule. For example, when a carbonyl group (>C=O) is present, an absorption at about 290 nm is normally observed, although its precise location depends on the nature of the rest of the molecule. Groups with characteristic optical absorptions are called **chromophores** (from the Greek for 'colour bringer'), and their presence often accounts for the colours of substances (Table 45.2).

(a) d-Metal complexes

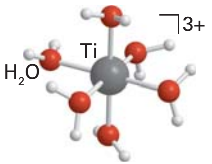
In a free atom, all five d orbitals of a given shell are degenerate. In a d-metal complex, where the immediate environment of the atom is no longer spherical, the d orbitals are not all degenerate, and electrons can absorb energy by making transitions between them.

Table 45.2* Absorption characteristics of some groups and molecules

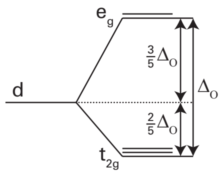
Group	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\lambda_\mathrm{max}/\mathrm{nm}$	$\varepsilon/(\mathrm{dm}^3\,\mathrm{mol}^{-1}\,\mathrm{cm}^{-1})$
C=C ($\pi^* \leftarrow \pi$)	61 000	163	15 000
C=O ($\pi^* \leftarrow \mathrm{n}$)	35 000–37 000	270–290	10–20
$\mathrm{H_2O}$ ($\pi^* \leftarrow \mathrm{n}$)	60 000	167	7000

* More values are given in the *Resource section*.

To see the origin of this splitting in an octahedral complex such as $[Ti(OH_2)_6]^{3+}$ (**1**), we regard the six ligands as point negative charges that repel the d electrons of the central ion (Fig. 45.11). As a result, the orbitals fall into two groups, with $d_{x^2-y^2}$ and d_{z^2} pointing directly towards the ligand positions, and d_{xy}, d_{yz}, and d_{zx} pointing between them. An electron occupying an orbital of the former group has a less favourable potential energy than when it occupies any of the three orbitals of the other group, and so the d orbitals split into the two sets shown in (**2**) with an energy difference Δ_O: a triply degenerate set comprising the d_{xy}, d_{yz}, and d_{zx} orbitals and labelled t_{2g}, and a doubly degenerate set comprising the $d_{x^2-y^2}$ and d_{z^2} orbitals and labelled e_g. The three t_{2g} orbitals lie below the two e_g orbitals in energy; the difference in energy Δ_O is called the **ligand-field splitting parameter** (the O denoting octahedral symmetry). The ligand-field splitting is typically about 10 per cent of the overall energy of interaction between the ligands and the central metal atom, which is largely responsible for the existence of the complex. The d orbitals also divide into two sets in a tetrahedral complex, but in this case the e orbitals lie below the t_2 orbitals (the g,u classification is no longer relevant as a tetrahedral complex has no centre of inversion) and their separation is written Δ_T.



1 $[Ti(OH_2)_6]^{3+}$



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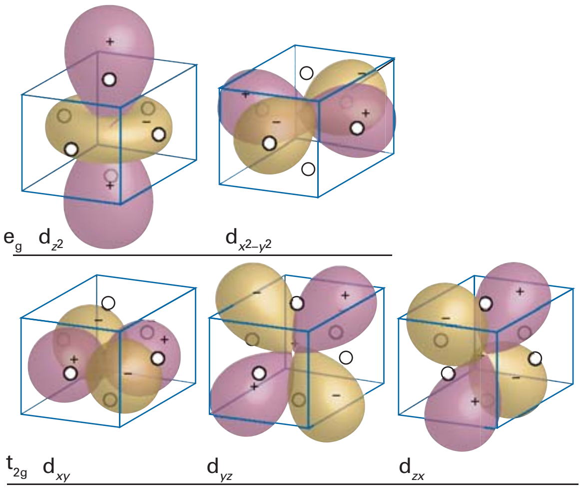

Figure 45.11 The classification of d orbitals in an octahedral environment. The open circles represent the positions of the six (point-charge) ligands. The classification as e_g or t_{2g} arises from considerations of their symmetry characteristics (Topic 33).

Neither Δ_O nor Δ_T is large, so transitions between the two sets of orbitals typically occur in the visible region of the spectrum. The transitions are responsible for many of the colours that are so characteristic of d-metal complexes.

Brief illustration 45.6 The electronic spectrum of a d-metal complex

The spectrum of $[Ti(OH_2)_6]^{3+}$ (**1**) near 20 000 cm^{-1} (500 nm) is shown in Fig. 45.12, and can be ascribed to the promotion of its single d electron from a t_{2g} orbital to an e_g orbital. The wavenumber of the absorption maximum suggests that $\Delta_O \approx 20\,000$ cm^{-1} for this complex, which corresponds to about 2.5 eV.

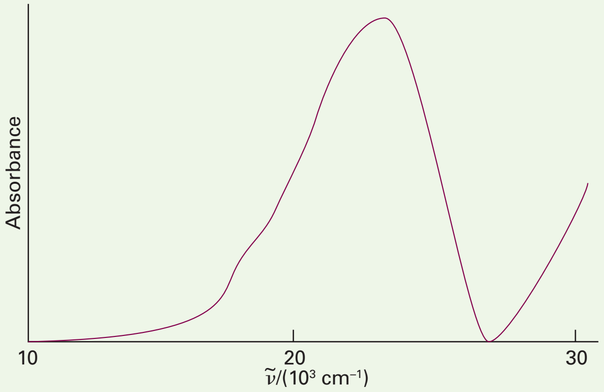

Figure 45.12 The electronic absorption spectrum of $[Ti(OH_2)_6]^{3+}$ in aqueous solution.

Self-test 45.8 Can a complex of the Zn^{2+} ion have a d–d electronic transition? Explain your answer.

Answer: No; all five d orbitals are fully occupied

According to the Laporte rule (Section 45.1b), d–d transitions are parity-forbidden in octahedral complexes because they are g→g transitions (more specifically $e_g \leftarrow t_{2g}$ transitions). However, d–d transitions become weakly allowed as vibronic transitions, joint vibrational and electronic transitions, as a result of coupling to asymmetrical vibrations such as that shown in Fig. 45.4.

A d-metal complex may also absorb radiation as a result of the transfer of an electron from the ligands into the d orbitals of the central atom, or vice versa. In such **charge-transfer transitions** the electron moves through a considerable distance, which means that the transition dipole moment may be large and the absorption correspondingly intense. In the permanganate ion, MnO_4^-, the charge redistribution that accompanies the migration of an electron from the O atoms to the central Mn atom results in strong transition in the range 420–700 nm that accounts for the intense purple colour of the ion. Such an electronic migration from the ligands to the metal corresponds to a **ligand-to-metal charge-transfer transition** (LMCT). The reverse migration, a **metal-to-ligand charge-transfer transition** (MLCT), can also occur. An example is the migration of a d electron into the antibonding π orbitals of an aromatic ligand. The resulting excited state may have a very long lifetime if the electron is extensively delocalized over several aromatic rings.

In common with other transitions, the intensities of charge-transfer transitions are proportional to the square of the transition dipole moment. We can think of the transition moment as a measure of the distance moved by the electron as it migrates from metal to ligand or vice versa, with a large distance of migration corresponding to a large transition dipole moment and therefore a high intensity of absorption. However, because the integrand in the transition dipole is proportional to the product of the initial and final wavefunctions, it is zero unless the two wavefunctions have nonzero values in the same region of space. Therefore, although large distances of migration favour high intensities, the diminished overlap of the initial and final wavefunctions for large separations of metal and ligands favours low intensities (see Problem 45.9).

(b) $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow$ n transitions

Absorption by a C=C double bond results in the excitation of a π electron into an antibonding π* orbital (Fig. 45.13). The chromophore activity is therefore due to a **$\pi^* \leftarrow \pi$ transition** (which is normally read 'π to π-star transition'). Its energy is about 7 eV for an unconjugated double bond, which corresponds to an absorption at 180 nm (in the ultraviolet). When the double bond is part of a conjugated chain, the energies of the molecular orbitals lie closer together and the $\pi^* \leftarrow \pi$ transition moves to longer wavelength; it may even lie in the visible region if the conjugated system is long enough.

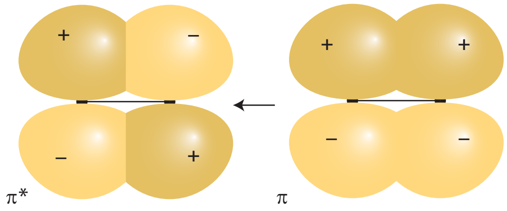

Figure 45.13 A C=C double bond acts as a chromophore. One of its important transitions is the $\pi^* \leftarrow \pi$ transition illustrated here, in which an electron is promoted from a π orbital to the corresponding antibonding orbital.

One of the transitions responsible for absorption in carbonyl compounds can be traced to the lone pairs of electrons on the O atom. The Lewis concept of a 'lone pair' of electrons is represented in molecular orbital theory by a pair of electrons in an orbital confined largely to one atom and not appreciably involved in bond formation. One of these electrons may be excited into an empty π* orbital of the carbonyl group (Fig. 45.14), which gives rise to an **$\pi^* \leftarrow$ n transition** (an 'n to π-star transition'). Typical absorption energies are about 4 eV (290 nm). Because $\pi^* \leftarrow$ n transitions in carbonyls are symmetry forbidden, the absorptions are weak.

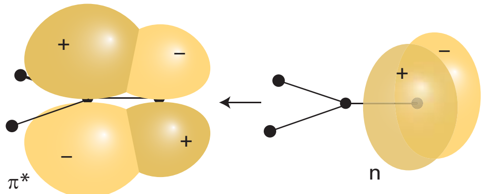

Figure 45.14 A carbonyl group (C=O) acts as a chromophore partly on account of the excitation of a nonbonding O lone-pair electron to an antibonding CO π orbital.

Brief illustration 45.7 $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow$ n transitions

The compound $CH_3CH{=}CHCHO$ has a strong absorption in the ultraviolet at 46 950 cm^{-1} (213 nm) and a weak absorption at 30 000 cm^{-1} (330 nm). The former is a $\pi^* \leftarrow \pi$ transition associated with the delocalized π system C=C−C=O. Delocalization extends the range of the C=O $\pi^* \leftarrow \pi$ transition to lower wavenumbers (longer wavelengths). The latter is an $\pi^* \leftarrow$ n transition associated with the carbonyl chromophore.

Self-test 45.9 Account for the observation that propanone (acetone, $(CH_3)_2CO$) has a strong absorption at 189 nm and a weaker absorption at 280 nm.

Answer: Both transitions are associated with the C=O chromophore, with the weaker being an $\pi^* \leftarrow$ n transition and the stronger a $\pi^* \leftarrow \pi$ transition.

Checklist of concepts

☐ 1. The term symbols of diatomic molecules express the components of electronic angular momentum around the internuclear axis.

☐ 2. Selection rules for electronic transitions are based on considerations of angular momentum and symmetry.

☐ 3. The **Laporte selection rule** states that, for centrosymmetric molecules, only u → g and g → u transitions are allowed.

☐ 4. The **Franck–Condon principle** provides a basis for explaining the vibrational structure of electronic transitions.

☐ 5. In gas-phase samples, rotational structure is present too, and can give rise to **band heads**.

☐ 6. **Chromophores** are groups with characteristic optical absorptions.

☐ 7. In d-metal complexes, the presence of ligands removes the degeneracy of d orbitals and vibrationally allowed **d–d transitions** can occur between them.

☐ 8. **Charge-transfer transitions** typically involve the migration of electrons between the ligands and the central metal atom.

☐ 9. Other chromophores include double bonds (**π* ← π transitions**) and carbonyl groups (**π* ← n transitions**).

Checklist of equations

Property	Equation	Comment	Equation number
Selection rules (angular momentum)	$\Delta\Lambda=0, \pm1$; $\Delta S=0$; $\Delta\Sigma=0$; $\Delta\Omega=0, \pm1$	Linear molecules	45.4
Franck–Condon factor	$\lvert S(v_\mathrm{f},v_\mathrm{i})\rvert^2=\left(\int \psi_{v,\mathrm{f}}^{*}\psi_{v,\mathrm{i}}\,\mathrm{d}\tau_\mathrm{n}\right)^2$		45.6
Rotational structure of electronic spectra (diatomic molecules)	$\tilde{\nu}_\mathrm{P}(J)=\tilde{\nu}-(\tilde{B}'+\tilde{B})J+(\tilde{B}'-\tilde{B})J^2$	P branch ($\Delta J=-1$)	45.8a
	$\tilde{\nu}_\mathrm{Q}(J)=\tilde{\nu}+(\tilde{B}'-\tilde{B})J(J+1)$	Q branch ($\Delta J=0$)	45.8b
	$\tilde{\nu}_\mathrm{R}(J)=\tilde{\nu}+(\tilde{B}'+\tilde{B})(J+1)+(\tilde{B}'-\tilde{B})(J+1)^2$	R branch ($\Delta J=+1$)	45.8c

TOPIC 46

Decay of excited states

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➤ Why do you need to know this material?

Considerable information can be obtained from the photons emitted when excited electronic states decay radiatively back to the ground state. The process also has great technological importance: for instance, lasers have brought unprecedented precision to spectroscopy and are used in medicine and telecommunications.

➤ What is the key idea?

Molecules in excited electronic states decay by emission of electromagnetic radiation or by energy transfer as heat to surrounding molecules.

➤ What do you need to know already?

You need to be familiar with electronic absorption processes in molecules (Topic 45), the difference between spontaneous and stimulated emission of radiation (Topic 16), and the general features of spectroscopy (Topic 40). You need to be aware of the difference between singlet and triplet states (Topic 21) and of the Franck–Condon principle (Topic 45).

A **radiative decay process** is a process in which a molecule discards its excitation energy as a photon, as discussed in Topic 40. In this Topic we pay particular attention to spontaneous radiative decay processes, which include fluorescence and phosphorescence. A very important example of stimulated radiative decay is that responsible for the action of lasers, and we see how this stimulated emission may be achieved and employed.

A more common fate of an electronically excited molecule is **nonradiative decay**, in which the excess energy is transferred into the vibration, rotation, and translation of the surrounding molecules. This thermal degradation converts the excitation energy into thermal motion of the environment (that is, to 'heat'). An excited molecule may also take part in a chemical reaction, as we discuss in Topic 93.

46.1 Fluorescence and phosphorescence

In **fluorescence**, spontaneous emission of radiation occurs while the sample is being irradiated and ceases within milliseconds to nanoseconds of the exciting radiation being extinguished (Fig. 46.1). In **phosphorescence**, the spontaneous emission may persist for long periods (even hours, but characteristically seconds or fractions of seconds). The difference suggests that fluorescence is a fast conversion of absorbed radiation into re-emitted energy, and that phosphorescence involves the storage of energy in a reservoir from which it slowly leaks.

Figure 46.2 shows the sequence of steps involved in fluorescence. The initial stimulated absorption takes the molecule to an excited electronic state, and if the absorption spectrum were monitored it would look like the one shown in

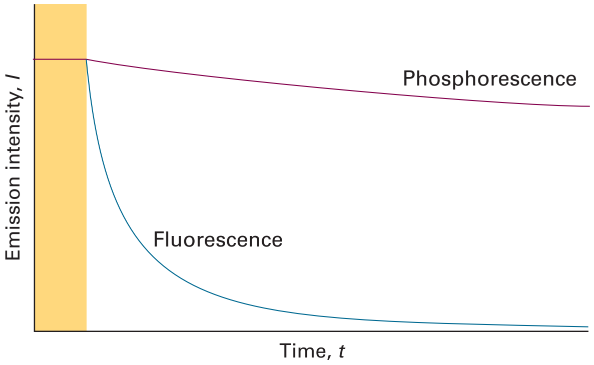


Figure 46.1 The empirical (observation-based) distinction between fluorescence and phosphorescence is that the former is extinguished very quickly after the exciting source is removed, whereas the latter continues with relatively slowly diminishing intensity.

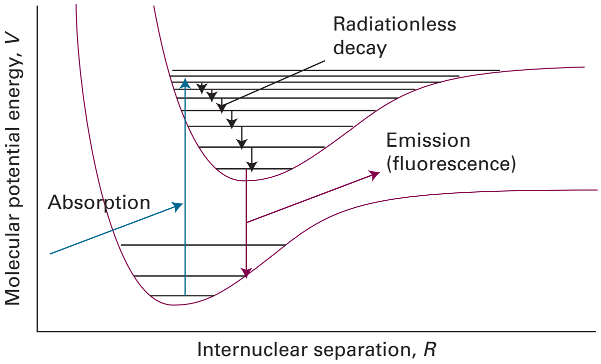


Figure 46.2 The sequence of steps leading to fluorescence. After the initial absorption, the upper vibrational states undergo radiationless decay by giving up energy to the surroundings. A radiative transition then occurs from the vibrational ground state of the upper electronic state.

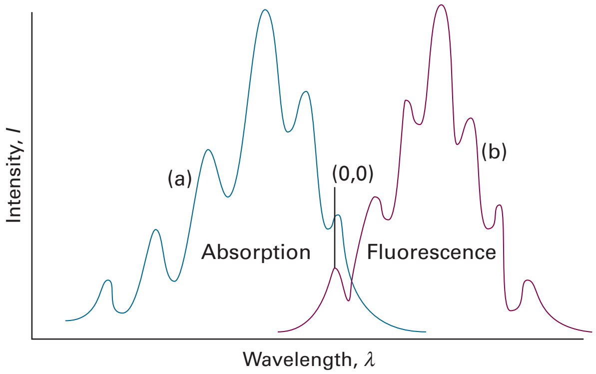


Figure 46.3 An absorption spectrum (a) shows a vibrational structure characteristic of the upper state. A fluorescence spectrum (b) shows a structure characteristic of the lower state; it is also displaced to lower frequencies (but the 0–0 transitions are coincident) and resembles a mirror image of the absorption.

Fig. 46.3a. The excited molecule is subjected to collisions with the surrounding molecules, and as it gives up energy nonradiatively it steps down the ladder of vibrational levels to the lowest vibrational level of the electronically excited molecular state. The surrounding molecules, however, might now be unable to accept the larger energy difference needed to lower the molecule to the ground electronic state. It might therefore survive long enough to undergo spontaneous emission and emit the remaining excess energy as radiation. The downward electronic transition is vertical, in accord with the Franck–Condon principle (Topic 45), and the fluorescence spectrum has a vibrational structure characteristic of the *lower* electronic state (Fig. 46.3b).

Provided they can be seen, the 0–0 absorption and fluorescence transitions can be expected to be coincident. The absorption spectrum arises from $1\leftarrow 0$, $2\leftarrow 0$, … transitions that occur at progressively higher wavenumber and with intensities governed by the Franck–Condon principle. The fluorescence spectrum arises from $0\rightarrow 0$, $0\rightarrow 1$, … *downward* transitions that occur with decreasing wavenumbers. The 0–0 absorption and fluorescence peaks are not always exactly coincident, however, because the solvent may interact differently with the solute in the ground and excited states (for instance, the hydrogen bonding pattern might differ). Because the solvent molecules do not have time to rearrange during the transition, the absorption occurs in an environment characteristic of the solvated ground state; however, the fluorescence occurs in an environment characteristic of the solvated excited state (Fig. 46.4).

Fluorescence occurs at lower frequencies (longer wavelengths) than the incident radiation because the emissive transition occurs after some vibrational energy has been discarded into the surroundings. The vivid oranges and greens of fluorescent dyes are an everyday manifestation of this effect:

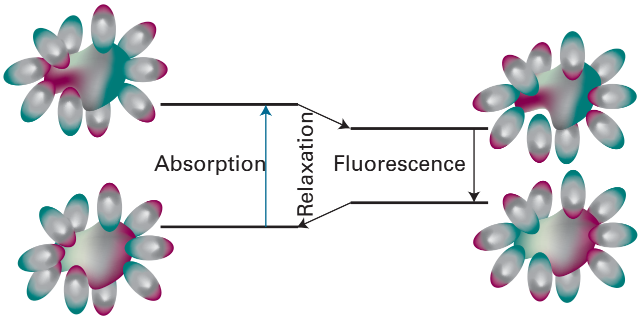


Figure 46.4 The solvent can shift the fluorescence spectrum relative to the absorption spectrum. On the left we see that the absorption occurs with the solvent (the ellipses) in the arrangement characteristic of the ground electronic state of the molecule (the sphere). However, before fluorescence occurs, the solvent molecules relax into a new arrangement, and that arrangement is preserved during the subsequent radiative transition.

they absorb in the ultraviolet and blue, and fluoresce in the visible. The mechanism also suggests that the intensity of the fluorescence ought to depend on the ability of the solvent molecules to accept the electronic and vibrational quanta. It is indeed found that a solvent composed of molecules with widely spaced vibrational levels (such as water) can in some cases accept the large quantum of electronic energy and so extinguish, or 'quench', the fluorescence. The rate at which fluorescence is quenched by other molecules also gives valuable kinetic information (Topic 93).

Figure 46.5 shows the sequence of events leading to phosphorescence for a molecule with a singlet ground state. The first steps are the same as in fluorescence, but the presence of a triplet excited state at an energy close to that of the singlet excited state plays a decisive role. The singlet and triplet excited states share a common geometry at the point where their potential energy curves intersect. Hence, if there is a mechanism for unpairing two electron spins (and achieving the conversion of ↑↓ to ↑↑), the molecule may undergo **intersystem crossing**, a nonradiative transition between states of different multiplicity, and become a triplet state. As in the discussion of atomic spectra (Topic 21), singlet–triplet transitions may occur in the presence of spin–orbit coupling. Intersystem crossing is expected to be important when a molecule contains a moderately heavy atom (such as sulfur), because then the spin–orbit coupling is large.

If an excited molecule crosses into a triplet state, it continues to discard energy into the surroundings. However, it is now stepping down the triplet's vibrational ladder, and at the lowest energy level it is trapped because the triplet state is at a lower energy than the corresponding singlet (Hund's rule, Topic 19). The solvent cannot absorb the final, large quantum of electronic excitation energy, and the molecule cannot radiate its energy because return to the ground state is spin-forbidden. The radiative transition, however, is not totally forbidden because the spin–orbit coupling that was responsible for the intersystem crossing also breaks the selection rule. The molecules are therefore able to emit weakly, and the emission may continue long after the original excited state was formed.

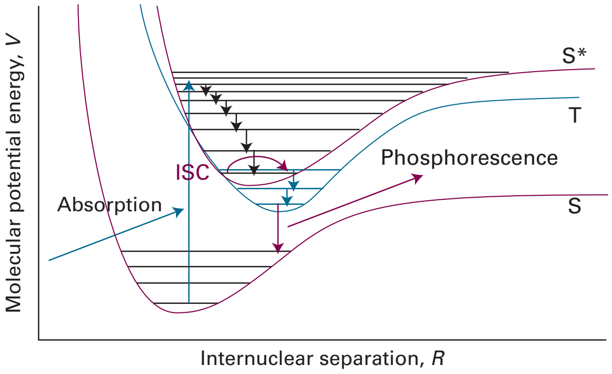


Figure 46.5 The sequence of steps leading to phosphorescence. The important step is the intersystem crossing (ISC), the switch from a singlet state to a triplet state brought about by spin–orbit coupling. The triplet state acts as a slowly radiating reservoir because the return to the ground state is spin-forbidden.

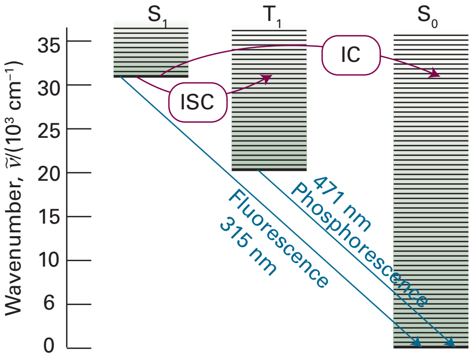


Figure 46.6 A Jablonski diagram (here, for naphthalene) is a simplified portrayal of the relative positions of the electronic energy levels of a molecule. Vibrational levels of states of a given electronic state lie above each other, but the relative horizontal locations of the columns bear no relation to the nuclear separations in the states. The ground vibrational states of each electronic state are correctly located vertically but the other vibrational states are shown only schematically. (IC: internal conversion; ISC: intersystem crossing.)

The mechanism accounts for the observation that the excitation energy seems to get trapped in a slowly leaking reservoir. It also suggests (as is confirmed experimentally) that phosphorescence should be most intense from solid samples: energy transfer is then less efficient and intersystem crossing has time to occur as the singlet excited state steps slowly past the intersection point. The mechanism also suggests that the phosphorescence efficiency should depend on the presence of a moderately heavy atom (with strong spin–orbit coupling), which is in fact the case.

The various types of nonradiative and radiative transitions that can occur in molecules are often represented on a schematic **Jablonski diagram** of the type shown in Fig. 46.6.

Brief illustration 46.1 Fluorescence and phosphorescence of organic molecules

Fluorescence efficiency decreases, and the phosphorescence efficiency increases, in the series of compounds: naphthalene, 1-chloronaphthalene, 1-bromonaphthalene, 1-iodonaphthalene. The replacement of an H atom by successively heavier atoms enhances both intersystem crossing from the first excited singlet state to the first excited triplet state (thereby decreasing the efficiency of fluorescence) and the radiative transition from the first excited triplet state to the ground singlet state (thereby increasing the efficiency of phosphorescence).

Self-test 46.1 Consider an aqueous solution of a chromophore that fluoresces strongly. Is the addition of iodide ion to the solution likely to increase or decrease the efficiency of phosphorescence of the chromophore?

Answer: Increase

46.2 Dissociation and predissociation

Another fate for an electronically excited molecule is **dissociation**, the breaking of bonds (Fig. 46.7). The onset of dissociation can be detected in an absorption spectrum by seeing that the vibrational structure of a band terminates at a certain energy. Absorption occurs in a continuous band above this **dissociation limit** because the final state is an unquantized translational motion of the fragments. Locating the dissociation limit is a valuable way of determining the bond dissociation energy.

In some cases, the vibrational structure disappears but resumes at higher photon energies. This effect provides evidence of **predissociation**, which can be interpreted in terms of the molecular potential energy curves shown in Fig. 46.8. When a molecule is excited to a vibrational level, its electrons may undergo a redistribution that results in it undergoing an **internal conversion**, a radiationless conversion to another state of the same multiplicity. An internal conversion occurs most readily at the point of intersection of the two molecular potential energy curves, because there the nuclear geometries of the two states are the same. The state into which the molecule converts may be dissociative, so the states near the intersection have a finite lifetime and hence their energies are imprecisely defined (lifetime broadening, Topic 40). As a result, the absorption spectrum is blurred in the vicinity of the intersection. When the incoming photon brings enough energy to excite the molecule to a vibrational level high above the intersection, the internal conversion does not occur (the nuclei are unlikely to have the same geometry). Consequently, the levels resume their well-defined, vibrational character with correspondingly well-defined energies, and the line structure resumes on the high-frequency side of the blurred region.

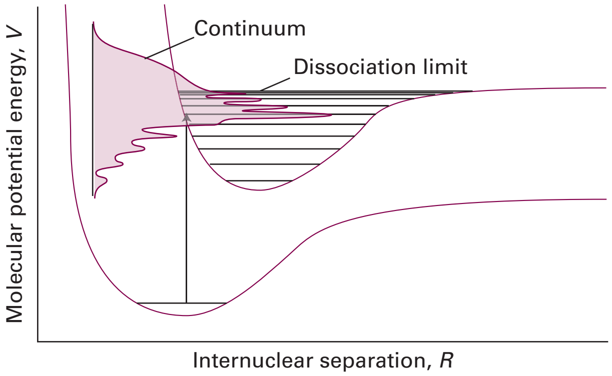


Figure 46.7 When absorption occurs to unbound states of the upper electronic state, the molecule dissociates and the absorption is a continuum. Below the dissociation limit the electronic spectrum shows a normal vibrational structure.

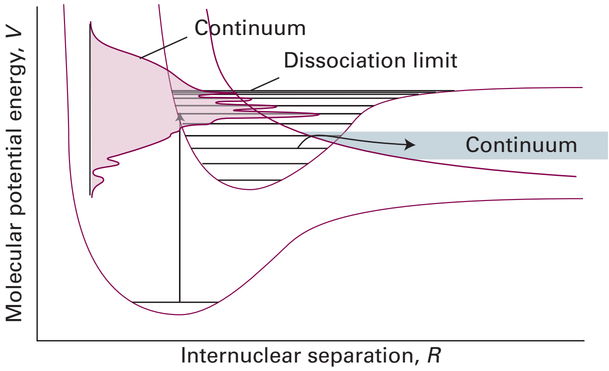


Figure 46.8 When a dissociative state crosses a bound state, as in the upper part of the illustration, molecules excited to levels near the crossing may dissociate. This process is called predissociation, and is detected in the spectrum as a loss of vibrational structure that resumes at higher frequencies.

Brief illustration 46.2 The effect of predissociation on an electronic spectrum

The O_2 molecule absorbs ultraviolet radiation in a transition from its ${}^3\Sigma_g^-$ ground electronic state to a ${}^3\Sigma_u^-$ excited state that is energetically close to a dissociative ${}^3\Pi_u$ state. In this case, the effect of predissociation is more subtle than the abrupt loss of vibrational–rotational structure in the spectrum; instead, the absorption band has a relatively large experimental linewidth. As before, spectral broadening is explained by short lifetimes of the excited vibrational states near the intersection of the curves describing the bound and dissociative excited electronic states.

Self-test 46.2 What can be estimated from the wavenumber of onset of predissociation?

Answer: See Fig. 46.8; an upper limit on the dissociation energy of the ground electronic state

46.3 Laser action

The word 'laser' is an acronym formed from light amplification by stimulated emission of radiation. In stimulated emission (Topic 16), an excited state is stimulated to emit a photon by

Table 46.1 Characteristics of laser radiation and their chemical applications

Characteristic	Advantage	Application
High power	Multiphoton process	Spectroscopy
	Low detector noise	Improved sensitivity
	High scattering intensity	Raman spectroscopy (Topics 40, 42–44)
Monochromatic	High resolution	Spectroscopy
	State selection	Photochemical studies (Topic 93)
Collimated beam	Long path lengths	Improved sensitivity
	Forward scattering observable	Raman spectroscopy (Topics 40, 42–44)
Coherent	Interference between separate beams	Coherent anti-Stokes Raman spectroscopy*
Pulsed	Precise timing of excitation	Fast reactions (Topic 93)
		Relaxation (Topic 84)
		Energy transfer (Topic 93)

*See our other *Physical chemistry* (2014).

radiation of the same frequency: the more photons that are present, the greater the probability of the emission. The essential feature of laser action is positive feedback: the more photons present of the appropriate frequency, the more photons of that frequency that will be stimulated to form.

Laser radiation has a number of striking characteristics (Table 46.1). Each of them (sometimes in combination with the others) opens up interesting opportunities in physical chemistry. Raman spectroscopy has flourished on account of the high-intensity monochromatic radiation available from lasers (Topics 40 and 42–44), and the ultrashort pulses that lasers can generate make possible the study of light-initiated reactions on timescales of femtoseconds and even attoseconds.

(a) Population inversion

One requirement of laser action is the existence of a **metastable excited state**, an excited state with a long enough lifetime for it to participate in stimulated emission. Another requirement is the existence of a greater population in the metastable state than in the lower state where the transition terminates, for then there will be a net emission of radiation. Because at thermal equilibrium the opposite is true, it is necessary to achieve a **population inversion** in which there are more molecules in the upper state than in the lower.

One way of achieving population inversion is illustrated in Fig. 46.9. The molecule is excited to an intermediate state I, which then gives up some of its energy nonradiatively and changes into a lower state A; the laser transition is the return of A to the ground state X. Because three energy levels are involved overall, this arrangement leads to a **three-level laser**. In practice, I consists of many states, all of which can convert to the upper of the two laser states A. The I←X transition is stimulated with an intense flash of light in the process called **pumping**. The pumping is often achieved with an electric discharge through xenon or with the light of another laser. The conversion of I to A should be rapid, and the laser transitions from A to X should be relatively slow.

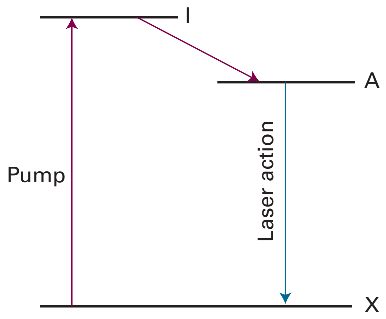


Figure 46.9 The transitions involved in one kind of three-level laser. The pumping pulse populates the intermediate state I, which in turn populates the laser state A. The laser transition is the stimulated emission A→X.

The disadvantage of the three-level arrangement is that it is difficult to achieve population inversion, because so many ground-state molecules must be converted to the excited state by the pumping action. The arrangement adopted in a **four-level laser** simplifies this task by having the laser transition terminate in a state A′ other than the ground state (Fig. 46.10). Because A′ is unpopulated initially, any population in A corresponds to a population inversion and we can expect laser action if A is sufficiently metastable. Moreover, this population inversion can be maintained if the A′→X transitions are rapid, for these transitions will deplete any population in A′ that stems from the laser transition, and keep the state A′ relatively empty.

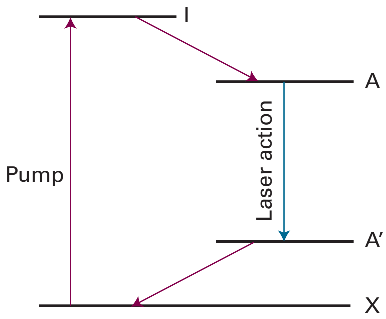


Figure 46.10 The transitions involved in a four-level laser. Because the laser transition terminates in an excited state (A′), the population inversion between A and A′ is much easier to achieve.

Brief illustration 46.3 Simple lasers

The ruby laser is an example of a three-level laser (Fig. 46.11). Ruby is Al_2O_3 containing a small proportion of Cr^{3+} ions. The lower level of the laser transition is the $^4A_2$ ground state of the Cr^{3+} ion. The process of pumping a majority of the Cr^{3+} ions into the $^4T_2$ and $^4T_1$ excited states is followed by a radiationless transition to the ^2E excited state. The laser transition is $^2E \rightarrow {}^4A_2$, and gives rise to red 694 nm radiation.

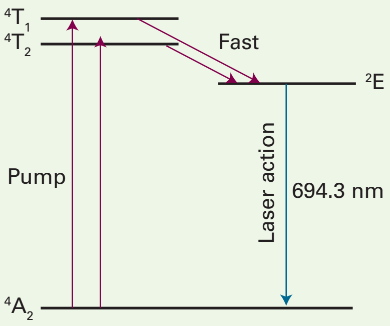


Figure 46.11 The transitions involved in a ruby laser.

The neodymium laser is an example of a four–level laser (Fig. 46.12). In one form it consists of Nd^{3+} ions at low concentration in yttrium aluminium garnet (YAG, specifically $Y_3Al_5O_{12}$), and is then known as a Nd:YAG laser. A neodymium laser operates at a number of wavelengths in the infrared, the band at 1064 nm being most common.

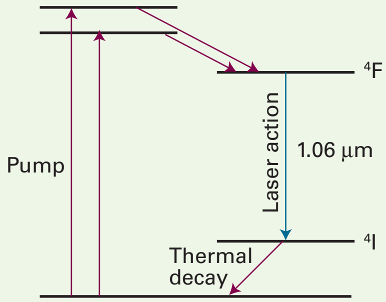


Figure 46.12 The transitions involved in a neodymium laser.

Self-test 46.3 In the arrangement discussed above, does a ruby laser more easily generate pulses of light or a continuous beam of light?

Answer: Pulses of light

(b) Cavity and mode characteristics

The laser medium is confined to a cavity that ensures that only certain photons of a particular frequency, direction of travel, and state of polarization are generated abundantly. The cavity is essentially a region between two mirrors, which reflect the light back and forth. This arrangement can be regarded as a version of the particle in a box, with the particle now being a photon. As in the treatment of a particle in a box (Topic 9), the only wavelengths that can be sustained satisfy

$$n \times \tfrac{1}{2}\lambda = L \qquad \text{Resonant modes} \qquad (46.1)$$

where n is an integer and L is the length of the cavity. That is, only an integral number of half-wavelengths fit into the cavity; all other waves undergo destructive interference with themselves. In addition, not all wavelengths that can be sustained by the cavity are amplified by the laser medium (many fall outside the range of frequencies of the laser transitions), so only a few contribute to the laser radiation. These wavelengths are the **resonant modes** of the laser.

Brief illustration 46.4 Resonant modes

It follows from eqn 46.1 that the frequencies of the resonant modes are $\nu = c/\lambda = (c/2L)\times n$. For a laser cavity of length 30.0 cm, the allowed frequencies are

$$\nu = \frac{\overbrace{2.998\times10^{8}\,\mathrm{m\,s^{-1}}}^{c}}{2\times\underbrace{(0.300\,\mathrm{m})}_{L}}\times n = (5.00\times10^{8}\,\mathrm{s^{-1}})\times n$$
$$= (500\,\mathrm{MHz})\times n$$

with $n = 1, 2, \ldots$, and therefore $\nu = 500$ MHz, 1000 MHz, ….

Self-test 46.4 Consider a laser cavity of length 1.0 m. What is the frequency difference between successive resonant modes?

Answer: 150 MHz

Photons with the correct wavelength for the resonant modes of the cavity and the correct frequency to stimulate the laser transition are highly amplified. One photon might be generated spontaneously and travel through the medium. It stimulates the emission of another photon, which in turn stimulates more (Fig. 46.13). The cascade of energy builds up rapidly, and soon the cavity is an intense reservoir of radiation at all the resonant modes it can sustain. Some of this radiation can be withdrawn if one of the mirrors is partially transmitting.

The resonant modes of the cavity have various natural characteristics, and to some extent may be selected. Only photons that are travelling strictly parallel to the axis of the cavity undergo more than a couple of reflections, so only they are amplified, all others simply vanishing into the surroundings. Hence, laser light generally forms a beam with very low divergence. It may also be polarized, with its electric vector in a particular plane (or in some other state of polarization), by

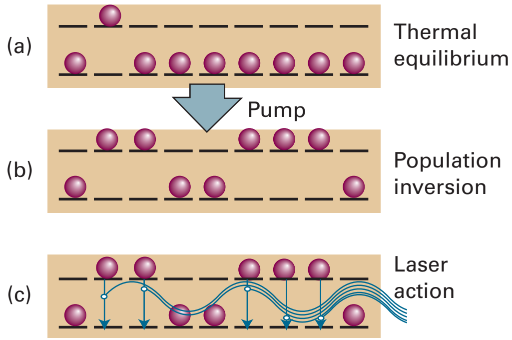


Figure 46.13 A schematic illustration of the steps leading to laser action. (a) The Boltzmann population of states, with more atoms in the ground state. (b) When the initial state absorbs, the populations are inverted (the atoms are pumped to the excited state). (c) A cascade of radiation then occurs, as one emitted photon stimulates another atom to emit, and so on. The radiation is coherent (phases in step).

including a polarizing filter into the cavity or by making use of polarized transitions in a solid medium.

Laser radiation is **coherent** in the sense that the electromagnetic waves are all in step. In **spatial coherence** the waves are in step across the cross-section of the beam emerging from the cavity. In **temporal coherence** the waves remain in step along the beam. The former is normally expressed in terms of a **coherence length**, l_C, the distance over which the waves remain coherent, and is related to the range of wavelengths, $\Delta\lambda$, present in the beam:

$$l_C = \frac{\lambda^2}{2\Delta\lambda} \qquad \text{Coherence length} \qquad (46.2)$$

When many wavelengths are present, and $\Delta\lambda$ is large, the waves get out of step in a short distance and the coherence length is small.

Brief illustration 46.5 Coherence length

A typical light bulb gives out light with a coherence length of only about 400 nm. By contrast, a He–Ne laser with $\lambda = 633$ nm and $\Delta\lambda = 2.0$ pm has a coherence length of

$$l_C = \frac{\overbrace{(633\,\text{nm})^2}^{\lambda^2}}{2\times\underbrace{(0.0020\,\text{nm})}_{\Delta\lambda}} = 1.0\times10^8\,\text{nm} = 0.10\,\text{m} = 10\,\text{cm}$$

Self-test 46.5 What is the condition that would lead to an infinite coherence length?

Answer: A perfectly monochromatic beam, or $\Delta\lambda = 0$

(c) Pulsed lasers

A laser can generate radiation for as long as the population inversion is maintained. A laser can operate continuously when heat is easily dissipated, for then the population of the upper level can be replenished by pumping. When overheating is a problem, the laser can be operated only in pulses, perhaps of microsecond or millisecond duration, so that the medium has a chance to cool or the lower state discard its population. However, it is sometimes desirable to have pulses of radiation rather than a continuous output, with a lot of power concentrated into a brief pulse. One way of achieving pulses is by ***Q*-switching**, the modification of the resonance characteristics of the laser cavity. The name comes from the '*Q*-factor' used as a measure of the quality of a resonance cavity in microwave engineering.

Example 46.1 Relating the power and energy of a laser

A laser rated at 0.10 J can generate radiation in 3.0 ns pulses at a pulse repetition rate of 10 Hz. Assuming that the pulses are rectangular, calculate the peak power output and the average power output of this laser.

Method The power output is the energy released in an interval divided by the duration of the interval, and is expressed in watts ($1\,\text{W} = 1\,\text{J s}^{-1}$). To calculate the peak power output, P_{peak}, we divide the energy released during the pulse by the duration of the pulse. The average power output, P_{average}, is the total energy released by a large number of pulses divided by the duration of the time interval over which the total energy was measured. So, the average power is simply the energy released by one pulse multiplied by the pulse repetition rate.

Answer From the data,

$$P_{\text{peak}} = \frac{0.10\,\text{J}}{3.0\times10^{-9}\,\text{s}} = 3.3\times10^{7}\,\text{J s}^{-1} = 33\,\text{MJ s}^{-1} = 33\,\text{MW}$$

The pulse repetition rate is 10 Hz, so ten pulses are emitted by the laser in every second of operation. It follows that the average power output is

$$P_{\text{average}} = 0.10\,\text{J}\times10\,\text{s}^{-1} = 1.0\,\text{J s}^{-1} = 1.0\,\text{W}$$

The peak power is much higher than the average power because this laser emits light for only 30 ns during each second of operation.

Self-test 46.6 Calculate the peak power and average power output of a laser with a pulse energy of 2.0 mJ, a pulse duration of 30 ps, and a pulse repetition rate of 38 MHz.

Answer: $P_{\text{peak}} = 67\,\text{MW}$, $P_{\text{average}} = 76\,\text{kW}$

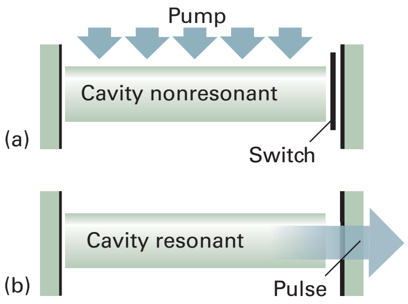


Figure 46.14 The principle of *Q*-switching. (a) The excited state is populated while the cavity is nonresonant. (b) Then the resonance characteristics are suddenly restored, and the stimulated emission emerges in a giant pulse.

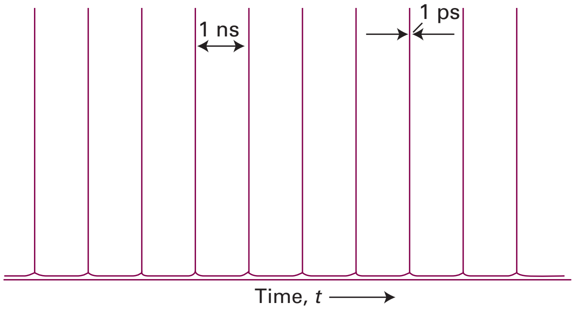


Figure 46.15 The output of a mode-locked laser consists of a stream of very narrow pulses (here 1 ps in duration) separated by an interval equal to the time it takes for light to make a round trip inside the cavity (here 1 ns).

The aim of *Q*-switching is to achieve a healthy population inversion in the absence of the resonant cavity, then to plunge the population-inverted medium into a cavity and hence to obtain a sudden pulse of radiation. The switching may be achieved by impairing the resonance characteristics of the cavity in some way while the pumping pulse is active and then suddenly improving them (Fig. 46.14). One technique is to use the ability of some crystals, such as those of potassium dihydrogenphosphate (KH_2PO_4), to change their optical properties when an electrical potential difference is applied. Switching the potential on and off can store and then release energy in a laser cavity, resulting in an intense pulse of stimulated emission.

The technique of **mode locking** can produce pulses of picosecond duration and less. A laser radiates at a number of different frequencies, depending on the precise details of the resonance characteristics of the cavity and in particular on the number of half-wavelengths of radiation that can be trapped between the mirrors (the cavity modes). The resonant modes differ in frequency by multiples of $c/2L$ (*Brief illustration* 46.4). Normally, these modes have random phases relative to each other. However, it is possible to lock their phases together. As we show in the following *Justification*, interference then occurs to give a series of sharp peaks, and the energy of the laser is obtained in short bursts (Fig. 46.15). More specifically, the intensity, I, of the radiation varies with time as

$$I(t) \propto \mathcal{E}_0^2 \frac{\sin^2(N\pi ct/2L)}{\sin^2(\pi ct/2L)} \qquad \text{Mode-locked laser output} \qquad (46.3)$$

where $\mathcal{E}_0$ is the amplitude of the electromagnetic wave describing the laser beam and N is the number of locked modes. This function is shown in Fig. 46.16. We see that it is a series of peaks with maxima separated by $t = 2L/c$, the round-trip transit time of the light in the cavity, and that the peaks become sharper as N is increased. In a laser with a cavity of length 30 cm, the peaks are separated by 2 ns. If 1000 modes contribute, the width of the pulses is 4 ps.

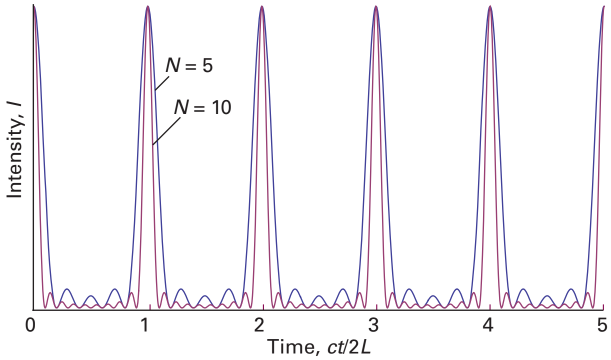


Figure 46.16 The structure of the pulses generated by a mode-locked laser for $N = 5$ and 10. Note that the peaks become sharper as N increases. In each case the pulses have been adjusted to have the same maximum amplitude.

Justification 46.1 The origin of mode locking

The general expression for a (complex) wave of amplitude $\mathcal{E}_0$ and frequency ω is $\mathcal{E}_0 e^{i\omega t}$. Therefore, each wave that can be supported by a cavity of length L has the form

$$\mathcal{E}_n(t) = \mathcal{E}_0 e^{2\pi i(\nu + nc/2L)t}$$

where ν is the lowest frequency. A wave formed by superimposing N modes with $n = 0, 1, \ldots, N-1$ has the form

$$\mathcal{E}(t) = \sum_{n=0}^{N-1} \mathcal{E}_n(t) = \mathcal{E}_0 e^{2\pi i t} \sum_{n=0}^{N-1} e^{i\pi nct/L}$$

The sum simplifies to:

$$S = \sum_{n=0}^{N-1} e^{i\pi nct/L} = 1 + e^{i\pi ct/L} + e^{2i\pi ct/L} + \cdots + e^{(N-1)i\pi ct/L}$$

At this point we recognize that the sum is a geometrical series:

$$1+e^{x}+e^{2x}+\cdots+e^{(N-1)x}=\frac{e^{Nx}-1}{e^{x}-1}$$

with $x=e^{i\pi ct/L}$, so

$$S=\frac{e^{Ni\pi ct/L}-1}{e^{i\pi ct/L}-1}$$

The term on the right can be written

$$\frac{e^{Ni\pi ct/L}-1}{e^{i\pi ct/L}-1}=\frac{e^{Ni\pi ct/2L}-e^{-Ni\pi ct/2L}}{e^{i\pi ct/2L}-e^{-i\pi ct/2L}}\times e^{(N-1)i\pi ct/2L}$$

Finally, we use the relation $\sin x=(1/2i)(e^{ix}-e^{-ix})$ to conclude that

$$S=\frac{\sin(N\pi ct/2L)}{\sin(\pi ct/2L)}\times e^{(N-1)i\pi ct/2L}$$

The intensity, $I(t)$, of the radiation is proportional to the square modulus of the total amplitude, so

$$I(t)\propto\mathcal{E}^{*}\mathcal{E}\overset{\mathcal{E}=\mathcal{E}_0 S}{=}\mathcal{E}_0^{2}\frac{\sin^{2}(N\pi ct/2L)}{\sin^{2}(\pi ct/2L)}$$

which is eqn 46.3.

Mode locking is achieved by varying the Q-factor of the cavity periodically at the frequency $c/2L$. The modulation can be pictured as the opening of a shutter in synchrony with the round-trip travel time of the photons in the cavity, so only photons making the journey in that time are amplified. The modulation can be achieved by linking a prism in the cavity to a transducer driven by a radiofrequency source at a frequency $c/2L$. The transducer sets up standing-wave vibrations in the prism and modulates the loss it introduces into the cavity.

Another mechanism for mode-locking lasers is based on the **optical Kerr effect**, which arises from a change in refractive index of a well-chosen medium, the **Kerr medium**, when it is exposed to intense laser pulses. Because a beam of light changes direction when it passes from a region of one refractive index to a region with a different refractive index, changes in refractive index result in the self-focusing of an intense laser pulse as it travels through the Kerr medium (Fig. 46.17).

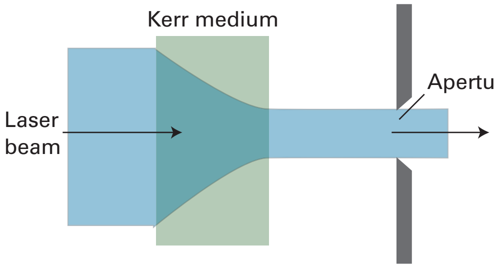


Figure 46.17 An illustration of the optical Kerr effect. An intense laser beam is focused inside a Kerr medium and passes through a small aperture in the laser cavity. This effect may be used to mode-lock a laser, as explained in the text.

To bring about mode locking, a Kerr medium is included in the laser cavity and next to it is a small aperture. The procedure makes use of the fact that the **gain**, the growth in intensity, of a frequency component of the radiation in the cavity is very sensitive to amplification, and once a particular frequency begins to grow, it can quickly dominate. When the power inside the cavity is low, a portion of the photons will be blocked by the aperture, creating a significant loss. A spontaneous fluctuation in intensity—a bunching of photons—may begin to turn on the optical Kerr effect and the changes in the refractive index of the Kerr medium will result in a **Kerr lens,** which is the self-focusing of the laser beam. The bunch of photons can pass through and travel to the far end of the cavity, amplifying as it goes. The Kerr lens immediately disappears (if the medium is well chosen), but is re-created when the intense pulse returns from the mirror at the far end. In this way, that particular bunch of photons may grow to considerable intensity because it alone is stimulating emission in the cavity. Sapphire is an example of a Kerr medium that facilitates the mode locking of titanium sapphire lasers, resulting in very short laser pulses of duration in the femtosecond range.

Checklist of concepts

☐ 1. **Fluorescence** is radiative decay between states of the same multiplicity; it ceases as soon as the exciting source is removed.

☐ 2. **Phosphorescence** is radiative decay between states of different multiplicity; it persists after the exciting radiation is removed.

☐ 3. **Intersystem crossing** is the nonradiative conversion to a state of different multiplicity.

☐ 4. A **Jablonski diagram** is a schematic diagram of the types of nonradiative and radiative transitions that can occur in molecules.

☐ 5. An additional fate of an electronically excited species is **dissociation**.

☐ 6. **Internal conversion** is a nonradiative conversion to a state of the same multiplicity.

☐ 7. **Predissociation** is the observation of the effects of dissociation before the dissociation limit is reached.

☐ 8. **Laser action** is the stimulated emission of coherent radiation between states related by a population inversion.

☐ 9. A **population inversion** is a condition in which the population of an upper state is greater than that of a relevant lower state.

☐ 10. The **resonant modes** of a laser are the wavelengths of radiation sustained inside a laser cavity.

☐ 11. Laser pulses are generated by the techniques of **Q-switching** and **mode locking**.

Checklist of equations

Property	Equation	Comment	Equation number
Resonant modes	$n \times \frac{1}{2}\lambda = L$	Laser cavity of length L	46.1
Coherence length	$l_C = \lambda^2/2\Delta\lambda$		46.2
Mode-locked laser output	$I(t) \propto \mathcal{E}_0^2\{\sin^2(N\pi ct/2L)/\sin^2(\pi ct/2L)\}$	N locked modes	46.3

Focus 9 on Molecular spectroscopy

Note: The masses of nuclides are listed in Table 0.2 of the *Resource section*.

Topic 40 General features

Discussion questions

40.1 Distinguish between the basic experimental arrangements commonly used for absorption, emission, and Raman spectroscopy.

40.2 Describe the physical origins of linewidths in absorption and emission spectra. Do you expect the same contributions for species in condensed and gas phases?

Exercises

40.1(a) The molar absorption coefficient of a substance dissolved in hexane is known to be 723 $dm^3 mol^{-1} cm^{-1}$ at 260 nm. Calculate the percentage reduction in intensity when light of that wavelength passes through 2.50 mm of a solution of concentration 4.25 $mmol\,dm^{-3}$.

40.1(b) The molar absorption coefficient of a substance dissolved in hexane is known to be 227 $dm^3 mol^{-1} cm^{-1}$ at 290 nm. Calculate the percentage reduction in intensity when light of that wavelength passes through 2.00 mm of a solution of concentration 2.52 $mmol\,dm^{-3}$.

40.2(a) A solution of an unknown component of a biological sample when placed in an absorption cell of path length 1.00 cm transmits 18.1 per cent of light of 320 nm incident upon it. If the concentration of the component is 0.139 $mmol\,dm^{-3}$, what is the molar absorption coefficient?

40.2(b) When light of wavelength 400 nm passes through 2.5 mm of a solution of an absorbing substance at a concentration 0.717 $mmol\,dm^{-3}$, the transmission is 61.5 per cent. Calculate the molar absorption coefficient of the solute at this wavelength and express the answer in $cm^2 mol^{-1}$.

40.3(a) The molar absorption coefficient of a solute at 540 nm is 386 $dm^3 mol^{-1} cm^{-1}$. When light of that wavelength passes through a 5.00 mm cell containing a solution of the solute, 38.5 per cent of the light was absorbed. What is the concentration of the solution?

40.3(b) The molar absorption coefficient of a solute at 440 nm is 423 $dm^3 mol^{-1} cm^{-1}$. When light of that wavelength passes through a 6.50 mm cell containing a solution of the solute, 48.3 per cent of the light was absorbed. What is the concentration of the solution?

40.4(a) The absorption associated with a particular transition begins at 220 nm, peaks sharply at 270 nm, and ends at 300 nm. The maximum value of the molar absorption coefficient is 2.21×10^4 $dm^3 mol^{-1} cm^{-1}$. Estimate the integrated absorption coefficient of the transition assuming a triangular lineshape.

40.4(b) The absorption associated with a certain transition begins at 156 nm, peaks sharply at 210 nm, and ends at 275 nm. The maximum value of the molar absorption coefficient is 3.35×10^4 $dm^3 mol^{-1} cm^{-1}$. Estimate the integrated absorption coefficient of the transition assuming an inverted parabolic lineshape (Fig. F9.1).

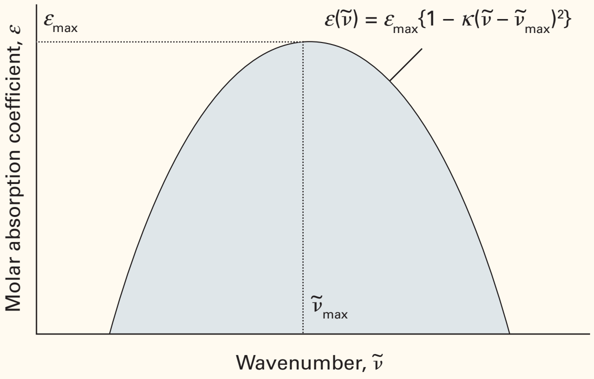


Figure F9.1 A model parabolic absorption lineshape.

40.5(a) The following data were obtained for the absorption by Br_2 in carbon tetrachloride using a 2.0 mm cell. Calculate the molar absorption coefficient of bromine at the wavelength employed:

$[Br_2]/(mol\,dm^{-3})$	0.0010	0.0050	0.0100	0.0500
$T/(\%)$	81.4	35.6	12.7	3.0×10^{-3}

40.5(b) The following data were obtained for the absorption by a dye dissolved in methylbenzene using a 2.50 mm cell. Calculate the molar absorption coefficient of the dye at the wavelength employed:

$[dye]/(mol\,dm^{-3})$	0.0010	0.0050	0.0100	0.0500
$T/(\%)$	68	18	3.7	1.03×10^{-5}

40.6(a) A 2.0 mm cell was filled with a solution of benzene in a non-absorbing solvent. The concentration of the benzene was 0.010 $mol\,dm^{-3}$ and the wavelength of the radiation was 256 nm (where there is a maximum in the absorption). Calculate the molar absorption coefficient of benzene at this wavelength given that the transmission was 48 per cent. What will the transmittance be in a 4.0 mm cell at the same wavelength?

40.6(b) A 5.00 mm cell was filled with a solution of a dye. The concentration of the dye was 18.5 $mmol\,dm^{-3}$. Calculate the molar absorption coefficient of the dye at this wavelength given that the transmission was 29 per cent. What will the transmittance be in a 2.50 mm cell at the same wavelength?

40.7(a) A swimmer enters a gloomier world (in one sense) on diving to greater depths. Given that the mean molar absorption coefficient of seawater in the visible region is 6.2×10^{-3} $dm^3 mol^{-1} cm^{-1}$, calculate the depth at which a diver will experience (a) half the surface intensity of light, (b) one-tenth the surface intensity.

40.7(b) Given that the maximum molar absorption coefficient of a molecule containing a carbonyl group is 30 $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$ near 280 nm, calculate the thickness of a sample that will result in (a) half the initial intensity of radiation, (b) one-tenth the initial intensity.

40.8(a) What is the Doppler-shifted wavelength of a red (680 nm) traffic light approached at 60 $\mathrm{km\,h^{-1}}$?

40.8(b) At what speed of approach would a red (680 nm) traffic light appear green (530 nm)?

40.9(a) Estimate the lifetime of a state that gives rise to a line of width (a) 0.20 $\mathrm{cm^{-1}}$, (b) 2.0 $\mathrm{cm^{-1}}$.

40.9(b) Estimate the lifetime of a state that gives rise to a line of width (a) 200 MHz, (b) 2.45 $\mathrm{cm^{-1}}$.

40.10(a) A molecule in a liquid undergoes about 1.0×10^{13} collisions in each second. Suppose that (i) every collision is effective in deactivating the molecule vibrationally and (ii) that one collision in 100 is effective. Calculate the width (in $\mathrm{cm^{-1}}$) of vibrational transitions in the molecule.

40.10(b) A molecule in a gas undergoes about 1.0×10^{9} collisions in each second. Suppose that (i) every collision is effective in deactivating the molecule rotationally and (ii) that one collision in 10 is effective. Calculate the width (in hertz) of rotational transitions in the molecule.

Problems

40.1 Refer to Fig. 40.4 describing a Michelson interferometer. The mirror M_1 moves in finite distance increments, so the path difference p is also incremented in finite steps. Explore the effect of increasing the step size on the shape of the interferogram for a monochromatic beam of wavenumber $\tilde{\nu}$ and intensity I_0. That is, draw plots of $I(p)/I_0$ against $\tilde{\nu}p$ each with a different number of data points spanning the same total distance path taken by the movable mirror M_1.

40.2 Using mathematical software, elaborate on the results of Example 40.1 by (a) exploring the effect of varying the wavenumbers and intensities of the three components of the radiation on the shape of the interferogram, and (b) calculating the Fourier transforms of the functions you generated in part (a).

40.3 The flux of visible photons reaching Earth from the North Star is about $4\times10^{3}\ \mathrm{mm^{-2}\,s^{-1}}$. Of these photons, 30 per cent are absorbed or scattered by the atmosphere and 25 per cent of the surviving photons are scattered by the surface of the cornea of the eye. A further 9 per cent are absorbed inside the cornea. The area of the pupil at night is about 40 $\mathrm{mm^2}$ and the response time of the eye is about 0.1 s. Of the photons passing through the pupil, about 43 per cent are absorbed in the ocular medium. How many photons from the North Star are focused onto the retina in 0.1 s? For a continuation of this story, see R.W. Rodieck, *The first steps in seeing,* Sinauer (1998).

40.4 A *Dubosq colorimeter* consists of a cell of fixed path length and a cell of variable path length. By adjusting the length of the latter until the transmission through the two cells is the same, the concentration of the second solution can be inferred from that of the former. Suppose that a plant dye of concentration 25 $\mathrm{\mu g\,dm^{-3}}$ is added to the fixed cell, the length of which is 1.55 cm. Then a solution of the same dye, but of unknown concentration, is added to the second cell. It is found that the same transmittance is obtained when the length of the second cell is adjusted to 1.18 cm. What is the concentration of the second solution?

40.5 The Beer–Lambert law is derived on the basis that the concentration of absorbing species is uniform. Suppose, instead, that the concentration falls exponentially as $[\mathrm{J}]=[\mathrm{J}]_0\mathrm{e}^{-x/\lambda}$. Derive an expression for the variation of I with sample length; suppose that $L\gg\lambda$.

40.6 It is common to make measurements of absorbance at two wavelengths and use them to find the individual concentrations of two components A and B in a mixture. Show that the molar concentrations of A and B are

$$[\mathrm{A}]=\frac{\varepsilon_{\mathrm{B}2}A_1-\varepsilon_{\mathrm{B}1}A_2}{(\varepsilon_{\mathrm{A}1}\varepsilon_{\mathrm{B}2}-\varepsilon_{\mathrm{A}2}\varepsilon_{\mathrm{B}1})L}\qquad[\mathrm{B}]=\frac{\varepsilon_{\mathrm{A}1}A_2-\varepsilon_{\mathrm{A}2}A_1}{(\varepsilon_{\mathrm{A}1}\varepsilon_{\mathrm{B}2}-\varepsilon_{\mathrm{A}2}\varepsilon_{\mathrm{B}1})L}$$

where A_1 and A_2 are absorbances of the mixture at wavelengths λ_1 and λ_2, and the molar extinction coefficients of A (and B) at these wavelengths are $\varepsilon_{\mathrm{A}1}$ and $\varepsilon_{\mathrm{A}2}$ (and $\varepsilon_{\mathrm{B}1}$ and $\varepsilon_{\mathrm{B}2}$).

40.7 When pyridine is added to a solution of iodine in carbon tetrachloride the 520 nm band of absorption shifts toward 450 nm. However, the absorbance of the solution at 490 nm remains constant: this feature is called an *isosbestic point*. Show that an isosbestic point should occur when two absorbing species are in equilibrium.

40.8[‡] Ozone absorbs ultraviolet radiation in a part of the electromagnetic spectrum energetic enough to disrupt DNA in biological organisms and that is absorbed by no other abundant atmospheric constituent. This spectral range, denoted UV-B, spans the wavelengths of about 290 nm to 320 nm. The molar extinction coefficient of ozone over this range is given in the table below (DeMore, et al., *Chemical kinetics and photochemical data for use in stratospheric modeling: Evaluation Number 11,* JPL Publication 94–26 (1994)).

λ/nm	292.0	296.3	300.8	305.4	310.1	315.0	320.0
$\varepsilon/(\mathrm{dm^3\,mol^{-1}\,cm^{-1}})$	1512	865	477	257	135.9	69.5	34.5

Compute the integrated absorption coefficient of ozone over the wavelength range 290–320 nm. (*Hint*: $\varepsilon(\tilde{\nu})$ can be fitted to an exponential function quite well.)

40.9 In many cases it is possible to assume that an absorption band has a Gaussian lineshape (one proportional to e^{-x^2}) centred on the band maximum. Assume such a lineshape, and show that $\mathcal{A}=\int\varepsilon(\tilde{\nu})\mathrm{d}\tilde{\nu}\approx1.0645\varepsilon_{\max}\Delta\tilde{\nu}_{1/2}$, where $\Delta\tilde{\nu}_{1/2}$ is the width at half-height. The absorption spectrum of azoethane ($\mathrm{CH_3CH_2N_2}$) between 24 000 $\mathrm{cm^{-1}}$ and 34 000 $\mathrm{cm^{-1}}$ is shown in Fig. F9.2. First, estimate $\mathcal{A}$ for the band by assuming that it is Gaussian. Then use mathematical software to fit a polynomial to the absorption band (or a Gaussian), and integrate the result analytically.

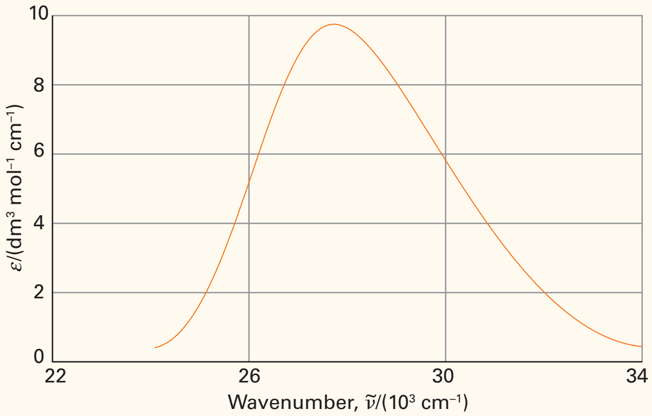


Figure F9.2 The absorption spectrum of azoethane.

40.10[‡] Wachewsky, et al. (*J. Phys. Chem.* **100**, 11559 (1996)) examined the UV absorption spectrum of $\mathrm{CH_3I}$, a species of interest in connection with stratospheric ozone chemistry. They found the integrated absorption coefficient to be dependent on temperature and pressure to an extent inconsistent with internal structural changes in isolated $\mathrm{CH_3I}$ molecules;

[‡] These problems were supplied by Charles Trapp and Carmen Giunta.

they explained the changes as due to dimerization of a substantial fraction of the CH_3I, a process which would naturally be pressure- and temperature-dependent. (a) Compute the integrated absorption coefficient over a triangular lineshape in the range 31 250 to 34 483 cm^{-1} and a maximal molar absorption coefficient of 150 $dm^3\,mol^{-1}\,cm^{-1}$ at 31 250 cm^{-1}. (b) Suppose 1 per cent of the CH_3I units in a sample at 2.4 Torr and 373 K exist as dimers. Compute the absorbance expected at 31 250 cm^{-1} in a sample cell of length 12.0 cm. (c) Suppose 18 per cent of the CH_3I units in a sample at 100 Torr and 373 K exists as dimers. Compute the absorbance expected at 31 250 cm^{-1} in a sample cell of length 12.0 cm; compute the molar absorption coefficient which would be inferred from this absorbance if dimerization was not considered.

40.11 *Laser light scattering* is a technique that uses the fact that the intensity of light scattered—by Rayleigh scattering—by a particle is proportional to the molar mass of the particle and to λ^{-4}, so shorter-wavelength radiation is scattered more intensely than longer wavelengths. Consider the experimental arrangement shown in Fig. F9.3 for the measurement of light scattering from solutions of macromolecules. Typically, the sample is irradiated with monochromatic light from a laser. The intensity of scattered light is then measured as a function of the angle θ that the line of propagation of the laser beam makes with a line from the sample to the detector. For dilute solutions of a spherical macromolecule with a diameter much smaller than the wavelength of incident radiation, the intensity, I_θ, of light scattered by a sample of mass concentration c_M (units: kg m^{-3}) is given by

$$\frac{I_0}{I_\theta}=\frac{1}{Kc_M M}+\frac{16\pi^2R^2}{5\lambda^2}\left(\frac{I_0}{I_\theta}\sin^2\frac{1}{2}\theta\right)$$

where I_0 is the intensity of the incident laser radiation, M is the molar mass, R is the radius of the particle, and K is a parameter that depends on the refractive index of the solution, the incident wavelength, and the distance between the detector and the sample, which is held constant during the experiment. It follows that structural properties, such as size and the molar mass of a macromolecule, can be obtained from measurements of light scattering by a sample at several angles θ relative to the direction of propagation of an incident beam. The following data for an aqueous solution of a macromolecule with c_M = 2.0 kg m^{-3} were obtained at 20 °C with laser light at $\lambda = 532$ nm. In a separate

$\theta/°$	15.0	45.0	70.0	85.0	90.0
$10^2 \times I_0/I_\theta$	4.20	4.37	4.63	4.83	4.90

experiment, it was determined that $K = 2.40 \times 10^{-2}$ mol $m^3\,kg^{-2}$. From this information, calculate R and M for the macromolecule.

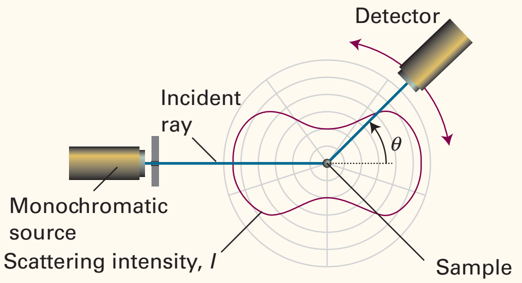


Figure F9.3 A typical experimental arrangement of a laser light scattering measurement.

40.12 The collision frequency z of a molecule of mass m in a gas at a pressure p is $z = 4\sigma(kT/\pi m)^{1/2}p/kT$, where σ is the collision cross-section. Find an expression for the collision-limited lifetime of an excited state assuming that every collision is effective. Estimate the width of rotational transition in HCl ($\sigma = 0.30\ nm^2$) at 25 °C and 1.0 atm. To what value must the pressure of the gas be reduced in order to ensure that collision broadening is less important than Doppler broadening?

40.13 The spectrum of a star is used to measure its *radial velocity* with respect to the Sun, the component of the star's velocity vector that is parallel to a vector connecting the star's centre to the centre of the Sun. The measurement relies on the Doppler effect. When a star emitting electromagnetic radiation of frequency ν moves with a speed s relative to an observer, the observer detects radiation of frequency $\nu_{\text{receding}} = \nu f$ or $\nu_{\text{approaching}} = \nu/f$, where $f = \{(1-s/c)/(1+s/c)\}^{1/2}$ and c is the speed of light. (a) Three Fe I lines of the star HDE 271 182, which belongs to the Large Magellanic Cloud, occur at 438.882 nm, 441.000 nm, and 442.020 nm. The same lines occur at 438.392 nm, 440.510 nm, and 441.510 nm in the spectrum of an Earth-bound iron arc. Determine whether HDE 271 182 is receding from or approaching the Earth and estimate the star's radial speed with respect to the Earth. (b) What additional information would you need to calculate the radial velocity of HDE 271 182 with respect to the Sun?

40.14 In Problem 40.13, we saw that Doppler shifts of atomic spectral lines are used to estimate the speed of recession or approach of a star. A spectral line of $^{48}Ti^{8+}$ (of mass $47.95m_u$) in a distant star was found to be shifted from 654.2 nm to 706.5 nm and to be broadened to 61.8 pm. What are the speed of recession and the surface temperature of the star?

40.15 The Gaussian shape of a Doppler-broadened spectral line reflects the Maxwell distribution of speeds in the sample at the temperature of the experiment. In a spectrometer that makes use of *phase-sensitive detection* the output signal is proportional to the first derivative of the signal intensity, $dI/d\nu$. Plot the resulting lineshape for various temperatures. How is the separation of the peaks related to the temperature?

Topic 41 Molecular rotation

Discussion questions

41.1 Account for the rotational degeneracy of the various types of rigid rotor. Would their lack of rigidity affect your conclusions?

41.2 Discuss the differences between an oblate and a prolate symmetric rotor and give several examples of each.

Exercises

41.1(a) Calculate the moment of inertia around the C_2 axis (the bisector of the OOO angle) and the corresponding rotational constant of an $^{16}O_3$ molecule (bond angle 117°; OO bond length 128 pm).

41.1(b) Calculate the moment of inertia around the C_3 axis (the threefold symmetry axis) and the corresponding rotational constant of a $^{31}P^1H_3$ molecule (bond angle 93.5°; PH bond length 142 pm).

41.2(a) Plot the expressions for the two moments of inertia of a symmetric-top version of an AB_4 molecule (Table 41.1) with equal bond lengths but with the angle θ increasing from 90° to the tetrahedral angle.

41.2(b) Plot the expressions for the two moments of inertia of a symmetric-top version of an AB_4 molecule (Table 41.1) with θ equal to the tetrahedral angle but with one A–B bond varying. *Hint*: Write $\rho = R'_{AB}/R_{AB}$, and allow ρ to vary from 2 to 1.

41.3(a) Classify the following rotors: (a) O_3, (b) CH_3CH_3, (c) XeO_4, (d) $FeCp_2$ (Cp denotes the cyclopentadienyl group, C_5H_5).

41.3(b) Classify the following rotors: (a) $CH_2{=}CH_2$, (b) SO_3, (c) ClF_3, (d) N_2O.

41.4(a) Determine the HC and CN bond lengths in HCN from the rotational constants $B(^1H^{12}C^{14}N) = 44.316$ GHz and $B(^2H^{12}C^{14}N) = 36.208$ GHz.

41.4(b) Determine the CO and CS bond lengths in OCS from the rotational constants $B(^{16}O^{12}C^{32}S) = 6081.5$ MHz, $B(^{16}O^{12}C^{34}S) = 5932.8$ MHz.

Problems

41.1 Show that the moment of inertia of a diatomic molecule composed of atoms of masses m_A and m_B and bond length R is equal to $m_{eff}R^2$, where $m_{eff} = m_A m_B/(m_A + m_B)$.

41.2 Confirm the expression given in Table 41.1 for the moment of inertia of a linear ABC molecule. *Hint*: Begin by locating the centre of mass.

Topic 42 Rotational spectroscopy

Discussion questions

42.1 Account for the existence of a rotational zero-point energy in molecular hydrogen.

42.2 Discuss the physical origins of the gross selection rules for microwave spectroscopy.

42.3 Discuss the physical origins of the gross selection rules for rotational Raman spectroscopy.

42.4 Discuss the role of nuclear statistics in the occupation of energy levels in $^1H^{12}C{\equiv}^{12}C^1H$, $^1H^{13}C{\equiv}^{13}C^1H$, and $^2H^{12}C{\equiv}^{12}C^2H$. For nuclear spin data, see Table 47.2.

Exercises

42.1(a) Which of the following molecules may show a pure rotational microwave absorption spectrum: (a) H_2, (b) HCl, (c) CH_4, (d) CH_3Cl, (e) CH_2Cl_2?

42.1(b) Which of the following molecules may show a pure rotational microwave absorption spectrum: (a) H_2O, (b) H_2O_2, (c) NH_3, (d) N_2O?

42.2(a) Calculate the frequency and wavenumber of the $J = 3 \leftarrow 2$ transition in the pure rotational spectrum of $^{14}N^{16}O$. The equilibrium bond length is 115 pm. Does the frequency increase or decrease if centrifugal distortion is considered?

42.2(b) Calculate the frequency and wavenumber of the $J = 2 \leftarrow 1$ transition in the pure rotational spectrum of $^{12}C^{16}O$. The equilibrium bond length is 112.81 pm. Does the frequency increase or decrease if centrifugal distortion is considered?

42.3(a) The wavenumber of the $J = 3 \leftarrow 2$ rotational transition of $^1H^{35}Cl$ considered as a rigid rotor is 63.56 cm^{-1}; what is the H—Cl bond length?

42.3(b) The wavenumber of the $J = 1 \leftarrow 0$ rotational transition of $^1H^{81}Br$ considered as a rigid rotor is 16.93 cm^{-1}; what is the H—Br bond length?

42.4(a) The spacing of lines in the microwave spectrum of $^{27}Al^1H$ is 12.604 cm^{-1}; calculate the moment of inertia and bond length of the molecule.

42.4(b) The spacing of lines in the microwave spectrum of $^{35}Cl^{19}F$ is 1.033 cm^{-1}; calculate the moment of inertia and bond length of the molecule.

42.5(a) Which of the following molecules may show a pure rotational Raman spectrum: (a) H_2, (b) HCl, (c) CH_4, (d) CH_3Cl?

42.5(b) Which of the following molecules may show a pure rotational Raman spectrum: (a) CH_2Cl_2, (b) CH_3CH_3, (c) SF_6, (d) N_2O?

42.6(a) The wavenumber of the incident radiation in a Raman spectrometer is 20 487 cm^{-1}. What is the wavenumber of the scattered Stokes radiation for the $J = 2 \leftarrow 0$ transition of $^{14}N_2$?

42.6(b) The wavenumber of the incident radiation in a Raman spectrometer is 20 623 cm^{-1}. What is the wavenumber of the scattered Stokes radiation for the $J = 4 \leftarrow 2$ transition of $^{16}O_2$?

42.7(a) The rotational Raman spectrum of $^{35}Cl_2$ shows a series of Stokes lines separated by 0.9752 cm^{-1} and a similar series of anti-Stokes lines. Calculate the bond length of the molecule.

42.7(b) The rotational Raman spectrum of $^{19}F_2$ shows a series of Stokes lines separated by 3.5312 cm^{-1} and a similar series of anti-Stokes lines. Calculate the bond length of the molecule.

42.8(a) What is the ratio of weights of populations due to the effects of nuclear statistics for $^{35}Cl_2$?

42.8(b) What is the ratio of weights of populations due to the effects of nuclear statistics for $^{12}C^{32}S_2$? What effect would be observed when ^{12}C is replaced by ^{13}C? For nuclear spin data, see Table 47.2.

Problems

42.1 The rotational constant of NH_3 is 298 GHz. Compute the separation of the pure rotational spectrum lines as a frequency in GHz, a wavenumber in cm^{-1}, and a wavelength in mm, and show that the value of B is consistent with an N–H bond length of 101.4 pm and a bond angle of 106.78°.

42.2 Rotational absorption lines from $^1H^{35}Cl$ gas were found at the following wavenumbers (R.L. Hausler and R.A. Oetjen, *J. Chem. Phys.* **21**, 1340 (1953)): 83.32, 104.13, 124.73, 145.37, 165.89, 186.23, 206.60, 226.86 cm^{-1}. Calculate the moment of inertia and the bond length of the molecule. Predict the positions of the corresponding lines in $^2H^{35}Cl$.

42.3 Is the bond length in HCl the same as that in DCl? The wavenumbers of the $J=1\leftarrow 0$ rotational transitions for $H^{35}Cl$ and $^2H^{35}Cl$ are 20.8784 and 10.7840 cm^{-1}, respectively. Accurate atomic masses are 1.007 825m_u and 2.0140m_u for ^1H and ^2H, respectively. The mass of ^{35}Cl is 34.968 85m_u. Based on this information alone, can you conclude that the bond lengths are the same or different in the two molecules?

42.4 Thermodynamic considerations suggest that the copper monohalides CuX should exist mainly as polymers in the gas phase, and indeed it proved difficult to obtain the monomers in sufficient abundance to detect spectroscopically. This problem was overcome by flowing the halogen gas over copper heated to 1100 K (Manson, et al. *J. Chem. Phys.* **63**, 2724 (1975)). For CuBr the $J=13$–14, 14–15, and 15–16 transitions occurred at 84 421.34, 90 449.25, and 96 476.72 MHz, respectively. Calculate the rotational constant and bond length of CuBr.

42.5 The microwave spectrum of $^{16}O^{12}CS$ gave absorption lines (in GHz) as follows:

J	1	2	3	4
^{32}S	24.325 92	36.488 82	48.651 64	60.814 08
^{34}S	23.732 33		47.462 40	

Using the expressions for moments of inertia in Table 41.1 and assuming that the bond lengths are unchanged by substitution, calculate the CO and CS bond lengths in OCS.

42.6 Equation 42.8b may be rearranged into

$$\tilde{\nu}(J+1\leftarrow J)/2(J+1)=\tilde{B}-2\tilde{D}_J(J+1)^2$$

which is the equation of a straight line when the left-hand side is plotted against $(J+1)^2$. The following wavenumbers of transitions (in cm^{-1}) were observed for $^{12}C^{16}O$:

J:	0	1	2	3	4
	3.845 033	7.689 919	11.534 510	15.378 662	19.222 223

Determine $\tilde{B}$, $\tilde{D}_J$, and the equilibrium bond length of CO.

42.7‡ In a study of the rotational spectrum of the linear FeCO radical, Tanaka, et al. (*J. Chem. Phys.* **106**, 6820 (1997)) reported the following $J+1\leftarrow J$ transitions:

J	24	25	26	27	28	29
$\tilde{\nu}/m^{-1}$	214 777.7	223 379.0	231 981.2	240 584.4	249 188.5	257 793.5

Evaluate the rotational constant of the molecule. Also, estimate the value of J for the most highly populated rotational energy level at 298 K and at 100 K.

42.8 The rotational terms of a symmetric top, allowing for centrifugal distortion, are commonly written

$$\tilde{F}(J,K)=\tilde{B}J(J+1)+(\tilde{A}-\tilde{B})K^2-\tilde{D}_J J^2(J+1)^2-\tilde{D}_{JK}J(J+1)K^2-\tilde{D}_K K^4$$

Derive an expression for the wavenumbers of the allowed rotational transitions. The following transition frequencies (in gigahertz, GHz) were observed for CH_3F:

51.0718	102.1426	102.1408	153.2103	153.2076

Determine the values of as many constants in the expression for the rotational terms as these values permit.

42.9 Derive an expression for the value of J corresponding to the most highly populated rotational energy level of a diatomic rotor at a temperature T, remembering that the degeneracy of each level is $2J+1$. Evaluate the expression for ICl (for which $\tilde{B}=0.1142$ cm^{-1}) at 25 °C. Repeat the problem for the most highly populated level of a spherical rotor, taking note of the fact that each level is $(2J+1)^2$-fold degenerate. Evaluate the expression for CH_4 (for which $\tilde{B}=5.24$ cm^{-1}) at 25 °C.

42.10 A. Dalgarno, in *Chemistry in the interstellar medium*, Frontiers of Astrophysics, ed. E.H. Avrett, Harvard University Press, Cambridge (1976), notes that although both CH and CN spectra show up strongly in the interstellar medium in the constellation Ophiuchus, the CN spectrum has become the standard for the determination of the temperature of the cosmic microwave background radiation. Demonstrate through a calculation why CH would not be as useful for this purpose as CN. The rotational constant $\tilde{B}_0$ for CH is 14.190 cm^{-1}.

42.11 The space immediately surrounding stars, the *circumstellar space*, is significantly warmer because stars are very intense black-body emitters with temperatures of several thousand kelvin. Discuss how such factors as cloud temperature, particle density, and particle velocity may affect the rotational spectrum of CO in an interstellar cloud. What new features in the spectrum of CO can be observed in gas ejected from and still near a star with temperatures of about 1000 K, relative to gas in a cloud with temperature of about 10 K? Explain how these features may be used to distinguish between circumstellar and interstellar material on the basis of the rotational spectrum of CO.

42.12 Pure rotational Raman spectra of gaseous C_6H_6 and C_6D_6 yield the following rotational constants: $\tilde{B}(C_6H_6)=0.189\,60$ cm^{-1}, $\tilde{B}(C_6D_6)=0.156\,81$ cm^{-1}. The moments of inertia of the molecules about any axis perpendicular to the C_6 axis were calculated from these data as $I(C_6H_6)=1.4759\times10^{-45}$ kg m^2, $I(C_6D_6)=1.7845\times10^{-45}$ kg m^2. Calculate the CC, CH, and CD bond lengths.

Topic 43 Vibrational spectroscopy: diatomic molecules

Discussion questions

43.1 Discuss the strengths and limitations of the parabolic and Morse functions as descriptors of the potential energy curve of a diatomic molecule.

43.2 Discuss the effect of vibrational excitation on the rotational constant of a diatomic molecule.

43.3 How is the method of combination differences used in rotation–vibration spectroscopy to determine rotational constants?

Exercises

43.1(a) An object of mass 100 g suspended from the end of a rubber band has a vibrational frequency of 2.0 Hz. Calculate the force constant of the rubber band.
43.1(b) An object of mass 1.0 g suspended from the end of a spring has a vibrational frequency of 10.0 Hz. Calculate the force constant of the spring.

43.2(a) Calculate the percentage difference in the fundamental vibrational wavenumbers of $^{23}Na^{35}Cl$ and $^{23}Na^{37}Cl$ on the assumption that their force constants are the same.
43.2(b) Calculate the percentage difference in the fundamental vibrational wavenumbers of $^{1}H^{35}Cl$ and $^{2}H^{37}Cl$ on the assumption that their force constants are the same.

43.3(a) The wavenumber of the fundamental vibrational transition of $^{35}Cl_2$ is 564.9 cm^{-1}. Calculate the force constant of the bond.
43.3(b) The wavenumber of the fundamental vibrational transition of $^{79}Br^{81}Br$ is 323.2 cm^{-1}. Calculate the force constant of the bond.

43.4(a) The hydrogen halides have the following fundamental vibrational wavenumbers: 4141.3 cm^{-1} (HF); 2988.9 cm^{-1} ($H^{35}Cl$); 2649.7 cm^{-1} ($H^{81}Br$); 2309.5 cm^{-1} ($H^{127}I$). Calculate the force constants of the hydrogen–halogen bonds.
43.4(b) From the data in Exercise 43.4(a), predict the fundamental vibrational wavenumbers of the deuterium halides.

43.5(a) For $^{16}O_2$, $\Delta\tilde{G}$ values for the transitions $v=1\leftarrow 0$, $2\leftarrow 0$, and $3\leftarrow 0$ are, respectively, 1556.22, 3088.28, and 4596.21 cm^{-1}. Calculate $\tilde{\nu}$ and x_e. Assume y_e to be zero.
43.5(b) For $^{14}N_2$, $\Delta\tilde{G}$ values for the transitions $v=1\leftarrow 0$, $2\leftarrow 0$, and $3\leftarrow 0$ are, respectively, 2329.91, 4631.20, and 6903.69 cm^{-1}. Calculate $\tilde{\nu}$ and x_e. Assume y_e to be zero.

43.6(a) Which of the following molecules may show infrared absorption spectra: (a) H_2, (b) HCl, (c) CO_2, (d) H_2O?
43.6(b) Which of the following molecules may show infrared absorption spectra: (a) CH_3CH_3, (b) CH_4, (c) CH_3Cl, (d) N_2?

Problems

43.1 The vibrational levels of NaI lie at the wavenumbers 142.81, 427.31, 710.31, and 991.81 cm^{-1}. Show that they fit the expression $(v+\frac{1}{2})\tilde{\nu}-(v+\frac{1}{2})^2 x_e\tilde{\nu}$, and deduce the force constant, zero-point energy, and dissociation energy of the molecule.

43.2 The HCl molecule is quite well described by the Morse potential with $D_e=5.33\,\mathrm{eV}$, $\tilde{\nu}=2989.7\,\mathrm{cm}^{-1}$, and $x_e\tilde{\nu}=52.05\,\mathrm{cm}^{-1}$. Assuming that the potential is unchanged on deuteration, predict the dissociation energies (D_0) of (a) HCl, (b) DCl.

43.3 The Morse potential (eqn 43.14) is very useful as a simple representation of the actual molecular potential energy. When RbH was studied, it was found that $\tilde{\nu}=936.8\,\mathrm{cm}^{-1}$ and $x_e\tilde{\nu}=14.15\,\mathrm{cm}^{-1}$. Plot the potential energy curve from 50 pm to 800 pm around $R_e=236.7$ pm. Then go on to explore how the rotation of a molecule may weaken its bond by allowing for the kinetic energy of rotation of a molecule and plotting $V^*=V+hc\tilde{B}J(J+1)$, with $\tilde{B}=\hbar/4\pi c\mu R^2$. Plot these curves on the same diagram for $J=40$, 80, and 100, and observe how the dissociation energy is affected by the rotation. (Taking $\tilde{B}=3.020\,\mathrm{cm}^{-1}$ at the equilibrium bond length will greatly simplify the calculation.)

43.4‡ Luo, et al. (*J. Chem. Phys.* **98**, 3564 (1993)) reported experimental observation of the He_2 complex, a species which had escaped detection for a long time. The fact that the observation required temperatures in the neighbourhood of 1 mK is consistent with computational studies which suggest that $hc\tilde{D}_e$ for He_2 is about 1.51×10^{-23} J, $hc\tilde{D}_0\approx 2\times10^{-26}$ J, and R_e about 297 pm. (See Problem 29.1.) (a) Estimate the fundamental vibrational wavenumber, force constant, moment of inertia, and rotational constant based on the harmonic-oscillator and rigid-rotor approximations. (b) Such a weakly bound complex is hardly likely to be rigid. Estimate the vibrational wavenumber and anharmonicity constant based on the Morse potential.

43.5 Confirm that a Morse oscillator has a finite number of bound states, the states with $V<hc\tilde{D}_e$. Determine the value of $v_{\max}$ for the highest bound state.

43.6 Provided higher-order terms are neglected, eqn 43.17 for the vibrational wavenumbers of an anharmonic oscillator, $\Delta\tilde{G}_{v+(1/2)}=\tilde{\nu}-2(v+1)x_e\tilde{\nu}+\ldots$, is the equation of a straight line when the left-hand side is plotted against $v+1$. Use the following data on CO to determine the values of $\tilde{\nu}$ and $x_e\tilde{\nu}$ for CO:

v	0	1	2	3	4
$\Delta\tilde{G}_{v+\frac{1}{2}}/\mathrm{cm}^{-1}$	2143.1	2116.1	2088.9	2061.3	2033.5

43.7 The rotational constant for CO is 1.9314 cm^{-1} and 1.6116 cm^{-1} in the ground and first excited vibrational states, respectively. By how much does the internuclear distance change as a result of this transition?

43.8 The average spacing between the rotational lines of the P and R branches of $^{12}C_2{}^{1}H_2$ and $^{12}C_2{}^{2}H_2$ is 2.352 cm^{-1} and 1.696 cm^{-1}, respectively. Estimate the CC and CH bond lengths.

43.9 Absorptions in the $v=1\leftarrow 0$ vibration–rotation spectrum of $^{1}H^{35}Cl$ were observed at the following wavenumbers (in cm^{-1}):

2998.05	2981.05	2963.35	2944.99	2925.92
2906.25	2865.14	2843.63	2821.59	2799.00

Assign the rotational quantum numbers and use the method of combination differences to determine the rotational constants of the two vibrational levels.

43.10 Suppose that the internuclear distance may be written $R=R_e+x$ where R_e is the equilibrium bond length. Also suppose that the potential well is symmetrical and confines the oscillator to small displacements. Deduce expressions for $1/\langle R\rangle^2$, $1/\langle R^2\rangle$, and $\langle 1/R^2\rangle$ to the lowest nonzero power of $\langle x^2\rangle/R_e^2$ and confirm that the values are not the same.

43.11 Continue the development of Problem 43.10 by using the virial expression to relate $\langle x^2\rangle$ to the vibrational quantum number. Does your result imply that the rotational constant increases or decreases as the oscillator becomes excited to higher quantum states? What would be the effect of anharmonicity?

43.12 The rotational constant for a diatomic molecule in the vibrational state v typically fits the expression $\tilde{B}_v=\tilde{B}_e-a(v+\frac{1}{2})$. For the interhalogen molecule IF it is found that $\tilde{B}_e=0.279\,71\,\mathrm{cm}^{-1}$ and $a=0.187\,\mathrm{m}^{-1}$ (note the change of units). Calculate $\tilde{B}_0$ and $\tilde{B}_1$ and use these values to calculate the wavenumbers of the $J'\rightarrow 3$ transitions of the P and R branches. You will need the following additional information: $\tilde{\nu}=610.258\,\mathrm{cm}^{-1}$ and $x_e\tilde{\nu}=3.141\,\mathrm{cm}^{-1}$. Estimate the dissociation energy of the IF molecule.

43.13 At low resolution, the strongest absorption band in the infrared absorption spectrum of $^{12}C^{16}O$ is centred at 2150 cm^{-1}. Upon closer examination at higher resolution, this band is observed to be split into two sets of closely spaced peaks, one on each side of the centre of the spectrum at 2143.26 cm^{-1}. The separation between the peaks immediately to the right and left of the centre is 7.655 cm^{-1}. Make the harmonic oscillator and rigid rotor approximations and calculate from these data: (a) the vibrational wavenumber of a CO molecule, (b) its molar zero-point vibrational energy, (c) the force constant of the CO bond, (d) the rotational constant $\tilde{B}$, and (e) the bond length of CO.

43.14 The analysis of combination differences summarized in Section 43.4b considered the R and P branches. Extend the analysis to the O and S branches of a Raman spectrum.

Topic 44 Vibrational spectroscopy: polyatomic molecules

Discussion questions

44.1 Discuss the physical origins of the gross selection rules for infrared spectroscopy.

44.2 Discuss the physical origins of the gross selection rules for vibrational Raman spectroscopy.

44.3 Suppose that you wish to characterize the normal modes of benzene in the gas phase. Why is it important to obtain both infrared absorption and Raman spectra of your sample?

Exercises

44.1(a) Which of the following molecules may show infrared absorption spectra: (a) H_2, (b) HCl, (c) CO_2, (d) H_2O?
44.1(b) Which of the following molecules may show infrared absorption spectra: (a) CH_3CH_3, (b) CH_4, (c) CH_3Cl, (d) N_2?

44.2(a) How many normal modes of vibration are there for the following molecules? (a) H_2O, (b) H_2O_2, (c) C_2H_4.
44.2(b) How many normal modes of vibration are there for the following molecules? (a) C_6H_6, (b) $C_6H_5CH_3$, (c) HC≡C–C≡C–H.

44.3(a) How many vibrational modes are there for the molecule NC–(C≡C–C≡C–)$_{10}$CN detected in an interstellar cloud?
44.3(b) How many vibrational modes are there for the molecule NC–(C≡C–C≡C–)$_8$CN detected in an interstellar cloud?

44.4(a) Write an expression for the vibrational term for the ground vibrational state of H_2O in terms of the wavenumbers of the normal modes. Neglect anharmonicities as in eqn 44.1.
44.4(b) Write an expression for the vibrational term for the ground vibrational state of SO_2 in terms of the wavenumbers of the normal modes. Neglect anharmonicities as in eqn 44.1.

44.5(a) Which of the three vibrations of an AB_2 molecule are infrared or Raman active when it is (a) angular, (b) linear?
44.5(b) Which of the vibrations of an AB_3 molecule are infrared or Raman active when it is (a) trigonal planar, (b) trigonal pyramidal?

44.6(a) Consider the vibrational mode that corresponds to the uniform expansion of the benzene ring. Is it (a) Raman, (b) infrared active?
44.6(b) Consider the vibrational mode that corresponds to the boat-like bending of a benzene ring. Is it (a) Raman, (b) infrared active?

44.7(a) The molecule CH_2Cl_2 belongs to the point group C_{2v}. The displacements of the atoms span $5A_1 + 2A_2 + 4B_1 + 4B_2$. What are the symmetries of the normal modes of vibration?
44.7(b) A carbon disulfide molecule belongs to the point group $D_{\infty h}$. The nine displacements of the three atoms span $A_{1g} + 2A_{1u} + 2E_{1u} + E_{1g}$. What are the symmetries of the normal modes of vibration?

44.8(a) Which of the normal modes of CH_2Cl_2 (Exercise 44.7(a)) are infrared active? Which are Raman active?
44.8(b) Which of the normal modes of carbon disulfide (Exercise 44.7(b)) are infrared active? Which are Raman active?

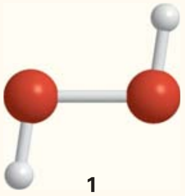
Problems

44.1 Suppose that the out-of-plane distortion of a planar molecule could be described by a potential energy $V = V_0(1 - e^{-bh^4})$, where h is the distance by which the central atom is displaced. Sketch this potential energy as a function of h (allow h to be both negative and positive). What could be said about (a) the force constant, (b) the vibrations? Sketch the form of the ground-state wavefunction.

44.2 Predict the shape of the nitronium ion, NO_2^+, from its Lewis structure and the VSEPR model. It has one Raman active vibrational mode at 1400 cm^{-1}, two strong IR active modes at 2360 and 540 cm^{-1}, and one weak IR mode at 3735 cm^{-1}. Are these data consistent with the predicted shape of the molecule? Assign the vibrational wavenumbers to the modes from which they arise.

44.3 Consider the molecule CH_3Cl. (a) To what point group does the molecule belong? (b) How many normal modes of vibration does the molecule have? (c) What are the symmetries of the normal modes of vibration for this molecule? (d) Which of the vibrational modes of this molecule are infrared active? (e) Which of the vibrational modes of this molecule are Raman active?

44.4 Suppose that three conformations are proposed for the nonlinear molecule H_2O_2 (**1**, **2**, and **3**). The infrared absorption spectrum of gaseous H_2O_2 has bands at 870, 1370, 2869, and 3417 cm^{-1}. The Raman spectrum of the same sample has bands at 877, 1408, 1435, and 3407 cm^{-1}. All bands correspond to fundamental vibrational wavenumbers and you may assume that (a) the 870 and 877 cm^{-1} bands arise from the same normal mode, and (b) the 3417 and 3407 cm^{-1} bands arise from the same normal mode. (i) If H_2O_2 were linear, how many normal modes of vibration would it have? (ii) Give the symmetry point group of each of the three proposed conformations of nonlinear H_2O_2. (iii) Determine which of the proposed conformations is inconsistent with the spectroscopic data. Explain your reasoning.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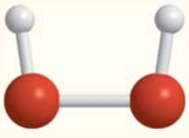
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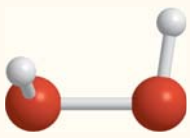
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Topic 45 Electronic spectroscopy

Discussion questions

45.1 Explain the origin of the term symbol $^3\Sigma_g^-$ for the ground state of dioxygen.

45.2 Explain the basis of the Franck–Condon principle and how it leads to the formation of a vibrational progression.

45.3 How do the band heads in P and R branches arise? Could the Q branch show a head?

45.4 Explain how colour can arise from molecules.

45.5 Suppose that you are a colour chemist and have been asked to intensify the colour of a dye without changing the type of compound, and that the dye in question was a polyene. (a) Would you choose to lengthen or to shorten the chain? (b) Would the modification to the length shift the apparent colour of the dye towards the red or the blue?

Exercises

45.1(a) One of the excited states of the C_2 molecule has the valence electron configuration $1\sigma_g^2 1\sigma_u^2 1\pi_u^3 1\pi_g^1$. Give the multiplicity and parity of the term.
45.1(b) One of the excited states of the C_2 molecule has the valence electron configuration $1\sigma_g^2 1\sigma_u^2 1\pi_u^2 1\pi_g^2$. Give the multiplicity and parity of the term.

45.2(a) Which of the following transitions are electric-dipole allowed? (a) $^2\Pi \leftrightarrow {}^2\Pi$, (b) $^1\Sigma \leftrightarrow {}^1\Sigma$, (c) $\Sigma \leftrightarrow \Delta$, (d) $\Sigma^+ \leftrightarrow \Sigma^-$, (e) $\Sigma^+ \leftrightarrow \Sigma^+$.
45.2(b) Which of the following transitions are electric-dipole allowed? (a) $^1\Sigma_g^+ \leftrightarrow {}^1\Sigma_u^+$, (b) $^3\Sigma_g^+ \leftrightarrow {}^3\Sigma_u^+$, (c) $\pi^* \leftrightarrow \mathrm{n}$.

45.3(a) The ground-state wavefunction of a certain molecule is described by the vibrational wavefunction $\psi_0 = N_0 \mathrm{e}^{-ax^2}$. Calculate the Franck–Condon factor for a transition to a vibrational state described by the wavefunction $\psi_v = N_v \mathrm{e}^{-b(x-x_0)^2}$ with $b = a/2$.
45.3(b) The ground-state wavefunction of a certain molecule is described by the vibrational wavefunction $\psi_0 = N_0 \mathrm{e}^{-ax^2}$. Calculate the Franck–Condon factor for a transition to a vibrational state described by the wavefunction $\psi_v = N_v x\mathrm{e}^{-b(x-x_0)^2}$, with $b = a/2$.

45.4(a) Suppose that the ground vibrational state of a molecule is modelled by using the particle-in-a-box wavefunction, $\psi_0 = (2/L)^{1/2}\sin(\pi x/L)$ for $0 \le x \le L$ and 0 elsewhere. Calculate the Franck–Condon factor for a transition to a vibrational state described by the wavefunction $\psi_v = (2/L)^{1/2}\sin\{\pi(x - L/2)/L\}$ for $L/4 \le x \le 5L/4$ and 0 elsewhere.
45.4(b) Suppose that the ground vibrational state of a molecule is modelled by using the particle-in-a-box wavefunction $\psi_0 = (2/L)^{1/2}\sin(\pi x/L)$ for $0 \le x \le L$ and 0 elsewhere. Calculate the Franck–Condon factor for a transition to a vibrational state described by the wavefunction $\psi_v = (2/L)^{1/2}\sin\{\pi(x - L/4)/L\}$ for $L/2 \le x \le 3L/2$ and 0 elsewhere.

45.5(a) Use eqn 45.8a to infer the value of J corresponding to the location of the band head of the P branch of a transition.
45.5(b) Use eqn 45.8c to infer the value of J corresponding to the location of the band head of the R branch of a transition.

45.6(a) The following parameters describe the electronic ground state and an excited electronic state of SnO: $\tilde{B} = 0.3540\,\mathrm{cm}^{-1}$, $\tilde{B}' = 0.3101\,\mathrm{cm}^{-1}$. Which branch of the transition between them shows a head? At what value of J will it occur?
45.6(b) The following parameters describe the electronic ground state and an excited electronic state of BeH: $\tilde{B} = 10.308\,\mathrm{cm}^{-1}$, $\tilde{B}' = 10.470\,\mathrm{cm}^{-1}$. Which branch of the transition between them shows a head? At what value of J will it occur?

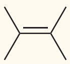
45.7(a) The R branch of the $^1\Pi_u \leftarrow {}^1\Sigma_g^+$ transition of H_2 shows a band head at the very low value of $J = 1$. The rotational constant of the ground state is $60.80\,\mathrm{cm}^{-1}$. What is the rotational constant of the upper state? Has the bond length increased or decreased in the transition?
45.7(b) The P branch of the $^2\Pi \leftarrow {}^2\Sigma^+$ transition of CdH shows a band head at $J = 25$. The rotational constant of the ground state is $5.437\,\mathrm{cm}^{-1}$. What is the rotational constant of the upper state? Has the bond length increased or decreased in the transition?

45.8(a) The complex ion $[\mathrm{Fe(OH_2)_6}]^{3+}$ has an electronic absorption spectrum with a maximum at 700 nm. Estimate a value of Δ_O for the complex.
45.8(b) The complex ion $[\mathrm{Fe(CN)_6}]^{3-}$ has an electronic absorption spectrum with a maximum at 305 nm. Estimate a value of Δ_O for the complex.

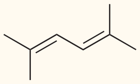
45.9(a) Suppose that we can model a charge-transfer transition in a one-dimensional system as a process in which a rectangular wavefunction that is nonzero in the range $0 \le x \le a$ makes a transition to another rectangular wavefunction that is nonzero in the range $\frac{1}{2}a \le x \le b$. Evaluate the transition moment $\int \psi_f x \psi_i \,\mathrm{d}x$. (Assume $a < b$.)
45.9(b) Suppose that we can model a charge-transfer transition in a one-dimensional system as a process in which an electron described by a rectangular wavefunction that is nonzero in the range $0 \le x \le a$ makes a transition to another rectangular wavefunction that is nonzero in the range $ca \le x \le a$ where $0 \le c \le 1$. Evaluate the transition moment $\int \psi_f x \psi_i \,\mathrm{d}x$ and explore its dependence on c.

45.10(a) Suppose that we can model a charge-transfer transition in a one-dimensional system as a process in which a Gaussian wavefunction centred on $x = 0$ and width a makes a transition to another Gaussian wavefunction of the same width centred on $x = \frac{1}{2}a$. Evaluate the transition moment $\int \psi_f x \psi_i \,\mathrm{d}x$.
45.10(b) Suppose that we can model a charge-transfer transition in a one-dimensional system as a process in which an electron described by a Gaussian wavefunction centred on $x = 0$ and width a makes a transition to another Gaussian wavefunction of width $a/2$ and centred on $x = 0$. Evaluate the transition moment $\int \psi_f x \psi_i \,\mathrm{d}x$.

45.11(a) The two compounds 2,3-dimethyl-2-butene (**4**) and 2,5-dimethyl-2,4-hexadiene (**5**) are to be distinguished by their ultraviolet absorption spectra. The maximum absorption in one compound occurs at 192 nm and in the other at 243 nm. Match the maxima to the compounds and justify the assignment.

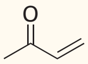


4 2,3-Dimethyl-2-butene



5 2,5-Dimethyl-2,4-hexadiene

45.11(b) 3-Buten-2-one (**6**) has a strong absorption at 213 nm and a weaker absorption at 320 nm. Justify these features and assign the ultraviolet absorption transitions.



6 3-Butene-2-one

Problems

45.1 The term symbol for the first excited state of N_2^+ is $^2\Pi_g$. Use the building-up principle to find the excited-state configuration to which this term symbol corresponds.

45.2‡ Dojahn, et al. (*J. Phys. Chem.* **100**, 9649 (1996)) characterized the potential energy curves of the ground and electronic states of homonuclear diatomic halogen anions. These anions have a $^2\Sigma_u^+$ ground state and $^2\Pi_g$, $^2\Pi_u$, and $^2\Sigma_g^+$ excited states. To which of the excited states are electric-dipole transitions allowed? Explain your conclusion.

45.3 The vibrational wavenumber of the oxygen molecule in its electronic ground state is 1580 cm^{-1}, whereas that in the excited state (B $^3\Sigma_u^-$), to which there is an allowed electronic transition, is 700 cm^{-1}. Given that the separation in energy between the minima in their respective potential energy curves of these two electronic states is 6.175 eV, what is the wavenumber of the lowest energy transition in the band of transitions originating from the $v=0$ vibrational state of the electronic ground state to this excited state? Ignore any rotational structure or anharmonicity.

45.4 We are now ready to understand more deeply the features of photoelectron spectra (Topic 24). Figure F9.4 shows the photoelectron spectrum of HBr. Disregarding for now the fine structure, the HBr lines fall into two main groups. The least tightly bound electrons (with the lowest ionization energies and hence highest kinetic energies when ejected) are those in the lone pairs of the Br atom. The next ionization energy lies at 15.2 eV, and corresponds to the removal of an electron from the HBr σ bond. (a) The spectrum shows that ejection of a σ electron is accompanied by a considerable amount of vibrational excitation. Use the Franck–Condon principle to account for this observation. (b) Go on to explain why the lack of much vibrational structure in the other band is consistent with the nonbonding role of the Br4p$_x$ and Br4p$_y$ lone-pair electrons.

45.5 The highest kinetic energy electrons in the photoelectron spectrum of H_2O using 21.22 eV radiation are at about 9 eV and show a large vibrational spacing of 0.41 eV. The symmetric stretching mode of the neutral H_2O molecule lies at 3652 cm^{-1}. (a) What conclusions can be drawn from the nature of the orbital from which the electron is ejected? (b) In the same spectrum of H_2O, the band near 7.0 eV shows a long vibrational series with spacing 0.125 eV. The bending mode of H_2O lies at 1596 cm^{-1}. What conclusions can you draw about the characteristics of the orbital occupied by the photoelectron?

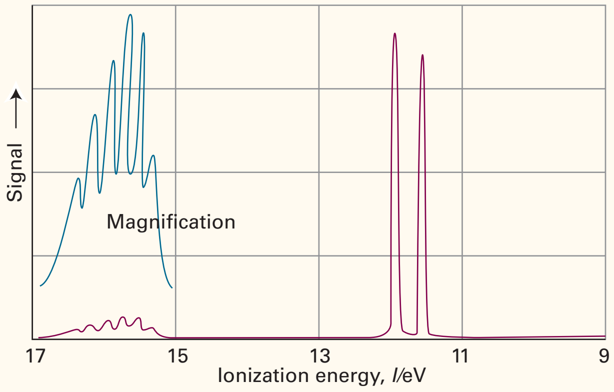


Figure F9.4 The photoelectron spectrum of HBr.

45.6 A lot of information about the energy levels and wavefunctions of small inorganic molecules can be obtained from their ultraviolet spectra. An example of a spectrum with considerable vibrational structure, that of gaseous SO_2 at 25 °C, is shown in Fig. 45.5. Estimate the integrated absorption coefficient for the transition. What electronic states are accessible from the A_1 ground state of this C_{2v} molecule by electric dipole transitions?

45.7 Assume that the electronic states of the π electrons of a conjugated molecule can be approximated by the wavefunctions of a particle in a one-dimensional box, and that the magnitude of the dipole moment can be related to the displacement along this length by $\mu=-ex$. Show that the transition probability for the transition $n=1\rightarrow n=2$ is nonzero, whereas that for $n=1\rightarrow n=3$ is zero. *Hints*: (a) The following relation will be useful: $\sin x\sin y=\frac{1}{2}\cos(x-y)-\frac{1}{2}\cos(x+y)$. (b) Relevant integrals are found in the *Resource section*.

45.8 1,3,5-Hexatriene (a kind of 'linear' benzene) was converted into benzene itself. On the basis of a free-electron molecular orbital model (in which hexatriene is treated as a linear box and benzene as a ring), would you expect the lowest-energy absorption to rise or fall in energy?

45.9 Estimate the magnitude of the transition dipole moment of a charge-transfer transition modelled as the migration of an electron from an H1s orbital on one atom to another H1s orbital on an atom a distance R away. Approximate the transition moment by $-eRS$, where S is the overlap integral of the two orbitals. Sketch the transition moment as a function of R using the curve for S given in Fig. 24.7. Why does the intensity of a charge-transfer transition fall to zero as R approaches zero and infinity?

45.10 Figure F9.5 shows the UV–visible absorption spectra of a selection of amino acids. Suggest reasons for their different appearances in terms of the structures of the molecules.

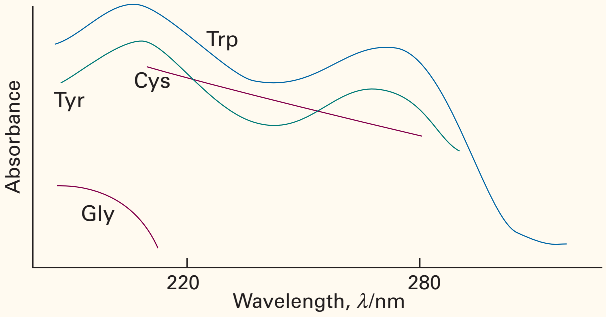


Figure F9.5 Electronic absorption spectra of selected amino acids.

Topic 46 Decay of excited states

Discussion questions

46.1 Describe the mechanism of fluorescence. In what respects is a fluorescence spectrum not the exact mirror image of the corresponding absorption spectrum?

46.2 What is the evidence for the correctness of the mechanism of fluorescence?

46.3 Describe the principles of (a) continuous-wave and (b) pulsed laser action.

46.4 How might you use a *Q*-switched or mode-locked laser in the study of a very fast chemical reaction that can be initiated by absorption of light?

Exercises

46.1(a) The line marked A in Fig. F9.6 is the fluorescence spectrum of benzophenone in solid solution in ethanol at low temperatures observed when the sample is illuminated with 360 nm light. What can be said about the vibrational energy levels of the carbonyl group in (a) its ground electronic state and (b) its excited electronic state?

46.1(b) When naphthalene is illuminated with 360 nm light it does not absorb, but the line marked B in Fig F9.6 is the phosphorescence spectrum of a solid solution of a mixture of naphthalene and benzophenone in ethanol. Now a component of fluorescence from naphthalene can be detected. Account for this observation.

46.2(a) The oxygen molecule absorbs ultraviolet radiation in a transition from its $^3\Sigma_g^-$ ground electronic state to an excited state that is energetically close to a dissociative $^5\Pi_u$ state. The absorption band has a relatively large experimental linewidth. Account for this observation.

46.2(b) The hydrogen molecule absorbs ultraviolet radiation in a transition from its $^1\Sigma_g^+$ ground electronic state to an excited state that is energetically close to a dissociative $^1\Sigma_u^+$ state. The absorption band has a relatively large experimental linewidth. Account for this observation.

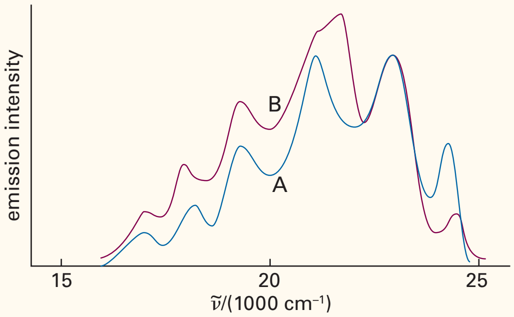


Figure F9.6 The fluorescence and phosphorescence spectra of two solutions.

46.3(a) A pulsed laser rated at 0.10 mJ can generate radiation with peak power output of 5.0 MW and average power output of 7.0 kW. What are the pulse duration and repetition rate?

46.3(b) A pulsed laser rated at 20.0 μJ can generate radiation with peak power output of 100 kW and average power output of 0.40 mW. What are the pulse duration and repetition rate?

Problems

46.1 The fluorescence spectrum of anthracene vapour shows a series of peaks of increasing intensity with individual maxima at 440 nm, 410 nm, 390 nm, and 370 nm followed by a sharp cut-off at shorter wavelengths. The absorption spectrum rises sharply from zero to a maximum at 360 nm with a trail of peaks of lessening intensity at 345 nm, 330 nm, and 305 nm. Account for these observations.

46.2 Use mathematical software or an electronic spreadsheet to simulate the output of a mode-locked laser (that is, plots such as that shown in Fig. 46.16) for $L = 30$ cm and $N = 100$ and 1000.

46.3 Matrix-assisted laser desorption/ionization (MALDI) is a type of mass spectrometry, a technique in which the sample is first ionized in the gas phase and then the mass-to-charge number ratios (m/z) of all ions are measured. *MALDI-TOF mass spectrometry*, so called because the MALDI technique is coupled to a time-of-flight (TOF) ion detector, is used widely in the determination of the molar masses of macromolecules. In a MALDI-TOF mass spectrometer, the macromolecule is first embedded in a solid matrix that often consists of an organic acid such as 2,5-dihydroxybenzoic acid, nicotinic acid, or α-cyanocarboxylic acid. This sample is then irradiated with a laser pulse. The pulse of electromagnetic energy ejects matrix ions, cations, and neutral macromolecules, thus creating a dense gas plume above the sample surface. The macromolecule is ionized by collisions and complexation with H^+ cations, resulting in molecular ions of varying charges. The spectrum of a mixture of polymers consists of multiple peaks arising from molecules with different molar masses. A MALDI-TOF mass spectrum consists of two intense features at $m/z = 9912$ and $4554\,\text{g mol}^{-1}$. Does the sample contain one or two distinct biopolymers? Explain your answer.

46.4 A certain molecule fluoresces at a wavelength of 400 nm with a half-life of 1.0 ns. It phosphoresces at 500 nm. If the ratio of the transition probabilities for stimulated emission for the $S^* \rightarrow S$ to the $T \rightarrow S$ transitions is 1.0×10^5, what is the half-life of the phosphorescent state?

Integrated activities

F9.1 In the group theoretical language developed in Topics 31–33, a spherical rotor is a molecule that belongs to a cubic or icosahedral point group, a symmetric rotor is a molecule with at least a threefold axis of symmetry, and an asymmetric rotor is a molecule without a threefold (or higher) axis. Linear molecules are linear rotors. Classify each of the following molecules as a spherical, symmetric, linear, or asymmetric rotor and justify your answers with group theoretical arguments: (a) CH_4, (b) CH_3CN, (c) CO_2, (d) CH_3OH, (e) benzene, (f) pyridine.

F9.2 Derive eqn 41.17 ($\tilde{D}_J = 4\tilde{B}^3/\tilde{\nu}^2$) for the centrifugal distortion constant $\tilde{D}_J$ of a diatomic molecule of effective mass m_{eff}. Treat the bond as an elastic spring with force constant k_f and equilibrium length r_e that is subjected to a centrifugal distortion to a new length r_c. Begin the derivation by letting the particles experience a restoring force of magnitude $k_f(r_c - r_e)$ that is countered perfectly by a centrifugal force $m_{\text{eff}}\omega^2 r_c$, where ω is the angular velocity of the rotating molecule. Then introduce quantum mechanical effects by writing the angular momentum as $\{J(J+1)\}^{1/2}\hbar$. Finally, write an expression for the energy of the rotating molecule, compare it with eqn 41.16, and infer an expression for $\tilde{D}_J$.

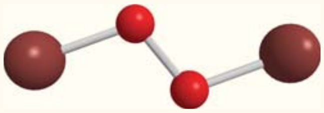
F9.3‡ The H_3^+ ion has recently been found in the interstellar medium and in the atmospheres of Jupiter, Saturn, and Uranus. The rotational energy levels of H_3^+, an oblate symmetric rotor, are given by eqn 41.13, with $\tilde{C}$ replacing $\tilde{A}$, when centrifugal distortion and other complications are ignored. Experimental values for vibrational–rotational constants are $\tilde{\nu}(E') = 2521.6\,\text{cm}^{-1}$, $\tilde{B} = 43.55\,\text{cm}^{-1}$, and $\tilde{C} = 20.71\,\text{cm}^{-1}$. (a) Show that, for a nonlinear planar molecule (such as H_3^+), $I_C = 2I_B$. The rather large discrepancy with the experimental values is due to factors ignored in eqn 41.13. (b) Calculate an approximate value of the H—H bond length in H_3^+. (c) The value of R_e obtained from the best quantum mechanical calculations by J.B. Anderson (*J. Chem. Phys.* **96**, 3702 (1991)) is 87.32 pm. Use this result to calculate the values of the rotational constants $\tilde{B}$ and $\tilde{C}$. (d) Assuming that the geometry and force constants are the same in D_3^+ and H_3^+, calculate the spectroscopic constants of D_3^+. The molecular ion D_3^+ was first produced by Shy, et al. (*Phys. Rev. Lett.* **45**, 535 (1980)), who observed the $\nu_2(E')$ band in the infrared.

F9.4 Use molecular modelling software and the computational method of your choice (semi-empirical, *ab initio*, or DFT method) to construct molecular potential energy curves like the one shown in Fig. 43.1. Consider the hydrogen halides (HF, HCl, HBr, and HI): (a) plot the calculated energy of each molecule against the bond length, and (b) identify the order of force constants of the H–Hal bonds.

F9.5 The semi-empirical, *ab initio*, and DFT methods discussed in Topics 28–30 can be used to simulate the vibrational spectrum of a molecule, and it is then possible to determine the correspondence between a vibrational frequency and the atomic displacements that give rise to a normal mode. (a) Using molecular modelling software and the computational method of your choice (semi-empirical, *ab initio*, or DFT method), calculate the fundamental vibrational wavenumbers and visualize the vibrational normal modes of SO_2 in the gas phase. (b) The experimental values of the fundamental vibrational wavenumbers of SO_2 in the gas phase are $525\,cm^{-1}$, $1151\,cm^{-1}$, and $1336\,cm^{-1}$. Compare the calculated and experimental values. Even if agreement is poor, is it possible to establish a correlation between an experimental value of the vibrational wavenumber with a specific vibrational normal mode?

F9.6 Use appropriate electronic structure software to perform calculations on H_2O and CO_2 using basis sets of your or your instructor's choosing. (a) Compute ground-state energies, equilibrium geometries, and vibrational frequencies for each molecule. (b) Compute the magnitude of the dipole moment of H_2O; the experimental value is 1.854 D. (c) Compare computed values to experiment and suggest reasons for any discrepancies.

F9.7 The protein haemerythrin is responsible for binding and carrying O_2 in some invertebrates. Each protein molecule has two Fe^{2+} ions that are in very close proximity and work together to bind one molecule of O_2. The Fe_2O_2 group of oxygenated haemerythrin is coloured and has an electronic absorption band at 500 nm. The resonance Raman spectrum of oxygenated haemerythrin obtained with laser excitation at 500 nm has a band at $844\,cm^{-1}$ that has been attributed to the O–O stretching mode of bound $^{16}O_2$. (a) Why is resonance Raman spectroscopy and not infrared spectroscopy the method of choice for the study of the binding of O_2 to haemerythrin? (b) Proof that the $844\,cm^{-1}$ band arises from a bound O_2 species may be obtained by conducting experiments on samples of haemerythrin that have been mixed with $^{18}O_2$, instead of $^{16}O_2$. Predict the fundamental vibrational wavenumber of the ^{18}O–^{18}O stretching mode in a sample of haemerythrin that has been treated with $^{18}O_2$. (c) The fundamental vibrational wavenumbers for the O–O stretching modes of O_2, O_2^- (superoxide anion), and O_2^{2-} (peroxide anion) are 1555, 1107, and $878\,cm^{-1}$, respectively. Explain this trend in terms of the electronic structures of O_2, O_2^-, and O_2^{2-}. *Hint*: Review Topic 24. What are the bond orders of O_2, O_2^-, and O_2^{2-}? (d) Based on the data given above, which of the following species best describes the Fe_2O_2 group of haemerythrin: $Fe_2^{2+}O_2$, $Fe^{2+}Fe^{3+}O_2^-$, or $Fe_2^{3+}O_2^{2-}$? Explain your reasoning. (e) The resonance Raman spectrum of haemerythrin mixed with $^{16}O^{18}O$ has two bands that can be attributed to the O–O stretching mode of bound oxygen. Discuss how this observation may be used to exclude one or more of the four proposed schemes (**7**–**10**) for binding of O_2 to the Fe_2 site of haemerythrin.



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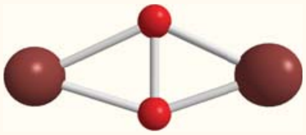

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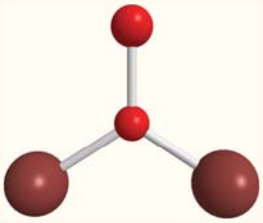

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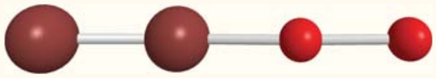

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F9.8‡ There is a gaseous interstellar cloud in the constellation Ophiuchus which is illuminated from behind by the star ζ-Ophiuci. Analysis of the electronic–vibrational–rotational absorption lines shows the presence of CN molecules in the interstellar medium. A strong absorption line in the ultraviolet region at $\lambda = 387.5\,nm$ was observed, corresponding to the transition $J = 0$–1. Unexpectedly, a second strong absorption line with 25 per cent of the intensity of the first was found at a slightly longer wavelength ($\Delta\lambda = 0.061\,nm$), corresponding to the transition $J = 1$–1 (here allowed). Calculate the temperature of the CN molecules. Gerhard Herzberg, who was later to receive the Nobel Prize for his contributions to spectroscopy, calculated the temperature as 2.3 K. Although puzzled by this result, he did not realize its full significance. If he had, his prize might have been for the discovery of the cosmic microwave background radiation.

F9.9‡ One of the principal methods for obtaining the electronic spectra of unstable radicals is to study the spectra of comets, which are almost entirely due to radicals. Many radical spectra have been found in comets, including that due to CN. These radicals are produced in comets by the absorption of far-ultraviolet solar radiation by their parent compounds. Subsequently, their fluorescence is excited by sunlight of longer wavelength. The spectra of comet Hale–Bopp (C/1995 O1) have been the subject of many recent studies. One such study is that of the fluorescence spectrum of CN in the comet at large heliocentric distances by R.M. Wagner and D.G. Schleicher (*Science* **275**, 1918 (1997)), in which the authors determine the spatial distribution and rate of production of CN in the coma. The (0–0) vibrational band is centred on 387.6 nm and the weaker (1–1) band with relative intensity 0.1 is centred on 386.4 nm. The band heads for (0–0) and (0–1) are known to be 388.3 and 421.6 nm, respectively. From these data, calculate the energy of the excited S_1 state relative to the ground S_0 state, the vibrational wavenumbers and the difference in the vibrational wavenumbers of the two states, and the relative populations of the $v = 0$ and $v = 1$ vibrational levels of the S_1 state. Also estimate the effective temperature of the molecule in the excited S_1 state. Only eight rotational levels of the S_1 state are thought to be populated. Is that observation consistent with the effective temperature of the S_1 state?

F9.10 The moments of inertia of the linear mercury(II) halides are very large, so the O and S branches of their vibrational Raman spectra show little rotational structure. Nevertheless, the peaks of both branches can be identified and have been used to measure the rotational constants of the molecules (R.J.H. Clark and D.M. Rippon, *J. Chem. Soc. Faraday Soc. II* **69**, 1496 (1973)). Show, from a knowledge of the value of J corresponding to the intensity maximum, that the separation of the peaks of the O and S branches is given by the Placzek–Teller relation, $\delta = (32\tilde{B}kT/hc)^{1/2}$. The following widths were obtained at the temperatures stated:

	$HgCl_2$	$HgBr_2$	HgI_2
$\theta/°C$	282	292	292
δ/cm^{-1}	23.8	15.2	11.4

Calculate the bond lengths in the three molecules.

F9.11‡ A mixture of carbon dioxide (2.1 per cent) and helium, at 1.00 bar and 298 K in a gas cell of length 10 cm, has an infrared absorption band centred at $2349\,cm^{-1}$ with absorbances, $A(\tilde{\nu})$, described by

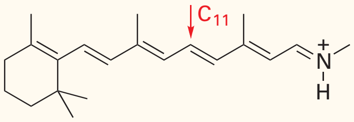
$$A(\tilde{\nu}) = \frac{a_1}{1 + a_2(\tilde{\nu} - a_3)^2} + \frac{a_4}{1 + a_5(\tilde{\nu} - a_6)^2}$$

where the coefficients are $a_1 = 0.932$, $a_2 = 0.005050\,cm^2$, $a_3 = 2333\,cm^{-1}$, $a_4 = 1.504$, $a_5 = 0.01521\,cm^2$, $a_6 = 2362\,cm^{-1}$. (a) Draw graphs of $A(\tilde{\nu})$ and

$\varepsilon(\tilde{\nu})$. What is the origin of both the band and the bandwidth? What are the allowed and forbidden transitions of this band? (b) Calculate the transition wavenumbers and absorbances of the band with a simple harmonic oscillator–rigid rotor model and compare the result with the experimental spectra. The CO bond length is 116.2 pm. (c) Within what height, h, is basically all the infrared emission from the Earth in this band absorbed by atmospheric carbon dioxide? The mole fraction of CO_2 in the atmosphere is 3.3×10^{-4} and $T/K = 288 - 0.0065(h/m)$ below 10 km. Draw a surface plot of the atmospheric transmittance of the band as a function of both height and wavenumber.

F9.12 Use a group theoretical arguments to decide which of the following transitions are electric-dipole allowed: (a) the $\pi^* \leftarrow \pi$ transition in ethene, (b) the $\pi^* \leftarrow n$ transition in a carbonyl group in a C_{2v} environment.

F9.13 Use molecule (**11**) as a model of the *trans* conformation of the chromophore found in rhodopsin. In this model, the methyl group bound to the nitrogen atom of the protonated Schiff's base replaces the protein. (a) Using molecular modelling software and the computational method of your instructor's choice, calculate the energy separation between the HOMO and LUMO of (**11**). (b) Repeat the calculation for the 11-*cis* form of (**11**). (c) Based on your results from parts (a) and (b), do you expect the experimental frequency for the $\pi^* \leftarrow \pi$ visible absorption of the *trans* form of (**11**) to be higher or lower than that for the 11-*cis* form of (**11**)?



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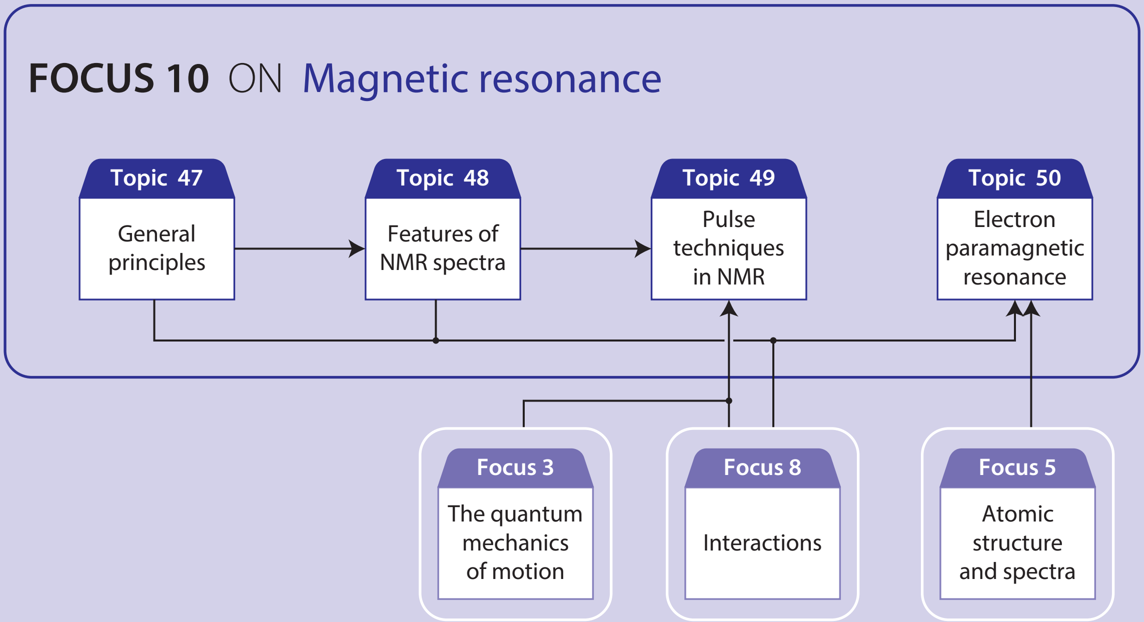
F9.14 Aromatic hydrocarbons and I_2 form complexes from which charge-transfer electronic transitions are observed. The hydrocarbon acts as an electron donor and I_2 as an electron acceptor. The energies $h\nu_{max}$ of the charge transfer transitions for a number of hydrocarbon–I_2 complexes are given below:

Hydrocarbon	Benzene	Biphenyl	Naphthalene	Phenanthrene	Pyrene	Anthracene
$h\nu_{max}$/eV	4.184	3.654	3.452	3.288	2.989	2.890

Investigate the hypothesis that there is a correlation between the energy of the HOMO of the hydrocarbon (from which the electron comes in the charge-transfer transition) and $h\nu_{max}$. Use one of the molecular electronic structure methods discussed in Topics 28–30 to determine the energy of the HOMO of each hydrocarbon in the data set.

F9.15 Spin angular momentum is conserved when a molecule dissociates into atoms. What atom multiplicities are permitted when (a) an O_2 molecule, (b) an N_2 molecule dissociates into atoms?

FOCUS 10 ON Magnetic resonance



In *Atomic structure and spectra* we see that electrons possess a property called ‘spin’. The techniques of ‘magnetic resonance’ which are treated in this set of Topics probe transitions between spin states of electrons and nuclei in molecules. ‘Nuclear magnetic resonance’ (NMR) spectroscopy, the main focus of this group of Topics, is one of the most widely used techniques in chemistry for the exploration of structural and dynamical properties of molecules as large as biopolymers. In **Topic 47** we begin our discussion of magnetic resonance with an account of the principles that govern spectroscopic transitions between spin states of nuclei and electrons in molecules.

Topic 48 is a discussion of conventional NMR, showing how the properties of a magnetic nucleus are affected by its electronic environment and the presence of magnetic nuclei in its vicinity. These concepts lead to understanding of how molecular structure governs the appearance of NMR spectra. Modern versions of NMR are based on the use of pulses of electromagnetic radiation and the processing of the resulting signal by ‘Fourier transform’ techniques (**Topic 49**); they also utilize concepts introduced in *Interactions* and *The quantum mechanics of motion*. It is through the application of these pulse techniques that NMR spectroscopy can probe a vast array of small and large molecules in a variety of environments.

The experimental techniques for electron paramagnetic resonance (EPR) resemble those used in the early days of NMR. The information obtained is used to investigate species with unpaired electrons, using concepts from *Atomic structure and spectra*. **Topic 50** is a brief survey of the applications of EPR to the study of organic radicals and d-metal complexes.

What is the impact of this material?

One of the most striking applications of nuclear magnetic resonance is in medicine. ‘Magnetic resonance imaging’ (MRI) is a portrayal of the concentrations of protons in a solid object (*Impact* 10.1). The technique is particularly useful for diagnosing disease. In *Impact* 10.2 we highlight an application of electron paramagnetic resonance in materials science and biochemistry: the use of a ‘spin probe’, a radical that interacts with a biopolymer or a nanostructure and has an EPR spectrum that reveals its structural and dynamical properties.

To read more about the impact of this material, scan the QR code or go to http://bcs.whfreeman.com/webpub/chemistry/qmc2e/impact/qchem_impact10.html.

TOPIC 47

General principles

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➤ Why do you need to know this material?

Nuclear magnetic resonance spectroscopy is used widely in chemistry and medicine. To understand the power of magnetic resonance, you need to understand the principles that govern spectroscopic transitions between spin states of electrons and nuclei in molecules.

➤ What is the key idea?

Resonant absorption occurs when the separation between the energy levels of spins in a magnetic field matches the energy of incident photons.

➤ What do you need to know already?

You need to be familiar with the quantum mechanical concept of spin (Topic 19) and the Boltzmann distribution (*Foundations,* Topic 2, and Topic 51).

When two pendulums share a slightly flexible support and one is set in motion, the other is forced into oscillation by the motion of the common axle. As a result, energy flows between the two pendulums. The energy transfer occurs most efficiently when the frequencies of the two pendulums are identical. The condition of strong effective coupling when the frequencies of two oscillators are identical is called **resonance**. Resonance is the basis of a number of everyday phenomena, including the response of radios to the weak oscillations of the electromagnetic field generated by a distant transmitter. Historically, spectroscopic techniques that measure transitions between nuclear and electron spin states have carried the term 'resonance' in their names because they have depended on matching a set of energy levels to a source of monochromatic radiation and observing the strong absorption that occurs at resonance. In fact, all spectroscopy is a form of resonant coupling between the electromagnetic field and the molecules; what distinguishes **magnetic resonance** is that the energy levels themselves are modified by the application of a magnetic field.

The Stern–Gerlach experiment (Topic 19) provided evidence for electron spin. It turns out that many nuclei also possess spin angular momentum. Orbital and spin angular momenta give rise to magnetic moments, and to say that electrons and nuclei have magnetic moments means that, to some extent, they behave like small bar magnets with energies that depend on their orientation in an applied magnetic field. Here we establish how the energies of electrons and nuclei depend on the applied field. This material sets the stage for the exploration of the structure and dynamics of complex molecules by magnetic resonance spectroscopy (Topics 48–50).

47.1 Nuclear magnetic resonance

The application of resonance that we describe here depends on the fact that many nuclei possess spin angular momentum characterized by a **nuclear spin quantum number** I (the analogue of s for electrons). To understand the **nuclear magnetic resonance** (NMR) experiment we must describe the behaviour of nuclei in magnetic fields, and then the basic techniques for detecting spectroscopic transitions.

(a) The energies of nuclei in magnetic fields

The nuclear spin quantum number, I, is a fixed characteristic property of a nucleus and, depending on the nuclide, is either an integer or a half-integer (Table 47.1). A nucleus with spin quantum number I has the following properties:

- An angular momentum of magnitude $\{I(I+1)\}^{1/2}\hbar$.
- A component of angular momentum $m_I\hbar$ on a specified axis ('the z-axis'), where $m_I = I, I-1, \ldots, -I$.
- If $I>0$, a magnetic moment with a constant magnitude and an orientation that is determined by the value of m_I.

Physical interpretation

According to the second property, the spin, and hence the magnetic moment, of the nucleus may lie in $2I+1$ different orientations relative to an axis. A proton has $I=\frac{1}{2}$ and its spin may adopt either of two orientations; a ^{14}N nucleus has $I=1$ and its spin may adopt any of three orientations; both ^{12}C and ^{16}O have $I=0$ and hence zero magnetic moment.

Classically, the energy of a magnetic moment $\boldsymbol{\mu}$ in a magnetic field $\mathcal{B}$ is equal to the scalar product (*Mathematical background* 4)

$$E = -\boldsymbol{\mu}\cdot\boldsymbol{\mathcal{B}} \tag{47.1}$$

More formally, $\mathcal{B}$ is the magnetic induction and is measured in tesla, T; $1\,\text{T} = 1\,\text{kg s}^{-2}\,\text{A}^{-1}$. The (non-SI) unit gauss, G, is also occasionally used: $1\,\text{T} = 10^4\,\text{G}$. Quantum mechanically, we write the hamiltonian as

$$\hat{H} = -\hat{\boldsymbol{\mu}}\cdot\boldsymbol{\mathcal{B}} \tag{47.2}$$

Table 47.1 Nuclear constitution and the nuclear spin quantum number*

Number of protons	Number of neutrons	I
Even	Even	0
Odd	Odd	Integer (1, 2, 3, …)
Even	Odd	Half-integer $\left(\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots\right)$
Odd	Even	Half-integer $\left(\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots\right)$

* The spin of a nucleus may be different if it is in an excited state; throughout this Topic we deal only with the ground state of nuclei.

To write an expression for $\hat{\boldsymbol{\mu}}$ we use the fact that, just as for electrons (Topic 21), the magnetic moment of a nucleus is proportional to its angular momentum. The operators in eqn 47.2 are then

$$\hat{\boldsymbol{\mu}} = \gamma_{\text{N}}\hat{\boldsymbol{I}} \quad \text{and} \quad \hat{H} = -\gamma_{\text{N}}\boldsymbol{\mathcal{B}}\cdot\hat{\boldsymbol{I}} \tag{47.3a}$$

where γ_{N} is the **nuclear magnetogyric ratio** of the specified nucleus, an empirically determined characteristic arising from its internal structure (Table 47.2). For a magnetic field of magnitude $\mathcal{B}_0$ along the z-direction, the hamiltonian in eqn 47.3a becomes

$$\hat{H} = -\gamma_{\text{N}}\mathcal{B}_0\hat{I}_z \tag{47.3b}$$

Because the eigenvalues of the operator $\hat{I}_z$ are $m_I\hbar$, the eigenvalues of this hamiltonian are

$$E_{m_I} = -\gamma_{\text{N}}\hbar\mathcal{B}_0 m_I \qquad \text{Energies of a nuclear spin in a magnetic field} \tag{47.4a}$$

The expression for the energy is often written in terms of the **nuclear magneton**, μ_{N},

$$\mu_{\text{N}} = \frac{e\hbar}{2m_{\text{p}}} \qquad \text{Nuclear magneton} \tag{47.4b}$$

where m_{p} is the mass of the proton and $\mu_{\text{N}} = 5.051\times10^{-27}\,\text{J T}^{-1}$, and in terms of an empirical constant called the **nuclear *g*-factor**, g_I, when eqn 47.4a becomes

$$E_{m_I} = -g_I\mu_{\text{N}}\mathcal{B}_0 m_I \quad g_I = \frac{\gamma_{\text{N}}\hbar}{\mu_{\text{N}}} \qquad \text{Energies of a nuclear spin in a magnetic field} \tag{47.4c}$$

Nuclear g-factors are experimentally determined dimensionless quantities with values typically between −6 and +6 (Table 47.2). Positive values of g_I and γ_{N} denote a magnetic

Table 47.2* Nuclear spin properties

Nuclide	Natural abundance/%	Spin I	g-factor, g_I	Magnetogyric ratio, $\gamma_{\text{N}}/(10^7\,\text{T}^{-1}\,\text{s}^{-1})$	NMR frequency at 1 T, ν/MHz
^{1}n		$\frac{1}{2}$	−3.826	−18.32	29.164
^{1}H	99.98	$\frac{1}{2}$	5.586	26.75	42.576
^{2}H	0.02	1	0.857	4.11	6.536
^{13}C	1.11	$\frac{1}{2}$	1.405	6.73	10.708
^{14}N	99.64	1	0.404	1.93	3.078

* More values are given in the *Resource section*.

moment that lies in the same direction as the spin angular momentum vector; negative values indicate that the magnetic moment and spin lie in opposite directions. A nuclear magnet is about 2000 times weaker than the magnet associated with electron spin.

For the remainder of our discussion of nuclear magnetic resonance we assume that γ_N is positive, as is the case for the majority of nuclei. In such cases, it follows from eqn 47.4 that states with $m_I<0$ lie above states with $m_I>0$. It follows that the energy separation between the lower $m_I=+\frac{1}{2}$ (α) and upper $m_I=-\frac{1}{2}$ (β) states of a **spin-$\frac{1}{2}$ nucleus**, a nucleus with $I=\frac{1}{2}$, is

$$\Delta E = E_{-1/2} - E_{+1/2} = \frac{1}{2}\gamma_N\hbar\mathcal{B}_0 - \left(-\frac{1}{2}\gamma_N\hbar\mathcal{B}_0\right) = \gamma_N\hbar\mathcal{B}_0 \qquad (47.5)$$

and resonant absorption occurs when the resonance condition (Fig. 47.1)

$$h\nu = \gamma_N\hbar\mathcal{B}_0 \quad \text{or} \quad \nu = \frac{\gamma_N\mathcal{B}_0}{2\pi} \qquad (47.6)$$

Spin-1/2 nuclei Resonance condition

is fulfilled. At resonance there is strong coupling between the spins and the radiation, and absorption occurs as the spins flip from the lower energy state to the upper state. The electromagnetic field also stimulates the spins to flip from the upper state to the lower state, with the emission of radiation. The net absorption is the difference of these two processes, as we discuss in more detail shortly.

Brief illustration 47.1 The resonance condition in NMR

To calculate the frequency at which radiation comes into resonance with proton ($s=\frac{1}{2}$) spins in a 12.0 T magnetic field we use eqn 47.6 as follows:

$$\nu = \frac{\overbrace{(2.6752\times10^{8}\,\mathrm{T^{-1}s^{-1}})}^{\gamma_N}\times\overbrace{(12.0\,\mathrm{T})}^{\mathcal{B}_0}}{2\pi} = 5.11\times10^{8}\,\mathrm{s^{-1}} = 511\,\mathrm{MHz}$$

Self-test 47.1 Determine the resonance frequency for ^{31}P nuclei, for which $\gamma_N = 1.0841\times10^{8}\,\mathrm{T^{-1}\,s^{-1}}$, under the same conditions.

Answer: 207 MHz

It is sometimes useful to compare the quantum mechanical and classical pictures of magnetic nuclei pictured as tiny bar magnets. A bar magnet in an externally applied magnetic field undergoes the motion called **precession** as it twists round the direction of the field (Fig. 47.2). The rate of precession ν_L is called the **Larmor precession frequency**:

$$\nu_L = \frac{\gamma_N\mathcal{B}_0}{2\pi} \qquad (47.7)$$

Definition Larmor frequency of a nucleus

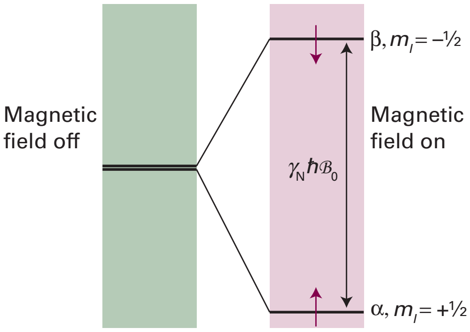

Figure 47.1 The nuclear spin energy levels of a spin-$\frac{1}{2}$ nucleus with positive magnetogyric ratio (for example, ^{1}H or ^{13}C) in a magnetic field. Resonance occurs when the energy separation of the levels matches the energy of the photons in the electromagnetic field.

It follows that resonance absorption by spin-$\frac{1}{2}$ nuclei occurs when the Larmor precession frequency is the same as the frequency of the applied electromagnetic field.

(b) The NMR spectrometer

In its simplest form, NMR is the study of the properties of molecules containing magnetic nuclei by applying a magnetic field and observing the frequency of the resonant electromagnetic field. Larmor frequencies of nuclei at the fields normally employed (about 12 T) typically lie in the radiofrequency region of the electromagnetic spectrum (close to 500 MHz), so NMR is a radiofrequency technique. For much of our discussion we consider spin-$\frac{1}{2}$ nuclei, but NMR is applicable to nuclei with any nonzero spin. As well as protons, which are the most common nuclei studied by NMR, spin-$\frac{1}{2}$ nuclei include ^{13}C, ^{19}F, and ^{31}P.

An NMR spectrometer consists of an appropriate source of radiofrequency radiation and a magnet that can produce a uniform, intense field. Most modern instruments use a superconducting magnet capable of producing fields of the order of 10 T and more (Fig. 47.3). The sample is rotated rapidly to average out magnetic inhomogeneities; however, although sample spinning is essential for the investigation of small molecules, for large molecules it can lead to irreproducible results and is often

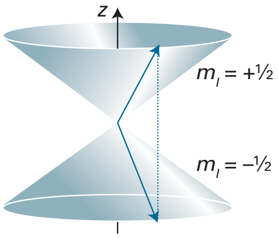

Figure 47.2 The interactions between the m_I states of a spin-$\frac{1}{2}$ nucleus and an external magnetic field may be visualized as the precession of the vectors representing the angular momentum.

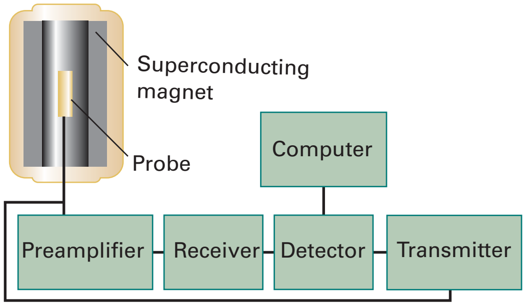

Figure 47.3 The layout of a typical NMR spectrometer. The link from the transmitter to the detector indicates that the high frequency of the transmitter is subtracted from the high-frequency received signal to give a low-frequency signal for processing.

avoided. Although a superconducting magnet (Topic 39) operates at the temperature of liquid helium (4 K), the sample itself is normally at room temperature or held in a variable-temperature enclosure between, typically, −150 and +100 °C.

Modern NMR spectroscopy uses pulses of radiofrequency radiation. These techniques of Fourier-transform (FT) NMR make possible the determination of structures of very large molecules in solution and in solids (Topic 49).

The intensity of an NMR transition depends on a number of factors. We show in the following *Justification* that

$$\text{Intensity} \propto (N_\alpha - N_\beta)\mathcal{B}_0 \tag{47.8a}$$

where

$$N_\alpha - N_\beta \approx \frac{N\gamma_N \hbar \mathcal{B}_0}{2kT} \tag{47.8b}$$

Nuclei Population difference

with N the total number of spins ($N = N_\alpha + N_\beta$). It follows that decreasing the temperature increases the intensity by increasing the population difference.

Brief illustration 47.2 Nuclear spin populations

For protons $\gamma_N = 2.675 \times 10^8\,\text{T}^{-1}\,\text{s}^{-1}$. Therefore, for 1 000 000 protons in a field of 10 T at 20 °C

$$N_\alpha - N_\beta \approx \frac{\overbrace{1000000}^{N} \times \overbrace{(2.675\times10^{8}\,\text{T}^{-1}\text{s}^{-1})}^{\gamma_N} \times \overbrace{(1.055\times10^{-34}\,\text{J s})}^{\hbar} \times \overbrace{(10\,\text{T})}^{\mathcal{B}_0}}{2\times\underbrace{(1.381\times10^{-23}\,\text{J K}^{-1})}_{k}\times\underbrace{(293\,\text{K})}_{T}}$$

$$\approx 35$$

Even in such a strong field there is only a tiny imbalance of population of about 35 in a million.

Self-test 47.2 For ^{13}C nuclei, $\gamma_N = 6.7283\times10^{7}\,\text{T}^{-1}\,\text{s}^{-1}$. Determine the magnetic field necessary to induce the same imbalance in the distribution of ^{13}C spins at 20 °C.

Answer: 40 T, an unrealistically high field for an NMR spectrometer

Justification 47.1 Intensities in NMR spectra

As indicated in the text, at resonance both absorption and emission are stimulated. From the general considerations of transition intensities in Topic 16, we know that the rate of absorption of electromagnetic radiation is proportional to the population of the lower-energy state (N_α in the case of a proton NMR transition) and the rate of stimulated emission is proportional to the population of the upper state (N_β). At the low frequencies typical of magnetic resonance, spontaneous emission can be neglected as it is very slow. Therefore, the net rate of absorption is proportional to the difference in populations, and we can write

$$\text{Rate of absorption} \propto N_\alpha - N_\beta$$

The intensity of absorption, the rate at which energy is absorbed, is proportional to the product of the rate of absorption (the rate at which photons are absorbed) and the energy of each photon, and the latter is proportional to the frequency ν of the incident radiation (through $E = h\nu$). At resonance, this frequency is proportional to the applied magnetic field (through $\nu = \nu_L = \gamma_N \mathcal{B}_0 / 2\pi$), so we can write

$$\text{Rate of absorption} \propto (N_\alpha - N_\beta)\mathcal{B}_0$$

as in eqn 47.8a. To write an expression for the population difference, we use the Boltzmann distribution (*Foundations*, Topic 2, and Topic 51) to write the ratio of populations as

$$\frac{N_\beta}{N_\alpha} = \mathrm{e}^{-\overbrace{\gamma_N \hbar \mathcal{B}_0}^{\Delta E}/kT} \overset{\mathrm{e}^{-x}=1-x+\ldots}{\overbrace{\approx}} 1 - \frac{\gamma_N \hbar \mathcal{B}_0}{kT}$$

The expansion of the exponential term is appropriate for $\Delta E = \gamma_N \hbar \mathcal{B}_0 \ll kT$, a condition usually met for nuclear spins. It follows that

$$\frac{N_\alpha - N_\beta}{\underbrace{N_\alpha + N_\beta}_{N}} = \frac{N_\alpha(1 - N_\beta/N_\alpha)}{N_\alpha(1 + N_\beta/N_\alpha)} = \frac{1 - \overbrace{N_\beta/N_\alpha}^{1-\gamma_N\hbar\mathcal{B}_0/kT}}{1 + \underbrace{N_\beta/N_\alpha}_{1-\gamma_N\hbar\mathcal{B}_0/kT}}$$

$$\approx \frac{1 - (1 - \gamma_N \hbar \mathcal{B}_0/kT)}{1 + \underbrace{(1 - \gamma_N \hbar \mathcal{B}_0/kT)}_{\approx 1}} = \frac{\gamma_N \hbar \mathcal{B}_0/kT}{2}$$

which is eqn 47.8b.

By combining eqns 47.8a and 47.8b we see that the intensity is proportional to $\mathcal{B}_0^2$, so NMR transitions can be enhanced significantly by increasing the strength of the applied magnetic field. The use of high magnetic fields also simplifies the appearance of spectra (Topic 48) and so allows them to be interpreted more readily. We can also conclude that absorptions of nuclei with large magnetogyric ratios (^{1}H, for instance) are more intense than those with small magnetogyric ratios (^{13}C, for instance).

47.2 Electron paramagnetic resonance

Electron paramagnetic resonance (EPR), or **electron spin resonance** (ESR), is the study of molecules and ions containing unpaired electrons by observing the magnetic field at which they come into resonance with radiation of known frequency. As we have done for NMR, we write expressions for the resonance condition in EPR and then describe the general features of EPR spectrometers.

(a) The energies of electrons in magnetic fields

The spin magnetic moment of an electron, which has a spin quantum number $s=\frac{1}{2}$ (Topic 19), is proportional to its spin angular momentum. The spin magnetic moment and hamiltonian operators are, respectively,

$$\hat{\boldsymbol{\mu}}=\gamma_e\hat{\boldsymbol{s}} \quad \text{and} \quad \hat{H}=-\gamma_e\boldsymbol{\mathcal{B}}\cdot\hat{\boldsymbol{s}} \qquad (47.9a)$$

where $\hat{\boldsymbol{s}}$ is the spin angular momentum operator, and γ_e is the **magnetogyric ratio of the electron**:

$$\gamma_e=-\frac{g_e e}{2m_e} \qquad (47.9b)$$

Electrons Magnetogyric ratio

with $g_e=2.002\,319\ldots$ as the ***g*-value of the electron**. Dirac's relativistic theory (his modification of the Schrödinger equation to make it consistent with Einstein's special relativity) gives $g_e=2$; the additional 0.002 319… arises from interactions of the electron with the electromagnetic fluctuations of the vacuum that surrounds the electron. The negative sign of γ_e (arising from the sign of the electron's charge) shows that the orbital moment is opposite in direction to the orbital angular momentum vector.

For a magnetic field of magnitude $\mathcal{B}_0$ in the z-direction,

$$\hat{H}=-\gamma_e\mathcal{B}_0\hat{s}_z \qquad (47.10)$$

Because the eigenvalues of the operator $\hat{s}_z$ are $m_s\hbar$ with $m_s=+\frac{1}{2}$ (α) and $m_s=-\frac{1}{2}$ (β), it follows that the energies of an electron spin in a magnetic field are

$$E_{m_s}=-\gamma_e\hbar\mathcal{B}_0 m_s \qquad (47.11a)$$

Energies of an electron spin in a magnetic field

and can also be expressed in terms of the **Bohr magneton**, μ_B, as

$$E_{m_s}=g_e\mu_B\mathcal{B}_0 m_s \qquad \mu_B=\frac{e\hbar}{2m_e} \qquad (47.11b)$$

Energies of an electron spin in a magnetic field

where m_e is the mass of the electron and $\mu_B=9.274\times10^{-24}JT^{-1}$. The Bohr magneton, a positive quantity, is often regarded as the fundamental quantum of magnetic moment.

In the absence of a magnetic field, the states with different values of m_s are degenerate. When a field is present, the degeneracy is removed: the state with $m_s=+\frac{1}{2}$ moves up in energy by $\frac{1}{2}g_e\mu_B\mathcal{B}_0$. and the state with $m_s=-\frac{1}{2}$ moves down by $\frac{1}{2}g_e\mu_B\mathcal{B}_0$ From eqn 47.11b, the separation between the (upper) $m_s=+\frac{1}{2}$ and (lower) $m_s=-\frac{1}{2}$ levels of an electron spin in a magnetic field of magnitude $\mathcal{B}_0$ in the z-direction is

$$\Delta E=E_{+1/2}-E_{-1/2}=\frac{1}{2}g_e\mu_B\mathcal{B}_0-\left(-\frac{1}{2}g_e\mu_B\mathcal{B}_0\right)=g_e\mu_B\mathcal{B}_0 \qquad (47.12a)$$

If the sample is exposed to radiation of frequency ν, the energy separations come into resonance with the radiation when the frequency satisfies the resonance condition (Fig. 47.4)

$$h\nu=g_e\mu_B\mathcal{B}_0 \qquad (47.12b)$$

Electrons Resonance condition

At resonance there is strong coupling between the electron spins and the radiation, and strong absorption occurs as the spins make the transition α←β. As for NMR, at resonance the opposite transition also occurs, and the detected signal is the net outcome taking into account the relative populations of the levels, as we explore in more detail shortly.

Brief illustration 47.3 The resonance condition in EPR

Magnetic fields of about 0.30 T (the value used in most commercial EPR spectrometers) correspond to resonance at

$$\nu=\frac{\overbrace{(2.0023)}^{g_e}\times\overbrace{(9.274\times10^{-24}\,\mathrm{J\,T^{-1}})}^{\mu_B}\times\overbrace{(0.30\,\mathrm{T})}^{\mathcal{B}_0}}{\underbrace{6.626\times10^{-34}\,\mathrm{J\,s}}_{h}}$$

$$=8.4\times10^{9}\,\mathrm{s^{-1}}=8.4\,\mathrm{GHz}$$

which corresponds to a wavelength of 3.6 cm.

Self-test 47.3 Determine the magnetic field for EPR transitions occurring at $\lambda=0.88$ cm.

Answer: 1.2 T

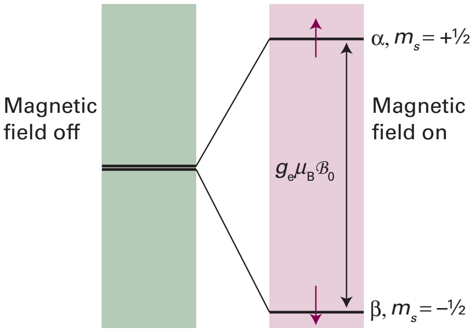

Figure 47.4 Electron spin levels in a magnetic field. Note that the β state is lower in energy than the α state (because the magnetogyric ratio of an electron is negative). Resonance is achieved when the frequency of the incident radiation matches the frequency corresponding to the energy separation.

(b) The EPR spectrometer

It follows from *Brief illustration* 47.3 that most commercial EPR spectrometers operate at wavelengths of approximately 3 cm. Because 3 cm radiation falls in the microwave region of the electromagnetic spectrum, EPR is a microwave technique.

Both Fourier-transform (FT) and continuous wave (CW) EPR spectrometers are available. The FT-EPR instrument is based on the concepts developed in Topic 49 for NMR spectroscopy, except that pulses of microwaves are used to excite electron spins in the sample. The layout of the more common CW-EPR spectrometer is shown in Fig. 47.5. It consists of a microwave source (a klystron or a Gunn oscillator), a cavity in which the sample is inserted in a glass or quartz container, a microwave detector, and an electromagnet with a field that can be varied in the region of 0.3 T. The EPR spectrum is obtained by monitoring the microwave absorption as the field is changed, and a typical spectrum (of the benzene radical anion, $C_6H_6^-$) is shown in Fig. 47.6. The peculiar appearance of the spectrum, which is in fact the first derivative of the absorption, arises from the detection technique, which is sensitive to the slope of the absorption curve (Fig. 47.7).

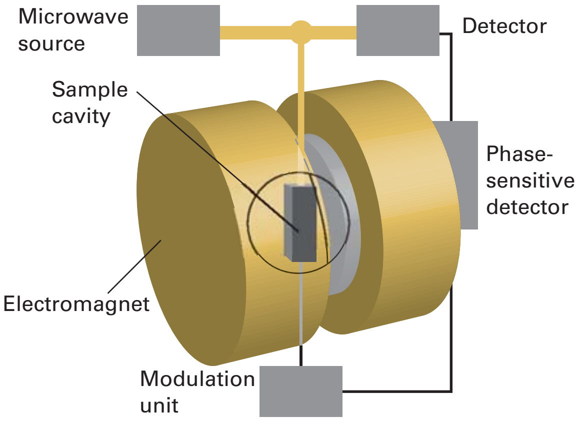

Figure 47.5 The layout of a continuous-wave EPR spectrometer. A typical magnetic field is 0.3 T, which requires 9 GHz (3 cm) microwaves for resonance.

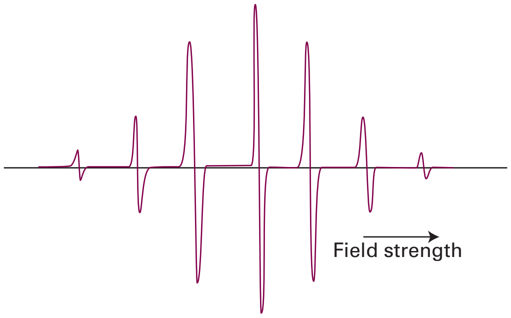

Figure 47.6 The EPR spectrum of the benzene radical anion, $C_6H_6^-$, in fluid solution.

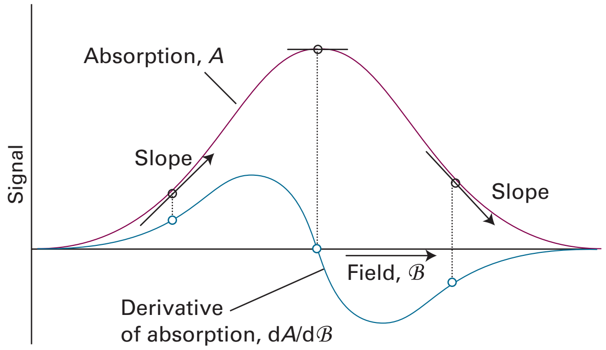

Figure 47.7 When phase-sensitive detection is used, the signal is the first derivative of the absorption intensity. Note that the peak of the absorption corresponds to the point where the derivative passes through zero.

As we have indicated, the intensities of spectral lines depend on the difference in populations between the ground and excited states. For an electron, the β state lies below the α state in energy and, by a similar argument to that for nuclei,

$$N_\beta - N_\alpha \approx \frac{N g_e \mu_B \mathcal{B}_0}{2kT} \qquad \textit{Electrons} \quad \text{Population difference} \qquad (47.13)$$

where N is the total number of spins.

Brief illustration 47.4 Electron spin populations

When 1000 electron spins are exposed to a 1.0 T magnetic field at 20 °C (293 K),

$$N_\beta - N_\alpha \approx \frac{\overbrace{1000}^{N}\times\overbrace{2.0023}^{g_e}\times\overbrace{(9.274\times10^{-24}\,\mathrm{J\,T^{-1}})}^{\mu_B}\times\overbrace{(1.0\,\mathrm{T})}^{\mathcal{B}_0}}{2\times\underbrace{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})}_{k}\times\underbrace{(293\,\mathrm{K})}_{T}}$$

$$\approx 2.3$$

There is an imbalance of populations of only about two electrons in a thousand. However the imbalance is much larger for electron spins than for nuclear spins (*Brief illustration* 47.2) because the energy separation between the spin states of electrons is larger than that for nuclear spins, even at the lower magnetic field strengths normally employed.

Self-test 47.4 It is common to conduct EPR experiments at very low temperatures. At what temperature would the imbalance in spin populations be 5 electrons in 100, with $\mathcal{B}_0 = 0.30\,\mathrm{T}$?

Answer: 4 K

Checklist of concepts

☐ **1.** The **nuclear spin quantum number**, I, of a nucleus is a non-negative integer or half-integer.

☐ **2.** Nuclei with different values of m_I have different energies in the presence of a magnetic field.

☐ **3.** **Nuclear magnetic resonance** (NMR) is the observation of the resonant absorption of electromagnetic radiation by nuclei in a magnetic field.

☐ **4.** NMR spectrometers consist of a source of radiofrequency radiation and a magnet that provides a strong, uniform field.

☐ **5.** The resonance absorption intensity increases with the strength of the applied magnetic field (as $\mathcal{B}_0^2$).

☐ **6.** Electrons with different values of m_s have different energies in the presence of a magnetic field.

☐ **7.** **Electron paramagnetic resonance** (EPR) is the observation of the resonant absorption of electromagnetic radiation by unpaired electrons in a magnetic field.

☐ **8.** EPR spectrometers consist of a microwave source, a cavity in which the sample is inserted, a microwave detector, and an electromagnet.

Checklist of equations

Property	Equation	Comment	Equation number
Nuclear magneton	$\mu_N = e\hbar/2m_p$		47.4b
Energies of a nuclear spin in a magnetic field	$E_{m_I} = -\gamma_N \hbar \mathcal{B}_0 m_I$ $= -g_I \mu_N \mathcal{B}_0 m_I$		47.4c
Resonance condition (spin-$\frac{1}{2}$ nuclei)	$h\nu = \gamma_N \hbar \mathcal{B}_0$	$\gamma_N > 0$	47.6
Larmor frequency	$\nu_L = \gamma_N \mathcal{B}_0 / 2\pi$	$\gamma_N > 0$	47.7
Population difference (nuclei)	$N_\alpha - N_\beta \approx N\gamma_N \hbar \mathcal{B}_0 / 2kT$		47.8b
Magnetogyric ratio (electron)	$\gamma_e = -g_e e/2m_e$	$g_e = 2.002\,319$	47.9b
Energies of an electron spin in a magnetic field	$E_{m_s} = -\gamma_e \hbar \mathcal{B}_0 m_s$ $= g_e \mu_B \mathcal{B}_0 m_s$		47.11a
Bohr magneton	$\mu_B = e\hbar/2m_e$		47.11b
Resonance condition (electrons)	$h\nu = g_e \mu_B \mathcal{B}_0$		47.12
Population difference (electrons)	$N_\beta - N_\alpha \approx N g_e \mu_B \mathcal{B}_0 / 2kT$		47.13

TOPIC 48

Features of NMR spectra

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➤ Why do you need to know this material?

To make progress with the analysis of NMR spectra and extract the wealth of information they contain you need to understand how the appearance of a spectrum correlates with molecular structure.

➤ What is the key idea?

The resonance frequency of a magnetic nucleus is affected by its electronic environment and the presence of magnetic nuclei in its vicinity.

➤ What do you need to know already?

You need to be familiar with the general principles of magnetic resonance (Topic 47).

Nuclear magnetic moments interact with the *local* magnetic field. The local field may differ from the applied field because the latter induces electronic orbital angular momentum (that is, the circulation of electronic currents) which gives rise to a small additional magnetic field $\delta\mathcal{B}$ at the nuclei. This additional field is proportional to the applied field, and it is conventional to write

$$\delta\mathcal{B} = -\sigma\mathcal{B}_0 \qquad \textit{Definition} \quad \text{Shielding constant} \qquad (48.1)$$

where the dimensionless quantity σ is called the **shielding constant** of the nucleus (σ is usually positive but may be negative). The ability of the applied field to induce an electronic current in the molecule, and hence affect the strength of the resulting local magnetic field experienced by the nucleus, depends on the details of the electronic structure near the magnetic nucleus of interest, so nuclei in different chemical groups have different shielding constants. The calculation of reliable values of the shielding constant is very difficult, but trends in it are quite well understood and we concentrate on them.

48.1 The chemical shift

Because the total local field $\mathcal{B}_{\text{loc}}$ is

$$\mathcal{B}_{\text{loc}} = \mathcal{B}_0 + \delta\mathcal{B} = (1-\sigma)\mathcal{B}_0 \qquad (48.2)$$

the nuclear Larmor frequency is

$$\nu_{\mathrm{L}} = \frac{\gamma_{\mathrm{N}}\mathcal{B}_{\mathrm{loc}}}{2\pi} = \frac{\gamma_{\mathrm{N}}\mathcal{B}_0}{2\pi}(1-\sigma) \qquad (48.3)$$

This frequency is different for nuclei in different environments. Hence, different nuclei, even of the same element, come into resonance at different frequencies if they are in different molecular environments.

The **chemical shift** of a nucleus is the difference between its resonance frequency and that of a reference standard. The standard for protons is the proton resonance in tetramethylsilane, Si(CH_3)$_4$, commonly referred to as TMS, which bristles with protons and dissolves without reaction in many solutions. For ^{13}C, the reference frequency is the ^{13}C resonance in TMS, and for ^{31}P it is the ^{31}P resonance in 85 per cent H_3PO_4(aq). Other references are used for other nuclei. The separation of the resonance of a particular group of nuclei from the standard increases with the strength of the applied magnetic field because the induced field is proportional to the applied field, and the stronger the latter, the greater the shift.

Chemical shifts are reported on the ***δ* scale**, which is defined as

$$\delta = \frac{\nu-\nu^{\circ}}{\nu^{\circ}}\times 10^6 \qquad \textit{Definition} \quad \delta\text{ scale} \qquad (48.4)$$

where ν° is the resonance frequency of the standard. The advantage of the δ scale is that shifts reported on it are independent of the applied field (because both numerator and denominator are proportional to the applied field). The resonance frequencies themselves, however, do depend on the applied field through

$$\nu = \nu^{\circ} + (\nu^{\circ}/10^6)\delta \qquad (48.5)$$

Brief illustration 48.1 The δ scale

A nucleus with $\delta = 1.00$ in a spectrometer where $\nu^{\circ} = 500\,\mathrm{MHz}$ (a '500 MHz NMR spectrometer') will have a shift relative to the reference equal to

$$\nu-\nu^{\circ} = (500\,\mathrm{MHz}/10^6)\times 1.00 = (500\,\mathrm{Hz})\times 1.00 = 500\,\mathrm{Hz}$$

because $1\,\mathrm{MHz} = 10^6$ Hz. In a spectrometer operating at $\nu^{\circ} = 100\,\mathrm{MHz}$, the shift relative to the reference would be only 100 Hz.

A note on good practice In much of the literature, chemical shifts are reported in parts per million, ppm, in recognition of the factor of 10^6 in the definition; this is unnecessary. If you see '$\delta = 10$ ppm', interpret it, and use it in eqn 48.5, as $\delta = 10$.

Self-test 48.1 What is the shift of the resonance from TMS of a group of nuclei with $\delta = 3.50$ and an operating frequency of 350 MHz?

Answer: 1.23 kHz

The relation between δ and σ is obtained by substituting eqn 48.3 into eqn 48.4:

$$\begin{aligned}\delta &= \frac{(1-\sigma)\mathcal{B}_0 - (1-\sigma^{\circ})\mathcal{B}_0}{(1-\sigma^{\circ})\mathcal{B}_0}\times 10^6 \\ &= \frac{\sigma^{\circ}-\sigma}{1-\sigma^{\circ}}\times 10^6 \approx (\sigma^{\circ}-\sigma)\times 10^6\end{aligned} \qquad \text{Relation between } \delta \text{ and } \sigma \qquad (48.6)$$

The last line follows from $\sigma^{\circ} \ll 1$. As the shielding σ gets smaller, δ increases. Therefore, we speak of nuclei with large chemical shifts as being strongly **deshielded**. Some typical chemical shifts are given in Fig. 48.1. As can be seen from the illustration, the nuclei of different elements have very different ranges of chemical shifts. The ranges exhibit the variety of electronic environments of the nuclei in molecules: the higher the atomic number of the element, the greater the number of electrons around the nucleus and hence the greater the range of the extent of shielding. By convention, NMR spectra are plotted with δ increasing from right to left.

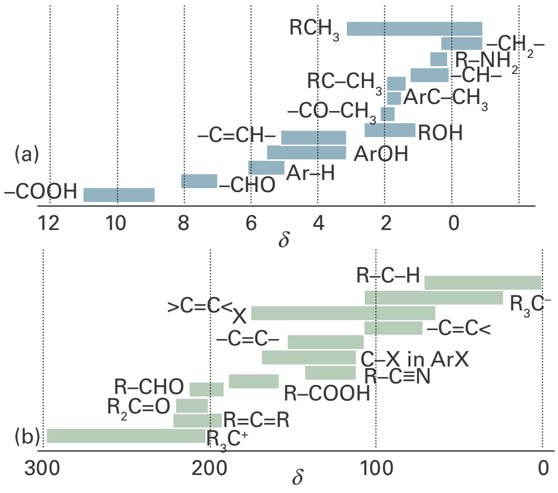

Figure 48.1 The range of typical chemical shifts for (a) ^1H resonances and (b) ^{13}C resonances.

Example 48.1 Interpreting the NMR spectrum of ethanol

Figure 48.2 shows the NMR spectrum of ethanol. Account for the observed chemical shifts.

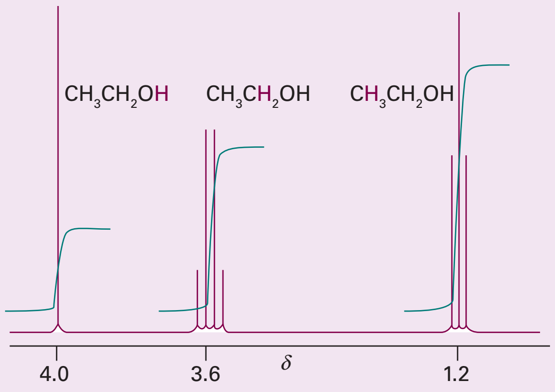

Figure 48.2 The ^{1}H-NMR spectrum of ethanol. The bold letters denote the protons giving rise to the resonance peak, and the step-like curve is the integrated signal.

Method Consider the effect of an electron-withdrawing atom: it deshields strongly those protons to which it is bound, and has a smaller effect on distant protons.

Answer The spectrum is consistent with the following assignments:

- The CH_3 protons form one group of nuclei with $\delta = 1.2$.
- The two CH_2 protons are in a different part of the molecule, experience a different local magnetic field, and resonate at $\delta = 3.6$.
- The OH proton is in another environment, and has a chemical shift of $\delta = 4.0$.

The increasing value of δ (that is, the decrease in shielding) is consistent with the electron-withdrawing power of the O atom: it reduces the electron density of the OH proton most, and that proton is strongly deshielded. It reduces the electron density of the distant methyl protons least, and those nuclei are least deshielded.

The relative intensities of the signals are commonly represented as the height of step-like curves superimposed on the spectrum, as in Fig. 48.2. In ethanol the group intensities are in the ratio 3:2:1 because there are three CH_3 protons, two CH_2 protons, and one OH proton in each molecule.

Self-test 48.2 The NMR spectrum of acetaldehyde (ethanal) has lines at $\delta = 2.20$ and $\delta = 9.80$. Which feature can be assigned to the CHO proton?

Answer: $\delta = 9.80$

48.2 The origin of shielding constants

The calculation of shielding constants is difficult, even for small molecules, for it requires detailed information (using the techniques outlined in Topics 28–30) about the distribution of electron density in the ground and excited states and the excitation energies of the molecule. Nevertheless, considerable success has been achieved with small molecules such as H_2O and CH_4 and even large molecules, such as proteins, are within the scope of some types of calculation. However, it is easier to understand the different contributions to chemical shifts by studying the large body of empirical information now available.

The empirical approach supposes that the observed shielding constant is the sum of three contributions:

$$\sigma = \sigma(\text{local}) + \sigma(\text{neighbour}) + \sigma(\text{solvent}) \qquad (48.7)$$

The **local contribution**, σ(local), is essentially the contribution of the electrons of the atom that contains the nucleus in question. The **neighbouring group contribution**, σ(neighbour), is the contribution from the groups of atoms that form the rest of the molecule. The **solvent contribution**, σ(solvent), is the contribution from the solvent molecules.

(a) The local contribution

It is convenient to regard the local contribution to the shielding constant as the sum of a **diamagnetic contribution**, σ_d, and a **paramagnetic contribution**, σ_p:

$$\sigma(\text{local}) = \sigma_d + \sigma_p \qquad (48.8)$$

Local contribution to the shielding constant

A diamagnetic contribution to σ(local) opposes the applied magnetic field and shields the nucleus in question. A paramagnetic contribution to σ(local) reinforces the applied magnetic field and deshields the nucleus in question. Therefore, $\sigma_d > 0$ and $\sigma_p < 0$. The total local contribution is positive if the diamagnetic contribution dominates, and is negative if the paramagnetic contribution dominates.

The diamagnetic contribution arises from the ability of the applied field to generate a circulation of charge in the ground-state electron distribution of the atom. The circulation generates a magnetic field that opposes the applied field and hence shields the nucleus. The magnitude of σ_d depends on the electron density close to the nucleus and can be calculated from the **Lamb formula**:[1]

$$\sigma_d = \frac{e^2\mu_0}{12\pi m_e}\left\langle \frac{1}{r} \right\rangle \qquad (48.9)$$

Lamb formula

where μ_0 is the vacuum permeability (a fundamental constant, see inside the front cover) and r is the electron–nucleus distance.

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[1] For a derivation, see our *Molecular quantum mechanics*, Oxford University Press, Oxford (2011).

Example 48.2 Using the Lamb formula

Calculate the shielding constant for the proton in a free H atom.

Method To calculate σ_d from the Lamb formula, calculate the expectation value of $1/r$ for a hydrogen 1s orbital. Wavefunctions are given in Table 18.1.

Answer The wavefunction for a hydrogen 1s orbital is

$$\psi=\left(\frac{1}{\pi a_0^3}\right)^{1/2} \mathrm{e}^{-r/a_0}$$

so, because $\mathrm{d}\tau=r^2\mathrm{d}r\,\sin\theta\,\mathrm{d}\theta\mathrm{d}\phi$, the expectation value of $1/r$ is written as

$$\left\langle\frac{1}{r}\right\rangle=\int\frac{\psi^*\psi}{r}\mathrm{d}\tau=\frac{1}{\pi a_0^3}\int_0^{2\pi}\mathrm{d}\phi\int_0^{\pi}\sin\theta\,\mathrm{d}\theta\int_0^{\infty}re^{-2r/a_0}\mathrm{d}r$$

$$=\frac{4}{a_0^3}\overbrace{\int_0^{\infty}re^{-2r/a_0}\mathrm{d}r}^{a_0^2/4\ \text{(Integral E.1)}}=\frac{1}{a_0}$$

where we used the integral listed in the *Resource section*. Therefore,

$$\sigma_d=\frac{e^2\mu_0}{12\pi m_e a_0}=\frac{(1.602\times10^{-19}\,\mathrm{C})^2\times\left(4\pi\times10^{-7}\ \overbrace{\mathrm{J}}^{\mathrm{kg\,m^2\,s^{-2}}}\ \mathrm{s^2\,C^{-2}\,m^{-1}}\right)}{12\pi\times(9.109\times10^{-31}\,\mathrm{kg})\times(5.292\times10^{-11}\,\mathrm{m})}$$

$$=1.775\times10^{-5}$$

Self-test 48.3 Derive a general expression for σ_d that applies to all hydrogenic atoms.

Answer: $Ze^2\mu_0/12\pi m_e a_0$

The diamagnetic contribution is the only contribution in closed-shell free atoms. It is also the only contribution to the local shielding for electron distributions that have spherical or cylindrical symmetry. Thus, it is the only contribution to the local shielding from inner cores of atoms, for cores remain nearly spherical even though the atom may be a component of a molecule and its valence electron distribution highly distorted. The diamagnetic contribution is broadly proportional to the electron density of the atom containing the nucleus of interest. It follows that the shielding is decreased if the electron density on the atom is reduced by the influence of an electronegative atom nearby. That reduction in shielding as the electronegativity of a neighbouring atom increases translates into an increase in the chemical shift δ (Fig. 48.3).

The local paramagnetic contribution, σ_p, arises from the ability of the applied field to force electrons to circulate through the molecule by making use of orbitals that are unoccupied in the ground state. It is zero in free atoms and around the axes of linear molecules (such as ethyne, HC≡CH) where the electrons can circulate freely and a field applied along the internuclear axis is unable to force them into other orbitals. We can expect large paramagnetic contributions from small atoms (because the induced currents are then close to the nucleus) in molecules with low-lying excited states (because an applied field can then induce significant currents). In fact, the paramagnetic contribution is the dominant local contribution for atoms other than hydrogen.

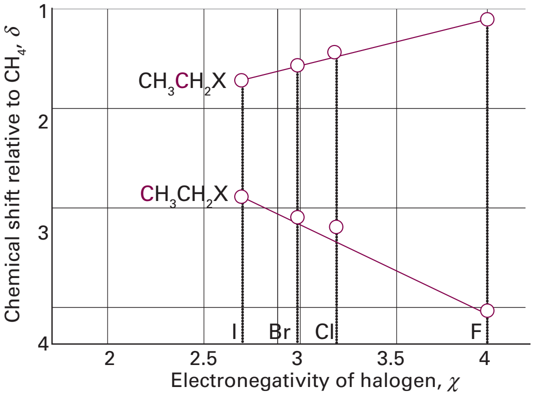


Figure 48.3 The variation of chemical shielding with electronegativity. The shifts for the methyl protons agree with the trend expected with increasing electronegativity. However, to emphasize that chemical shifts are subtle phenomena, notice that the trend for the methylene protons is opposite to that expected. For these protons another contribution (the magnetic anisotropy of C—H and C—X bonds) is dominant.

(b) Neighbouring group contributions

The neighbouring group contribution arises from the currents induced in nearby groups of atoms. Consider the influence of the neighbouring group X on the proton H in a molecule such as H—X. The applied field generates currents in the electron distribution of X and gives rise to an induced magnetic moment proportional to the applied field; the constant of proportionality is the magnetic susceptibility, χ (chi), of the group X: $\boldsymbol{\mu}_{\text{induced}}=\chi\boldsymbol{\mathcal{B}}_0$ (Topic 39). The susceptibility is negative for a diamagnetic group because the induced moment is opposite to the direction of the applied field. The induced moment gives rise to a magnetic field with a component parallel to the applied field and at a distance r and angle θ (1) that has the form (*The chemist's toolkit* 48.1)

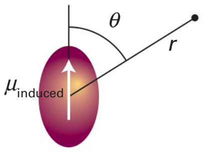
$$\mathcal{B}_{\text{local}}\propto\frac{\mu_{\text{induced}}}{r^3}(1-3\cos^2\theta) \qquad \text{Local dipolar field} \qquad (48.10a)$$

We see that the strength of the additional magnetic field experienced by the proton is inversely proportional to the cube of the distance r between H and X. If the magnetic susceptibility is independent of the orientation of the molecule (is 'isotropic'), because $1-3\cos^2\theta$ is zero when averaged over a sphere (see Problem 48.6) the local field averages to zero. To a good approximation, the shielding constant σ(neighbour) depends on the distance r as

$$\sigma(\text{neighbour}) \propto (\chi_{\parallel}-\chi_{\perp})\left(\frac{1-3\cos^2\theta}{r^3}\right) \qquad (48.10b)$$

Neighbouring group contribution

where $\chi_{\parallel}$ and $\chi_{\perp}$ are, respectively, the parallel and perpendicular components of the magnetic susceptibility, and θ is the angle between the X—H axis and the symmetry axis of the neighbouring group (**2**). Equation 48.10 shows that the neighbouring group contribution may be positive or negative according to the relative magnitudes of the two magnetic susceptibilities and the relative orientation of the nucleus with respect to X. If $54.7° < \theta < 125.3°$, then $1-3\cos^2\theta$ is positive, but it is negative otherwise (Figs 48.4 and 48.5).



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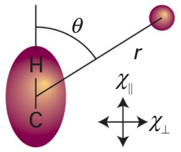


2

The chemist's toolkit 48.1 Dipolar fields

Standard electromagnetic theory gives the magnetic field at a point $\boldsymbol{r}$ from a point magnetic dipole $\boldsymbol{\mu}$ as

$$\mathcal{B}=\frac{\mu_0}{4\pi r^3}\left(\boldsymbol{\mu}-\frac{3(\boldsymbol{\mu}\cdot\boldsymbol{r})\boldsymbol{r}}{r^2}\right)$$

where μ_0 is the vacuum permeability (a fundamental constant with the defined value $4\pi\times10^{-7}\,\text{T}^2\,\text{J}^{-1}\,\text{m}^3$). The electric field due to a point electric dipole is given by a similar expression:

$$\mathcal{E}=\frac{1}{4\pi\varepsilon_0 r^3}\left(\boldsymbol{\mu}-\frac{3(\boldsymbol{\mu}\cdot\boldsymbol{r})\boldsymbol{r}}{r^2}\right)$$

where ε_0 is the vacuum permittivity, which is related to μ_0 by $\varepsilon_0=1/\mu_0c^2$. The component of magnetic field in the z-direction is

$$\mathcal{B}_z=\frac{\mu_0}{4\pi r^3}\left(\mu_z-\frac{3(\boldsymbol{\mu}\cdot\boldsymbol{r})z}{r^2}\right)$$

with $z=r\cos\theta$, the z-component of the distance vector $\boldsymbol{r}$. If the magnetic dipole is also parallel to the z-direction, it follows that

$$\mathcal{B}_z=\frac{\mu_0}{4\pi r^3}\left(\overbrace{\mu}^{\mu_z}-\frac{3\overbrace{(\mu r\cos\theta)}^{\boldsymbol{\mu}\cdot\boldsymbol{r}}\overbrace{(r\cos\theta)}^{z}}{r^2}\right)=\frac{\mu\mu_0}{4\pi r^3}(1-3\cos^2\theta)$$

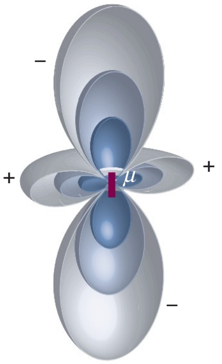


Figure 48.4 A depiction of the field arising from a point magnetic dipole. The three shades of colour represent the strength of field declining with distance (as $1/r^3$), and each surface shows the angle dependence of the z-component of the field for each distance.

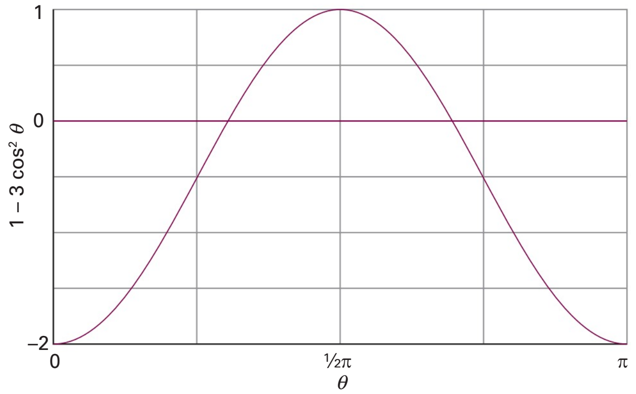


Figure 48.5 The variation of the function $1-3\cos^2\theta$ with the angle θ.

Brief illustration 48.2 Ring currents

A special case of a neighbouring group effect is found in aromatic compounds. The strong anisotropy of the magnetic susceptibility of the benzene ring is ascribed to the ability of the field to induce a *ring current*, a circulation of electrons around the ring, when it is applied perpendicular to the molecular plane. Protons in the plane are deshielded (Fig. 48.6), but any

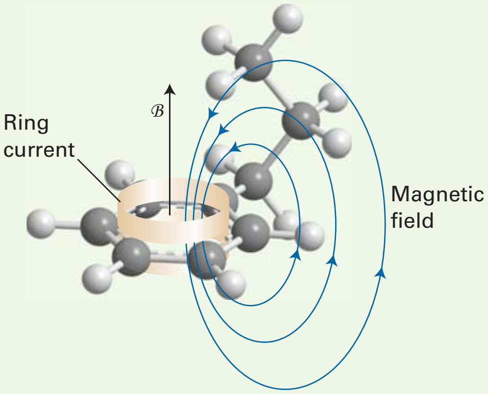


Figure 48.6 The shielding and deshielding effects of the ring current induced in the benzene ring by the applied field. Protons attached to the ring are deshielded but a proton attached to a substituent that projects above the ring is shielded.

that happen to lie above or below the plane (as members of substituents of the ring) are shielded.

Self-test 48.4 Consider ethyne, HC≡CH. Are its protons shielded or deshielded by currents induced by the triple bond?

Answer: Shielded

(c) The solvent contribution

A solvent can influence the local magnetic field experienced by a nucleus in a variety of ways. Some of these effects arise from specific interactions between the solute and the solvent (such as hydrogen-bond formation and other forms of Lewis acid–base complex formation). The anisotropy of the magnetic susceptibility of the solvent molecules, especially if they are aromatic, can also be the source of a local magnetic field. Moreover, if there are steric interactions that result in a loose but specific interaction between a solute molecule and a solvent molecule, then protons in the solute molecule may experience shielding or deshielding effects according to their location relative to the solvent molecule.

Brief illustration 48.3 The effect of aromatic solvents

An aromatic solvent like benzene can give rise to local currents that shield or deshield a proton in a solute molecule. The arrangement shown in Fig. 48.7 leads to shielding of a proton on the solute molecule.

Self-test 48.5 Refer to Fig. 48.7 and suggest an arrangement that leads to deshielding of a proton on the solute molecule.

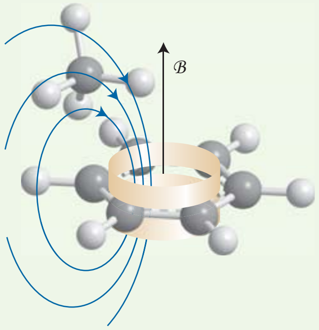


Figure 48.7 An aromatic solvent (benzene here) can give rise to local currents that shield or deshield a proton in a solute molecule. In this relative orientation of the solvent and solute, the proton on the solute molecule is shielded.

Answer: Proton on the solute molecule coplanar with the benzene ring

48.3 The fine structure

The splitting of resonances into individual lines by spin–spin coupling in Fig. 48.2 is called the **fine structure** of the spectrum. It arises because each magnetic nucleus may contribute to the local field experienced by the other nuclei and so modify their resonance frequencies. The strength of the interaction is expressed in terms of the **scalar coupling constant**, J, and reported in hertz (Hz). The scalar coupling constant is so called because the energy of interaction it describes is proportional to the scalar product of the two interacting spins: $E \propto \boldsymbol{I}_1 \cdot \boldsymbol{I}_2$. As explained in *Mathematical background* 4, a scalar product depends on the angle between the two vectors, so writing the energy in this way is simply a way of saying that the energy of interaction between two spins depends on their relative orientation. The constant of proportionality in this expression is written $hJ/\hbar^2$ (so $E = (hJ/\hbar^2)\boldsymbol{I}_1 \cdot \boldsymbol{I}_2$); because each spin angular momentum is proportional to $\hbar$, E is then proportional to hJ and J is a frequency (with units hertz). For nuclei that are constrained to align with the applied field in the z-direction, the only contribution to $\boldsymbol{I}_1 \cdot \boldsymbol{I}_2$ is $I_{1z}I_{2z}$, with eigenvalues $m_1 m_2 \hbar^2$, so in that case the energy due to spin–spin coupling is

$$E_{m_1 m_2} = hJm_1 m_2 \qquad \text{Spin–spin coupling energy} \qquad (48.11)$$

(a) The appearance of the spectrum

In NMR, letters far apart in the alphabet (typically A and X) are used to indicate nuclei with very different chemical shifts; letters close together (such as A and B) are used for nuclei with similar chemical shifts. We shall consider first an AX system, a molecule that contains two spin-$\frac{1}{2}$ nuclei A and X with very different chemical shifts in the sense that the difference in chemical shift corresponds to a frequency that is large compared to J.

For a spin-$\frac{1}{2}$ AX system there are four spin states: $\alpha_A\alpha_X$, $\alpha_A\beta_X$, $\beta_A\alpha_X$, $\beta_A\beta_X$. The energy depends on the orientation of the spins in the external magnetic field, and if spin–spin coupling is neglected

$$\begin{aligned} E_{m_A m_X} &= -\gamma_N \hbar(1-\sigma_A)\mathcal{B}_0 m_A - \gamma_N \hbar(1-\sigma_X)\mathcal{B}_0 m_X \\ &= -h\nu_A m_A - h\nu_X m_X \end{aligned} \tag{48.12a}$$

where ν_A and ν_X are the Larmor frequencies of A and X and m_A and m_X are their quantum numbers ($m_A = \pm\frac{1}{2}, m_X = \pm\frac{1}{2}$). This expression gives the four lines on the left of Fig. 48.8. When spin–spin coupling is included (by using eqn 48.11), the energy levels are

$$E_{m_A m_X} = -h\nu_A m_A - h\nu_X m_X + hJm_A m_X \tag{48.12b}$$

If $J > 0$, a lower energy is obtained when $m_A m_X < 0$, which is the case if one spin is α and the other is β. A higher energy is obtained if both spins are α or both spins are β. The opposite is true if $J < 0$. The resulting energy level diagram (for $J > 0$) is shown on the right of Fig. 48.8. We see that the αα and ββ states are both raised by $\frac{1}{4}hJ$ and that the αβ and βα states are both lowered by $\frac{1}{4}hJ$.

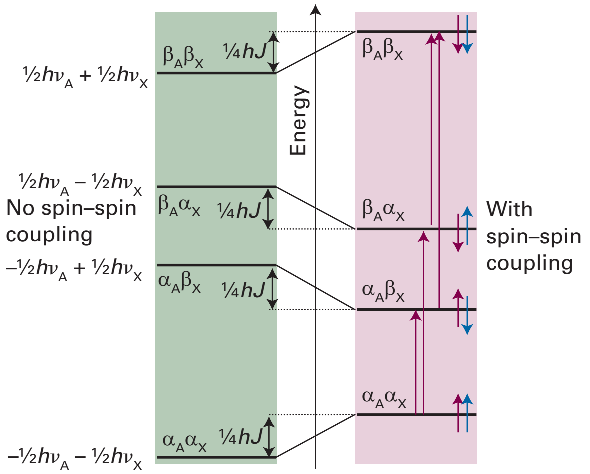


Figure 48.8 The energy levels of an AX system. The four levels on the left are those of the two spins in the absence of spin–spin coupling. The four levels on the right show how a positive spin–spin coupling constant affects the energies. The transitions shown are for β←α of A or X, the other nucleus (X or A, respectively) remaining unchanged. We have exaggerated the effect for clarity. In practice, the splitting caused by spin–spin coupling is much smaller than that caused by the applied field.

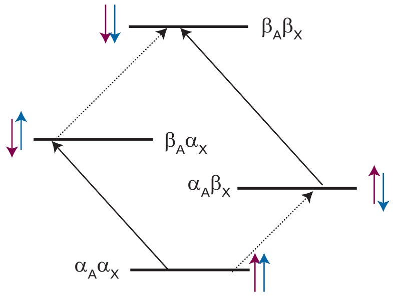


Figure 48.9 An alternative depiction of the energy levels and transitions shown in Fig. 48.8. Once again, we have exaggerated the effect of spin–spin coupling.

When a transition of nucleus A occurs, nucleus X remains unchanged. Therefore, the A resonance is a transition for which $\Delta m_A = +1$ and $\Delta m_X = 0$. There are two such transitions, one in which $\beta_A \leftarrow \alpha_A$ occurs when the X nucleus is α, and the other in which $\beta_A \leftarrow \alpha_A$ occurs when the X nucleus is β. They are shown in Fig. 48.8 and in a slightly different form in Fig. 48.9. The energies of the transitions are

$$\Delta E = h\nu_A \pm \tfrac{1}{2}hJ \tag{48.13a}$$

Therefore, the A resonance consists of a doublet of separation J centred on the chemical shift of A (Fig. 48.10). Similar remarks apply to the X resonance, which consists of two transitions according to whether the A nucleus is α or β (as shown in Fig. 48.9). The transition energies are

$$\Delta E = h\nu_X \pm \tfrac{1}{2}hJ \tag{48.13b}$$

It follows that the X resonance also consists of two lines of the same separation J, but they are centred on the chemical shift of X (as shown in Fig. 48.10).

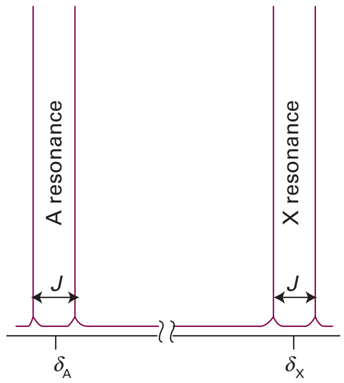


Figure 48.10 The effect of spin–spin coupling on an AX spectrum. Each resonance is split into two lines separated by J. The pairs of resonances are centred on the chemical shifts of the protons in the absence of spin–spin coupling.

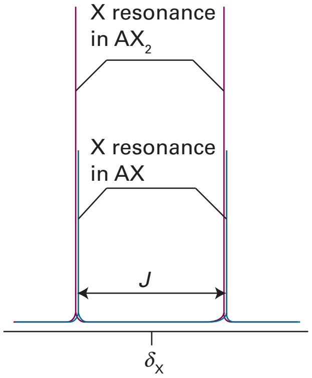


Figure 48.11 The X resonance of an AX_2 species is also a doublet, because the two equivalent X nuclei behave like a single nucleus; however, the overall absorption is twice as intense as that of an AX species.

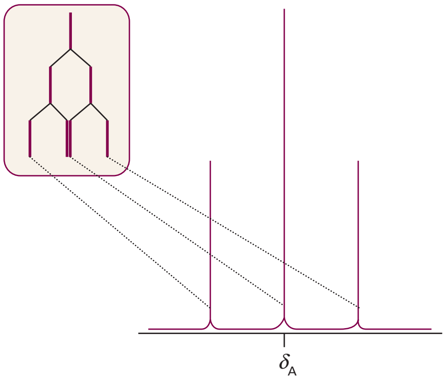
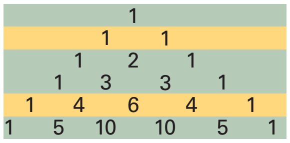


Figure 48.12 The origin of the 1:2:1 triplet in the A resonance of an AX_2 species. The resonance of A is split into two by coupling with one X nucleus (as shown in the inset), and then each of those two lines is split into two by coupling to the second X nucleus. Because each X nucleus causes the same splitting, the two central transitions are coincident and give rise to an absorption line of double the intensity of the outer lines.

If there is another X nucleus in the molecule with the same chemical shift as the first X (giving an AX_2 species), the X resonance of the AX_2 species is split into a doublet by A, as in the AX case discussed above (Fig. 48.11). The resonance of A is split into a doublet by one X, and each line of the doublet is split again by the same amount by the second X (Fig. 48.12). This splitting results in three lines in the intensity ratio 1:2:1 (because the central frequency can be obtained in two ways).



1
1 1
1 2 1
1 3 3 1
1 4 6 4 1
1 5 10 10 5 1

3

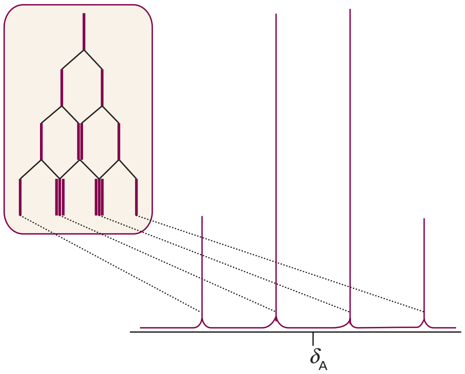


Figure 48.13 The origin of the 1:3:3:1 quartet in the A resonance of an AX_3 species. The third X nucleus splits each of the lines shown in Fig. 48.12 for an AX_2 species into a doublet, and the intensity distribution reflects the number of transitions that have the same energy.

Three equivalent X nuclei (an AX_3 species) split the resonance of A into four lines of intensity ratio 1:3:3:1 (Fig. 48.13). The X resonance remains a doublet as a result of the splitting caused by A. In general, N equivalent spin-$\frac{1}{2}$ nuclei split the resonance of a nearby spin or group of equivalent spins into $N+1$ lines with an intensity distribution given by Pascal's triangle (3). Successive rows of this triangle are formed by adding together the two adjacent numbers in the line above.

Example 48.3 Accounting for the fine structure in a spectrum

Account for the fine structure in the NMR spectrum of the C—H protons of ethanol.

Method Consider how each group of equivalent protons (for instance, three methyl protons) split the resonances of the other groups of protons. There is no splitting within groups of equivalent protons. Each splitting pattern can be decided by referring to Pascal's triangle.

Answer The three protons of the CH_3 group split the resonance of the CH_2 protons into a 1:3:3:1 quartet with a splitting J. Likewise, the two protons of the CH_2 group split the resonance of the CH_3 protons into a 1:2:1 triplet with the same splitting J. The OH resonance is not split because the OH protons migrate rapidly from molecule to molecule (including molecules of impurities in the sample) and their effect averages to zero. In gaseous ethanol, where this migration does not occur, the OH resonance appears as a triplet, showing that the CH_2 protons interact with the OH proton.

Self-test 48.6 What fine structure can be expected for the protons in $^{14}NH_4^+$? The spin quantum number of nitrogen-14 is 1.

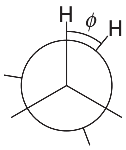
Answer: 1:1:1 triplet from N

(b) The magnitudes of coupling constants

The scalar coupling constant of two nuclei separated by N bonds is denoted ^{N}J, with subscripts for the types of nuclei involved. Thus, $^{1}J_{\mathrm{CH}}$ is the coupling constant for a proton joined directly to a ^{13}C atom, and $^{2}J_{\mathrm{CH}}$ is the coupling constant when the same two nuclei are separated by two bonds (as in ^{13}C—C—H). A typical value of $^{1}J_{\mathrm{CH}}$ is in the range 120 to 250 Hz; $^{2}J_{\mathrm{CH}}$ is between 10 and 20 Hz. Both ^{3}J and ^{4}J can give detectable effects in a spectrum, but couplings over larger numbers of bonds can generally be ignored. One of the longest-range couplings that has been detected is $^{9}J_{\mathrm{HH}}=0.4$ Hz between the CH_3 and CH_2 protons in $CH_3C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}CH_2OH$.

As remarked (in the discussion following eqn 48.12b), the sign of J_{XY} indicates whether the energy of two spins is lower when they are parallel ($J<0$) or when they are antiparallel ($J>0$). It is found that $^{1}J_{\mathrm{CH}}$ is often positive, $^{2}J_{\mathrm{HH}}$ is often negative, $^{3}J_{\mathrm{HH}}$ is often positive, and so on. An additional point is that J varies with the angle between the bonds (Fig. 48.14). Thus, a $^{3}J_{\mathrm{HH}}$ coupling constant is often found to depend on the dihedral angle ϕ (**4**) according to the **Karplus equation**:

$$^{3}J_{\mathrm{HH}}=A+B\cos\phi+C\cos 2\phi \qquad \text{Karplus equation} \qquad (48.14)$$



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with A, B, and C empirical constants with values close to +7 Hz, −1 Hz, and +5 Hz, respectively, for an HCCH fragment. It follows that the measurement of $^{3}J_{\mathrm{HH}}$ in a series of related compounds can be used to determine their conformations. The coupling constant $^{1}J_{\mathrm{CH}}$ also depends on the hybridization of the C atom, as the following values indicate:

	sp	sp^2	sp^3
$^{1}J_{\mathrm{CH}}$/Hz	250	160	125

Brief illustration 48.4 The Karplus equation

The investigation of H—N—C—H couplings in polypeptides can help reveal their conformation. For $^{3}J_{\mathrm{HH}}$ coupling in such a group, $A=+5.1$ Hz, $B=-1.4$ Hz, and $C=+3.2$ Hz. For a helical polymer, ϕ is close to 120°, which would give $^{3}J_{\mathrm{HH}}\approx 4$ Hz. For the sheet-like conformation, ϕ is close to 180°, which would give $^{3}J_{\mathrm{HH}}\approx 10$ Hz.

Self-test 48.7 NMR experiments reveal that for H—C—C—H coupling in polypeptides, $A=+3.5$ Hz, $B=-1.6$ Hz, and $C=+4.3$ Hz. In an investigation of the polypeptide flavodoxin, the $^{3}J_{\mathrm{HH}}$ coupling constant for such a grouping was determined to be 2.1 Hz. Is this value consistent with a helical or sheet conformation?

Answer: Helical conformation

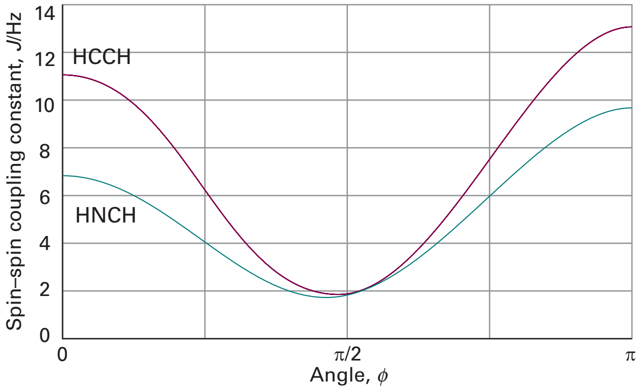


Figure 48.14 The variation of the spin–spin coupling constant with angle predicted by the Karplus equation for an HCCH group and an HNCH group.

(c) The origin of spin–spin coupling

Spin–spin coupling is a very subtle phenomenon and it is better to treat J as an empirical parameter than to use calculated values. However, we can get some insight into its origins, if not its precise magnitude—or always reliably its sign—by considering the magnetic interactions within molecules.

A nucleus with spin projection m_I gives rise to a magnetic field with z-component $\mathcal{B}_{\mathrm{nuc}}$ at a distance R, where, to a good approximation,

$$\mathcal{B}_{\mathrm{nuc}}=-\frac{\gamma_{\mathrm{N}}\hbar\mu_0}{4\pi R^3}(1-3\cos^2\theta)m_I \qquad (48.15)$$

The angle θ is defined in **1**; we saw a version of this expression in eqn 48.10a.

Brief illustration 48.5 Magnetic fields from nuclei

The z-component of the magnetic field arising from a proton ($m_I=\frac{1}{2}$) at $R=0.30$ nm, with its magnetic moment parallel to the z-axis ($\theta=0$) is

$$\mathcal{B}_{\mathrm{nuc}}=-\frac{\overbrace{(2.821\times10^{-26}\,\mathrm{J\,T^{-1}})}^{\gamma_{\mathrm{N}}\hbar}\times\overbrace{(4\pi\times10^{-7}\,\mathrm{T^2\,J^{-1}\,m^3})}^{\mu_0}}{4\pi\times(\underbrace{3.0\times10^{-10}\,\mathrm{m}}_{R})^3}\times\overbrace{(-1)}^{(1-3\cos^2\theta)m_I}$$

$$=1.0\times10^{-4}\,\mathrm{T}=0.10\,\mathrm{mT}$$

A field of this magnitude can give rise to the splitting of resonance signals in solid samples. In a liquid, the angle θ sweeps over all values as the molecule tumbles, and the factor $1-3\cos^2\theta$ averages to zero. Hence the direct dipolar interaction between spins cannot account for the fine structure of the spectra of rapidly tumbling molecules.

Self-test 48.8 In gypsum the splitting in the H_2O resonance can be interpreted in terms of a magnetic field of 0.715 mT generated by one proton and experienced by the other. With $\theta=0$, what is the separation of the protons in the H_2O molecule?

Answer: 158 pm

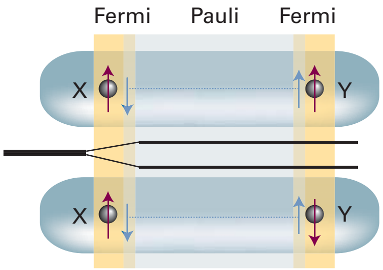


Figure 48.16 The polarization mechanism for spin–spin coupling ($^1J_{HH}$). The two arrangements have slightly different energies. In this case, J is positive, corresponding to a lower energy when the nuclear spins are antiparallel.

Spin–spin coupling in molecules in solution can be explained in terms of the **polarization mechanism**, in which the interaction is transmitted through the bonds. The simplest case to consider is that of $^1J_{XY}$, where X and Y are spin-$\frac{1}{2}$ nuclei joined by an electron-pair bond. The coupling mechanism depends on the fact that the energy depends on the relative orientation of the bonding electron and nuclear spins. This electron–nucleus coupling is magnetic in origin, and may be either a dipolar interaction or a **Fermi contact interaction**. A pictorial description of the latter is as follows. First, we regard the magnetic moment of the nucleus as arising from the circulation of a current in a tiny loop with a radius similar to that of the nucleus (Fig. 48.15). Far from the nucleus the field generated by this loop is indistinguishable from the field generated by a point magnetic dipole. Close to the loop, however, the field differs from that of a point dipole. The magnetic interaction between this non-dipolar field and the electron's magnetic moment is the contact interaction. The contact interaction—essentially the failure of the point-dipole approximation—depends on the very close approach of an electron to the nucleus and hence can occur only if the electron occupies an s orbital (which is the reason why $^1J_{CH}$ depends on the hybridization ratio). We shall suppose that it is energetically favourable for an electron spin and a nuclear spin to be antiparallel (as is the case for a proton and an electron in a hydrogen atom).

If the X nucleus is α, a β electron of the bonding pair will tend to be found nearby, because that is an energetically favourable arrangement (Fig. 48.16). The second electron in the bond, which must have α spin if the other is β (by the Pauli principle, Topic 19), will be found mainly at the far end of the bond because electrons tend to stay apart to reduce their mutual repulsion. Because it is energetically favourable for the spin of Y to be antiparallel to an electron spin, a Y nucleus with β spin has a lower energy than when it has α spin. The opposite is true when X is β, for now the α spin of Y has the lower energy. In other words, the antiparallel arrangement of nuclear spins lies lower in energy than the parallel arrangement as a result of

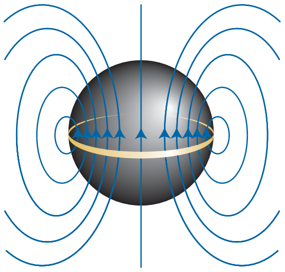


Figure 48.15 The origin of the Fermi contact interaction. From far away, the magnetic field pattern arising from a ring of current (representing the rotating charge of the nucleus, the pale grey sphere) is that of a point dipole. However, if an electron can sample the field close to the region indicated by the sphere, the field distribution differs significantly from that of a point dipole. For example, if the electron can penetrate the sphere, then the spherical average of the field it experiences is not zero.

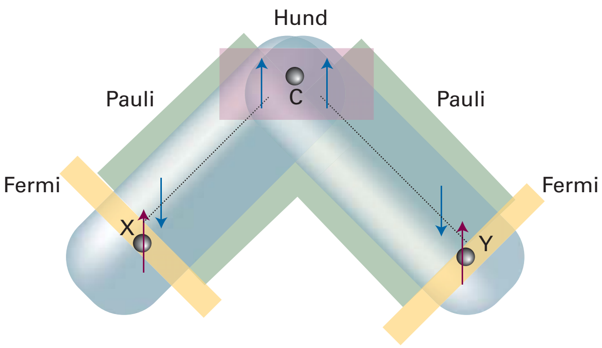


Figure 48.17 The polarization mechanism for $^2J_{HH}$ spin–spin coupling. The spin information is transmitted from one bond to the next by a version of the mechanism that accounts for the lower energy of electrons with parallel spins in different atomic orbitals (Hund's rule of maximum multiplicity). In this case, $J<0$, corresponding to a lower energy when the nuclear spins are parallel.

their magnetic coupling with the bond electrons. That is, ${}^1J_{\mathrm{CH}}$ is positive.

To account for the value of ${}^2J_{\mathrm{XY}}$, as in H—C—H, we need a mechanism that can transmit the spin alignments through the central C atom (which may be ^{12}C, with no nuclear spin of its own). In this case (Fig. 48.17), an X nucleus with α spin polarizes the electrons in its bond, and the α electron is likely to be found closer to the C nucleus. The more favourable arrangement of two electrons on the same atom is with their spins parallel (Hund's rule, Topic 19), so the more favourable arrangement is for the α electron of the neighbouring bond to be close to the C nucleus. Consequently, the β electron of that bond is more likely to be found close to the Y nucleus, and therefore that nucleus will have a lower energy if it is α. Hence, according to this mechanism, the lower energy will be obtained if the Y spin is parallel to that of X. That is, ${}^2J_{\mathrm{HH}}$ is negative.

The coupling of nuclear spin to electron spin by the Fermi contact interaction is most important for proton spins, but it is not necessarily the most important mechanism for other nuclei. These nuclei may also interact by a dipolar mechanism with the electron magnetic moments and with their orbital motion, and there is no simple way of specifying whether J will be positive or negative.

48.4 Conformational conversion and exchange processes

The appearance of an NMR spectrum is changed if magnetic nuclei can jump rapidly between different environments. Consider a molecule, such as *N*,*N*-dimethylformamide, that can jump between conformations; in this case, the methyl shifts depend on whether they are *cis* or *trans* to the carbonyl group (Fig. 48.18). When the jumping rate is low, the spectrum shows two sets of lines, one each from molecules in each conformation. When the interconversion is fast, the spectrum shows a single line at the mean of the two chemical shifts. At intermediate inversion rates, the line is very broad. This maximum broadening occurs when the lifetime, τ, of a conformation gives rise to a linewidth that is comparable to the difference of resonance frequencies, $\delta\nu$, and both broadened lines blend together into a very broad line. Coalescence of the two lines occurs when

$$\tau = \frac{2^{1/2}}{\pi\delta\nu} \qquad \text{Condition for coalescence of two NMR lines} \qquad (48.16)$$

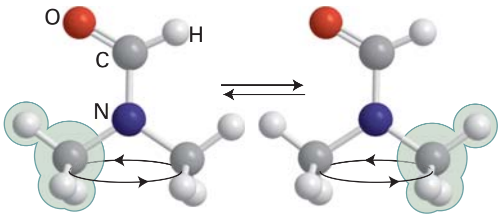


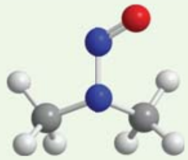
Figure 48.18 When a molecule changes from one conformation to another, the positions of its protons are interchanged and the protons jump between magnetically distinct environments.

Brief illustration 48.6 The effect of chemical exchange on NMR spectra

The NO group in *N*,*N*-dimethylnitrosamine, $(CH_3)_2N—NO$ (**5**), rotates about the N—N bond and, as a result, the magnetic environments of the two CH_3 groups are interchanged. The two CH_3 resonances are separated by 390 Hz in a 600 MHz spectrometer. According to eqn 48.16,

$$\tau = \frac{2^{1/2}}{\pi \times (390\ \mathrm{s}^{-1})} = 1.2\ \mathrm{ms}$$

It follows that the signal will collapse to a single line when the interconversion rate exceeds about $1/\tau = 830\ \mathrm{s}^{-1}$.



5 *N*,*N*-Dimethylnitrosamine

Self-test 48.9 What would you deduce from the observation of a single line from the same molecule in a 300 MHz spectrometer?

Answer: Conformation lifetime less than 2.3 ms

A similar explanation accounts for the loss of fine structure in solvents able to exchange protons with the sample. For example, hydroxyl protons are able to exchange with water protons. When this **chemical exchange** occurs, a molecule ROH with an α-spin proton (we write this ROH_{α}) rapidly converts to ROH_{β} and then perhaps to ROH_{α} again because the protons provided by the solvent molecules in successive exchanges have random spin orientations. Therefore, instead of seeing a spectrum composed of contributions from both ROH_{α} and ROH_{β} molecules (that is, a spectrum showing a doublet structure due to the OH proton), we see a spectrum that shows no splitting caused by coupling of the OH proton (as in Fig. 48.2 and as discussed in Example 48.3). The effect is observed when the lifetime of a molecule due to this chemical exchange is so short that the lifetime broadening is greater than the doublet splitting. Because this splitting is often very small (a few hertz), a proton must remain attached to the same molecule for longer than about 0.1 s for the splitting to be observable. In water, the exchange rate is much faster than that, so alcohols show no splitting from the OH protons. In dry dimethylsulfoxide (DMSO), the exchange rate may be slow enough for the splitting to be detected.

Checklist of concepts

☐ 1. The **chemical shift** of a nucleus is the difference between its resonance frequency and that of a reference standard.

☐ 2. The **shielding constant** is the sum of a local contribution, a neighbouring group contribution, and a solvent contribution.

☐ 3. The **local contribution** is the sum of a diamagnetic contribution and a paramagnetic contribution.

☐ 4. The **neighbouring** group contribution arises from the currents induced in nearby groups of atoms.

☐ 5. The **solvent contribution** can arise from specific molecular interactions between the solute and the solvent.

☐ 6. **Fine structure** is the splitting of resonances into individual lines by spin–spin coupling.

☐ 7. **Spin–spin coupling** is expressed in terms of the **spin–spin coupling constant** J and depends on the relative orientation of two nuclear spins.

☐ 8. The coupling constant decreases as the number of bonds separating two nuclei increases.

☐ 9. Spin–spin coupling can be explained in terms of the **polarization mechanism** and the **Fermi contact interaction**.

☐ 10. Coalescence of two NMR lines occurs when a conformational interchange or chemical exchange of nuclei is fast.

Checklist of equations

Property	Equation	Comment	Equation number
δ-Scale of chemical shifts	$\delta=\{(\nu-\nu^\circ)/\nu^\circ\}\times10^6$		48.4
Relation between chemical shift and shielding constant	$\delta\approx(\sigma^\circ-\sigma)\times10^6$		48.6
Local contribution to the shielding constant	$\sigma(\text{local})=\sigma_\text{d}+\sigma_\text{p}$		48.8
Lamb formula	$\sigma_\text{d}=(e^2\mu_0/12\pi m_\text{e})\langle 1/r\rangle$		48.9
Neighbouring group contribution to the shielding constant	$\sigma(\text{neighbour})\propto(\chi_\parallel-\chi_\perp)(1-3\cos^2\theta)/r^3$	The angle θ is defined in **1**	48.10b
Karplus equation	${}^3J_\text{HH}=A+B\cos\phi+C\cos 2\phi$	A, B, and C are empirical constants	48.14
Condition for coalescence of two NMR lines	$\tau=2^{1/2}/\pi\delta\nu$	Conformational conversions and exchange processes	48.16

TOPIC 49

Pulse techniques in NMR

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➤ Why do you need to know this material?

To understand how nuclear magnetic resonance spectroscopy is used to study large molecules and even diagnose disease, you need to understand how spectral information is obtained by analysing the response of nuclei to the application of strong pulses of radiofrequency radiation.

➤ What is the key idea?

Fourier-transform NMR spectroscopy is the analysis of the radiation emitted by nuclear spins as they return to equilibrium after stimulation by one or more pulses of radiofrequency radiation.

➤ What do you need to know already?

You need to be familiar with the general principles of magnetic resonance (Topic 47), the features of NMR spectra (Topics 48), the vector model of angular momentum (Topic 14), the magnetic properties of molecules (Topic 39), and Fourier transforms (Topic 40 and *Mathematical background* 6).

The common method of detecting the energy separation between nuclear spin states is more sophisticated than simply looking for the frequency at which resonance occurs. One of the best analogies that has been suggested to illustrate the preferred way of observing an NMR spectrum is that of detecting the spectrum of vibrations of a bell. We could stimulate the bell with a gentle vibration at a gradually increasing frequency, and note the frequencies at which it resonated with the stimulation. A lot of time would be spent getting zero response when the stimulating frequency was between the bell's vibrational modes. However, if we were simply to hit the bell with a hammer, we would immediately obtain a clang composed of all the frequencies that the bell can produce. The equivalent in NMR is to monitor the radiation nuclear spins emit as they return to equilibrium after the appropriate stimulation. The resulting **Fourier-transform NMR** (FT-NMR) spectroscopy gives greatly increased sensitivity, so opening up much of the periodic table to the technique. Moreover, multiple-pulse FT-NMR gives chemists unparalleled control over the information content and display of spectra.

49.1 The magnetization vector

Consider a sample composed of many identical spin-$\frac{1}{2}$ nuclei. By analogy with the discussion of angular momenta in Topic 14, a nuclear spin can be represented by a vector of length $\{I(I+1)\}^{1/2}$ units with a component of length m_I units along the z-axis. As the uncertainty principle does not allow us to specify the x- and y-components of the angular momentum, all we know is that the vector lies somewhere on a cone around the z-axis. For $I = \frac{1}{2}$, the length of the vector is $\frac{1}{2}3^{1/2}$ and it makes an angle of 55° to the z-axis (Fig. 49.1).

In the absence of a magnetic field, the sample consists of equal numbers of α and β nuclear spins with their vectors lying at random angles on the cones. These angles are unpredictable, and at this stage we picture the spin vectors as stationary. The **magnetization**, M, of the sample, its net nuclear magnetic moment, is zero (Fig. 49.2a).

Two changes occur in the magnetization when a magnetic field of magnitude $\mathcal{B}_0$ is present and aligned in the z-direction:

- The energies of the two orientations change, the α spins moving to low energy and the β spins to high energy (provided $\gamma_N > 0$).

At 10 T, the Larmor frequency for protons is 427 MHz, and in the vector model the individual vectors are pictured as precessing at this rate (Topic 48). This motion is a pictorial representation of the difference in energy of the spin states (it is not an actual representation of reality but is inspired by the motion of a classical bar magnet in a magnetic field). As the field is increased, the Larmor frequency increases and the precession becomes faster.

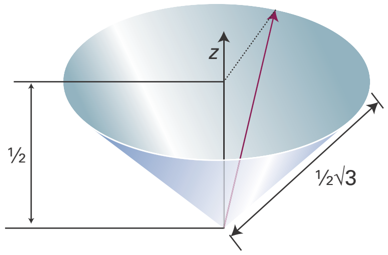


Figure 49.1 The vector model of angular momentum for a single spin-$\frac{1}{2}$ nucleus. The angle around the z–axis is indeterminate.

- The populations of the two spin states (the numbers of α and β spins) at thermal equilibrium change, with slightly more α spins than β spins (see Topic 47).

Despite its smallness, this imbalance means that there is a net magnetization that we can represent by a vector M pointing in the z-direction and with a length proportional to the population difference (Fig. 49.2b).

(a) The effect of the radiofrequency field

Now consider the effect of a radiofrequency field circularly polarized in the xy-plane, so that the magnetic component of the electromagnetic field (the only component we need to consider) is rotating around the z-direction in the same sense as the Larmor precession of the nuclei. The strength of the rotating magnetic field is $\mathcal{B}_1$.

To interpret the effects of radiofrequency pulses on the magnetization, it is useful to imagine stepping on to a platform, a so-called **rotating frame**, that rotates around the direction of the applied field. Suppose we choose the frequency of the radiofrequency field to be equal to the Larmor frequency of the spins, $\nu_L = \gamma_N \mathcal{B}_0/2\pi$; this choice is equivalent to selecting the resonance condition in the conventional experiment. The rotating magnetic field is in step with the precessing spins, and the nuclei experience a steady $\mathcal{B}_1$ field and precess about it at a frequency $\gamma_N \mathcal{B}_1/2\pi$ (Fig. 49.3). Now suppose that the $\mathcal{B}_1$ field is applied in a pulse of duration $\Delta\tau = \frac{1}{4} \times 2\pi/\gamma_N \mathcal{B}_1$. The magnetization tips through an angle of $\frac{1}{4} \times 2\pi = \pi/2$ (90°) in the

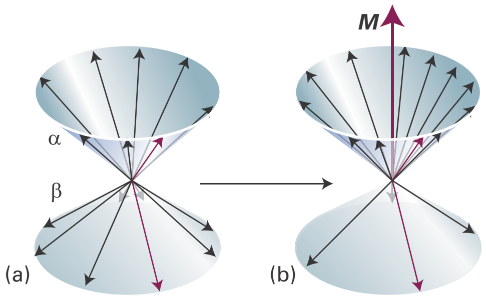


Figure 49.2 The magnetization of a sample of spin-$\frac{1}{2}$ nuclei is the resultant of all their magnetic moments. (a) In the absence of an externally applied field, there are equal numbers of α and β spins at random angles around the z-axis (the field direction) and the magnetization is zero. (b) In the presence of a field, the spins precess around their cones (that is, there is an energy difference between the α and β states) and there are slightly more α spins than β spins. As a result, there is a net magnetization along the z-axis.

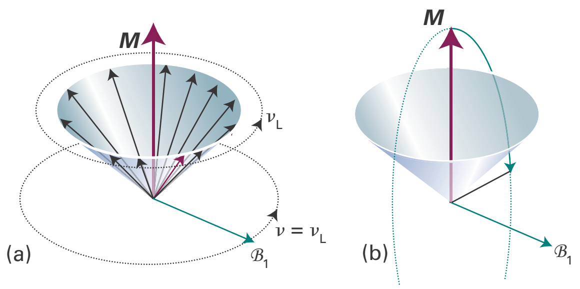


Figure 49.3 (a) In a resonance experiment, a circularly polarized radiofrequency magnetic field $\mathcal{B}_1$ is applied in the xy-plane (the magnetization vector lies along the z-axis). (b) If we step into a frame rotating at the radiofrequency, $\mathcal{B}_1$ appears to be stationary, as does the magnetization M if the Larmor frequency is equal to the radiofrequency. When the two frequencies coincide, the magnetization vector of the sample rotates around the direction of the $\mathcal{B}_1$ field.

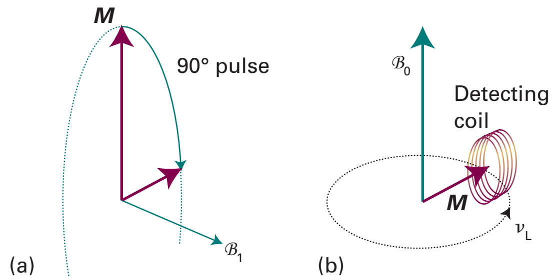


Figure 49.4 (a) If the radiofrequency field is applied for a certain time, the magnetization vector is rotated into the *xy*-plane. (b) To an external stationary observer (the coil), the magnetization vector is rotating at the Larmor frequency, and can induce a signal in the coil.

rotating frame and we say that we have applied a **90° pulse**, or a 'π/2 pulse' (Fig. 49.4a).

Brief illustration 49.1 Radiofrequency pulses

The duration of a radiofrequency pulse depends on the strength of the $\mathcal{B}_1$ field. If a 90° pulse requires 10 μs, then for protons

$$\mathcal{B}_1=\frac{\pi}{2\times\underbrace{(2.675\times10^{-8}\,\mathrm{T^{-1}s^{-1}})}_{\gamma_N}\times\underbrace{(1.0\times10^{-5}\,\mathrm{s})}_{\Delta\tau}}=5.9\times10^{-4}\,\mathrm{T}$$

Self-test 49.1 How long would a 180° pulse require for protons?

Answer: 20 μs

Now imagine stepping out of the rotating frame. To a fixed external observer (the role played by a radiofrequency coil), the magnetization vector is rotating at the Larmor frequency in the *xy*-plane (Fig. 49.4b). The rotating magnetization induces in the coil a signal that oscillates at the Larmor frequency and that can be amplified and processed. In practice, the processing takes place after subtraction of a constant high-frequency component (the radiofrequency used for $\mathcal{B}_1$), so that all the signal manipulation takes place at frequencies of a few kilohertz.

As time passes, the individual spins move out of step (partly because they are precessing at slightly different rates, as we explain later), so the magnetization vector shrinks exponentially with a time constant T_2 and induces an ever weaker signal in the detector coil. The form of the signal that we can expect is therefore the oscillating-decaying **free-induction decay** (FID) shown in Fig. 49.5. The *y*-component of the magnetization varies as

$$M_y(t)=M_0\cos(2\pi\nu_L t)e^{-t/T_2} \quad \text{Free-induction decay} \quad (49.1)$$

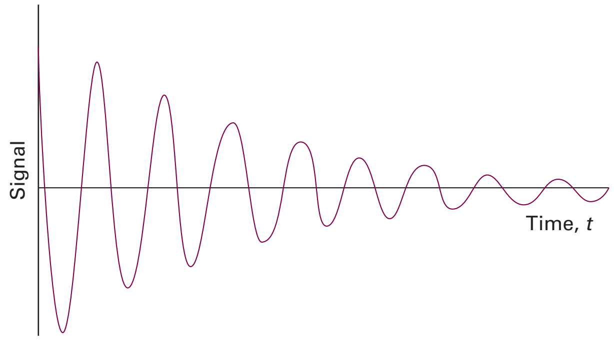


Figure 49.5 A simple free-induction decay of a sample of spins with a single resonance frequency.

We have considered the effect of a pulse applied at exactly the Larmor frequency. However, virtually the same effect is obtained off resonance, provided that the pulse is applied close to ν_L. If the difference in frequency is small compared to the inverse of the duration of the 90° pulse, the magnetization will end up in the *xy*-plane. Note that we do not need to know the Larmor frequency beforehand: the short pulse is the analogue of the hammer blow on the bell, exciting a range of frequencies. The detected signal shows that a particular resonant frequency is present.

(b) Time- and frequency-domain signals

We can think of the magnetization vector of a homonuclear AX spin system with spin–spin coupling constant $J=0$ as consisting of two parts, one formed by the A spins and the other by the X spins. When the 90° pulse is applied, both magnetization vectors are rotated into the *xy*-plane. However, because the A and X nuclei precess at different frequencies, they induce two signals in the detector coils, and the overall FID curve may resemble that in Fig. 49.6a. The composite FID curve is the analogue of the struck bell emitting a rich tone composed of all the frequencies (in this case, just the two resonance frequencies of the uncoupled A and X nuclei) at which it can vibrate.

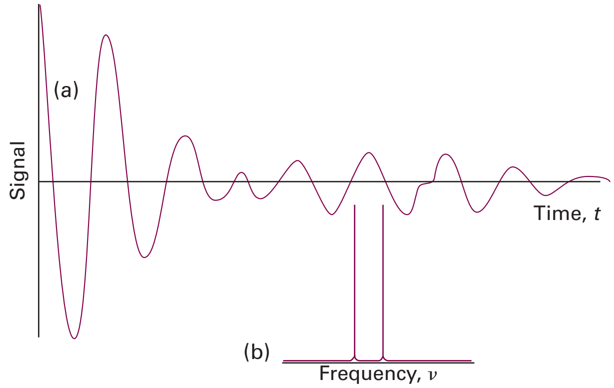


Figure 49.6 (a) A free-induction decay signal of a sample of AX species and (b) analysis into its frequency components.

The problem we must address is how to recover the resonance frequencies present in a free-induction decay. We know that the FID curve is a sum of decaying oscillating functions, so the problem is to analyse it into its components by carrying out a Fourier transformation (see the following *Justification*). When the signal in Fig. 49.6a is transformed in this way, we get the frequency-domain spectrum shown in Fig. 49.6b. One line represents the Larmor frequency of the A nuclei and the other that of the X nuclei.

Brief illustration 49.2 Fourier analysis

Fourier analysis is a common feature of most mathematical software packages, but one simple example is the Fourier transform of the function

$$S(t)=S(0)\cos(2\pi\nu_{\mathrm{L}}t)\mathrm{e}^{-t/T_2}$$

which describes the behaviour of the FID signal in eqn 49.1. The result is (Problem 49.4)

$$I(\nu)=\frac{S(0)T_2}{1+\left(\nu_{\mathrm{L}}-\nu\right)^2(2\pi T_2)^2}$$

which has the so-called 'Lorentzian' shape, with a maximum intensity at $I(\nu_{\mathrm{L}})=S(0)T_2$.

Self-test 49.2 What is the width at half-height, $\Delta\nu_{1/2}$, of the Lorentzian function above?

Answer: $\Delta\nu_{1/2}=1/\pi T_2$

Justification 49.1 Fourier transformation of the FID curve

The analysis of the FID curve is achieved by the standard mathematical technique of Fourier transformation, which is explained more fully in *Mathematical background* 6. We start by noting that the signal $S(t)$ in the time domain, the total FID curve, is the sum (more precisely, the integral) over all the contributing frequencies:

$$S(t)=\int_{-\infty}^{\infty}I(\nu)\mathrm{e}^{-2\pi\mathrm{i}\nu t}\mathrm{d}\nu \tag{49.2}$$

Because $\mathrm{e}^{2\pi\mathrm{i}\nu t}=\cos(2\pi\nu t)+\mathrm{i}\sin(2\pi\nu t)$, this expression is a sum over harmonically oscillating functions, with each one weighted by the intensity $I(\nu)$.

We need $I(\nu)$, the spectrum in the frequency domain; it is obtained by evaluating the integral

$$I(\nu)=2\mathrm{Re}\int_{0}^{\infty}S(t)\mathrm{e}^{2\pi\mathrm{i}\nu t}\mathrm{d}t \tag{49.3}$$

where 'Re' means take the real part of the following expression. This integral gives a nonzero value if $S(t)$ contains a component that matches the oscillating function $\mathrm{e}^{2\mathrm{i}\pi\nu t}$. The integration is carried out at a series of frequencies ν on a computer that is built into the spectrometer.

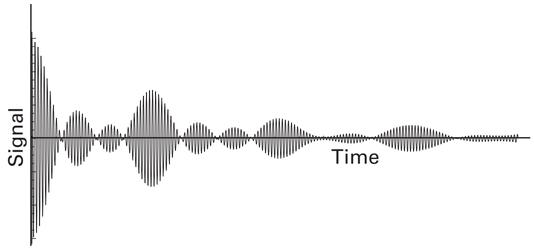


Figure 49.7 A free-induction decay signal of a sample of ethanol. Its Fourier transform is the frequency-domain spectrum shown in Fig. 48.2. The total length of the image corresponds to about 1 s.

The FID curve in Fig. 49.7 is obtained from a sample of ethanol. The frequency-domain spectrum obtained from it by Fourier transformation is the one discussed in Topic 48 (see Fig. 48.2). We can now see why the FID curve in Fig. 49.7 is so complex: it arises from the precession of a magnetization vector that is composed of eight components, each with a characteristic frequency.

49.2 Spin relaxation

There are two reasons why the component of the magnetization vector in the *xy*-plane shrinks. Both reflect the fact that the nuclear spins are not in thermal equilibrium with their surroundings (for then $\boldsymbol{M}$ lies parallel to z). At thermal equilibrium the spins have a Boltzmann distribution, with more α spins than β spins, and lie at random orientations on their precessional cones. The return to equilibrium is the process called **spin relaxation**.

Consider the effect of a 180° pulse, which may be visualized in the rotating frame as a flip of the net magnetization vector from one direction along the z-axis (with more α spins than β spins) to the opposite direction (with more β spins than α spins). After the pulse, the populations revert to their thermal equilibrium values exponentially. As they do so, the z-component of magnetization reverts to its equilibrium value M_0 with a time constant called the **longitudinal relaxation time**, T_1 (Fig. 49.8):

$$M_z(t)-M_0\propto\mathrm{e}^{-t/T_1} \tag{49.4}$$

Definition Longitudinal relaxation time

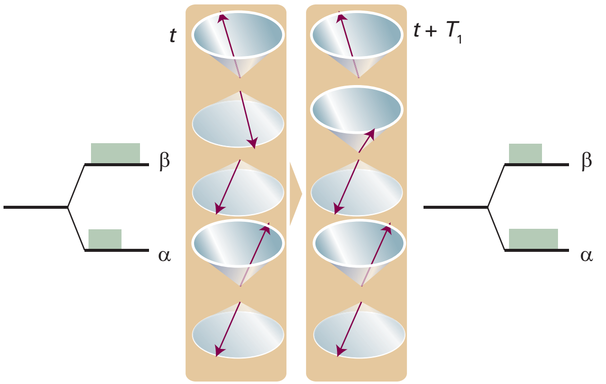


Figure 49.8 In longitudinal relaxation the spins relax back towards their thermal equilibrium populations. On the left we see the precessional cones representing spin-$\frac{1}{2}$ angular momenta, and they do not have their thermal equilibrium populations (there are more β spins than α spins). On the right, which represents the sample a long time after a time T_1 has elapsed, the populations are those characteristic of a Boltzmann distribution. In actuality, T_1 is the time constant for relaxation to the arrangement on the right and T_1 ln 2 is the half-life of the arrangement on the left.

Because this relaxation process involves giving up energy to the surroundings (the 'lattice') as β spins revert to α spins, the time constant T_1 is also called the **spin–lattice relaxation time**. Spin–lattice relaxation is caused by local magnetic fields that fluctuate at a frequency close to the resonance frequency of the $\beta \rightarrow \alpha$ transition. Such fields can arise from the tumbling motion of molecules in a fluid sample. If molecular tumbling is too slow or too fast compared to the resonance frequency, it will give rise to a fluctuating magnetic field with a frequency that is either too low or too high to stimulate a spin change from β to α, so T_1 will be long. Only if the molecule tumbles at about the resonance frequency will the fluctuating magnetic field be able to induce spin changes effectively, and only then will T_1 be short. The rate of molecular tumbling increases with temperature and with decreasing viscosity of the solvent, so we can expect a dependence like that shown in Fig. 49.9. The quantitative treatment of relaxation times depends on setting up models of molecular motion and using, for instance, the diffusion equation (Topic 81) adapted for rotational motion.

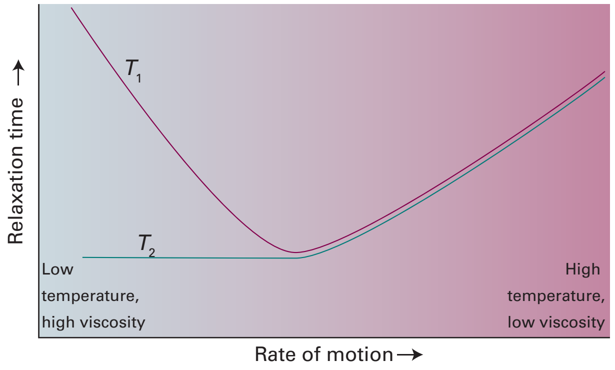


Figure 49.9 The variation of the two relaxation times with the rate at which the molecules move (either by tumbling or migrating through the solution). The horizontal axis can be interpreted as representing temperature or viscosity. Note that at rapid rates of motion, the two relaxation times coincide.

Now consider the events following a 90° pulse. The magnetization vector in the *xy*-plane is large when the spins are bunched together immediately after the pulse. However, this orderly bunching of spins is not at equilibrium and, even if there were no spin–lattice relaxation, we would expect the individual spins to spread out until they were uniformly distributed with all possible angles around the *z*-axis (Fig. 49.10). At that stage, the component of magnetization vector in the plane would be zero. The randomization of the spin directions occurs exponentially with a time constant called the **transverse relaxation time**, T_2:

$$M_y(t) \propto e^{-t/T_2} \qquad \textit{Definition} \qquad \text{Transverse relaxation time} \qquad (49.5)$$

Because the relaxation involves the relative orientation of the spins around their respective cones, T_2 is also known as the **spin–spin relaxation time**. Any relaxation process that changes the balance between α and β spins will also contribute to this randomization, so the time constant T_2 is almost always less than or equal to T_1.

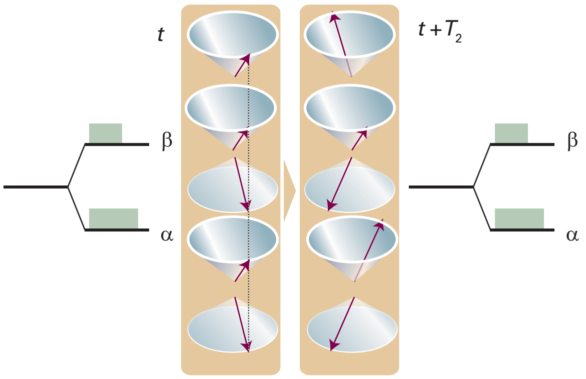


Figure 49.10 The transverse relaxation time, T_2, is the time constant for the phases of the spins to become randomized (another condition for equilibrium) and to change from the orderly arrangement shown on the left to the disorderly arrangement on the right (long after a time T_2 has elapsed). Note that the populations of the states remain the same; only the relative phase of the spins relaxes. In actuality, T_2 is the time constant for relaxation to the arrangement on the right and T_2 ln 2 is the half-life of the arrangement on the left.

Local magnetic fields also affect spin–spin relaxation. When the fluctuations are slow, each molecule lingers in its local magnetic environment and the spin orientations randomize quickly around their cones. If the molecules move rapidly from one magnetic environment to another, the effects of differences in local magnetic field average to zero: individual spins do not precess at very different rates, they can remain bunched for longer, and spin–spin relaxation does not take place as quickly. In other words, slow molecular motion corresponds to short T_2 and fast motion corresponds to long T_2 (as shown in Fig. 49.9). Calculations show that, when the motion is fast, the main randomizing effect arises from $\beta \rightarrow \alpha$ transitions rather than different precession rates on the cones, and then $T_2 \approx T_1$.

If the y-component of magnetization decays with a time constant T_2, the spectral line is broadened (Fig. 49.11), and its width at half-height becomes (see Self-test 49.2)

$$\Delta\nu_{1/2} = \frac{1}{\pi T_2} \qquad \text{Width at half-height of an NMR line} \qquad (49.6)$$

Typical values of T_2 in proton NMR are of the order of seconds, so linewidths of around 0.1 Hz can be anticipated, in broad agreement with observation.

So far, we have assumed that the equipment, and in particular the magnet, is perfect, and that the differences in Larmor frequencies arise solely from interactions within the sample. In practice, the magnet is not perfect, and the field is different at different locations in the sample. The inhomogeneity broadens the resonance, and in most cases this **inhomogeneous broadening** dominates the broadening we have discussed so far. It is common to express the extent of inhomogeneous broadening in terms of an **effective transverse relaxation time**, T_2^*, by using a relation like eqn 49.6, but writing

$$T_2^* = \frac{1}{\pi \Delta\nu_{1/2}} \qquad \text{Effective transverse relaxation time} \qquad (49.7)$$

where $\Delta\nu_{1/2}$ is the observed width at half-height of a line with a Lorentzian shape of the form $I \propto 1/(1+\nu^2)$.

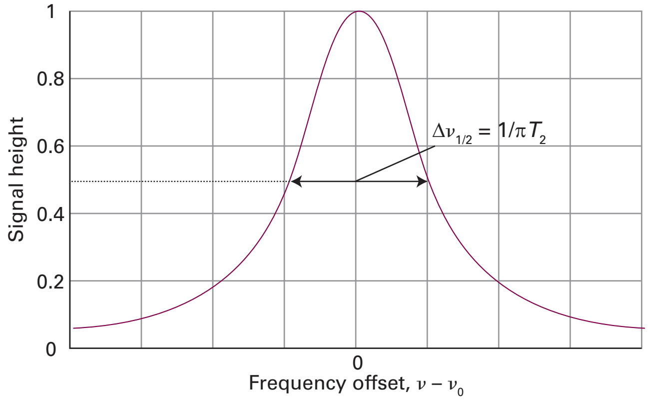


Figure 49.11 A Lorentzian absorption line. The width at half-height is inversely proportional to the parameter T_2 and the longer the transverse relaxation time, the narrower the line.

Brief illustration 49.3 Inhomogeneous broadening

Consider a line in a spectrum with a width of 10 Hz. It follows from eqn 49.7 that the effective transverse relaxation time is

$$T_2^* = \frac{1}{\pi \times (10\,\text{s}^{-1})} = 32\,\text{ms}$$

Self-test 49.3 Name two processes that could contribute to further broadening of the NMR line.

Answer: Conformational conversion or chemical exchange (see Topic 48)

49.3 The nuclear Overhauser effect

One advantage of protons in NMR is their high magnetogyric ratio, which results in relatively large Boltzmann population differences and strong coupling to the radiofrequency field, and hence greater resonance intensities than for most other nuclei. In the steady-state **nuclear Overhauser effect** (NOE), spin relaxation processes involving internuclear dipole–dipole interactions are used to transfer this population advantage to another nucleus (such as ^{13}C or another proton), so that the latter's resonances are modified. In a dipole–dipole interaction between two nuclei, one nucleus influences the behaviour of another nucleus in much the same way that the orientation of a bar magnet is influenced by the presence of another bar magnet nearby.

To understand the effect, consider the populations of the four levels of a homonuclear (for instance, proton) AX system; these levels were shown in Fig. 48.8. At thermal equilibrium, the population of the $\alpha_A\alpha_X$ level is the greatest and that of the $\beta_A\beta_X$ level is the least; the other two levels have the same energy and an intermediate population. The thermal equilibrium absorption intensities reflect these populations, as shown in Fig. 49.12. Now consider the combined effect of spin relaxation and keeping the X spins saturated. When we saturate the X transition, the populations of the X levels are equalized ($N_{\alpha_X} = N_{\beta_X}$) and all transitions involving $\alpha_X \leftrightarrow \beta_X$ spin flips are no longer observed. At this stage there is no change in the populations of the A levels. If that were all there were to happen, all we would see would be the loss of the X resonance and no effect on the A resonance.

Now consider the effect of spin relaxation. Relaxation can occur in a variety of ways if there is a dipolar interaction between the A and X spins. One possibility is for the magnetic field acting between the two spins to cause them *both* to flip

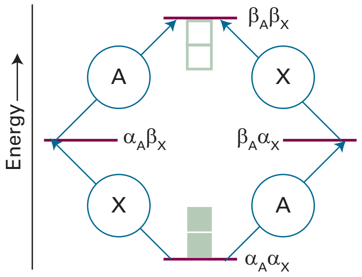


Figure 49.12 The energy levels of an AX system and an indication of their relative populations. Each green square above the line represents an excess population and each white square below the line represents a population deficit. The transitions of A and X are marked.

simultaneously from β to α, so the $\alpha_A\alpha_X$ and $\beta_A\beta_X$ states regain their thermal equilibrium populations. However, the populations of the $\alpha_A\beta_X$ and $\beta_A\alpha_X$ levels remain unchanged at the values characteristic of saturation. As we see from Fig. 49.13, the population difference between the states joined by transitions of A is now greater than at equilibrium, so the resonance absorption is enhanced. Another possibility is for the dipolar interaction between the two spins to cause α_A to flip to β_A and simultaneously β_X to flip to α_X (or vice versa). This transition equilibrates the populations of $\alpha_A\beta_X$ and $\beta_A\alpha_X$ but leaves the $\alpha_A\alpha_X$ and $\beta_A\beta_X$ populations unchanged. Now we see from the illustration that the population differences in the states involved in the A transitions are decreased, so the resonance absorption is diminished.

Which effect wins? Does the NOE enhance the A absorption or does it diminish it? As in the discussion of relaxation times in Section 49.2, the efficiency of the intensity-enhancing $\beta_A\beta_X \leftrightarrow \alpha_A\alpha_X$ relaxation is high if the dipole field oscillates at a frequency close to the transition frequency, which in this case is about 2ν; likewise, the efficiency of the intensity-diminishing $\alpha_A\beta_X \leftrightarrow \beta_A\alpha_X$ relaxation is high if the dipole field is stationary (as there is no frequency difference between the initial and final states). A large molecule rotates so slowly that there is very little motion at 2ν, so we expect an intensity decrease (Fig. 49.14). A small molecule rotating rapidly can be expected to have substantial motion at 2ν, and a consequent enhancement of the signal. In practice, the enhancement lies somewhere between the two extremes and is reported in terms of the parameter η (eta), where

$$\eta = \frac{I_A - I_A^\circ}{I_A^\circ} \qquad \text{NOE enhancement parameter} \qquad (49.8)$$

Here I_A° and I_A are the intensities of the NMR signals due to nucleus A before and after application of the long ($> T_1$) radiofrequency pulse that saturates transitions due to the X nucleus. When A and X are nuclei of the same species, such as protons, η lies between -1 (diminution) and $+\frac{1}{2}$ (enhancement). However, η also depends on the values of the magnetogyric

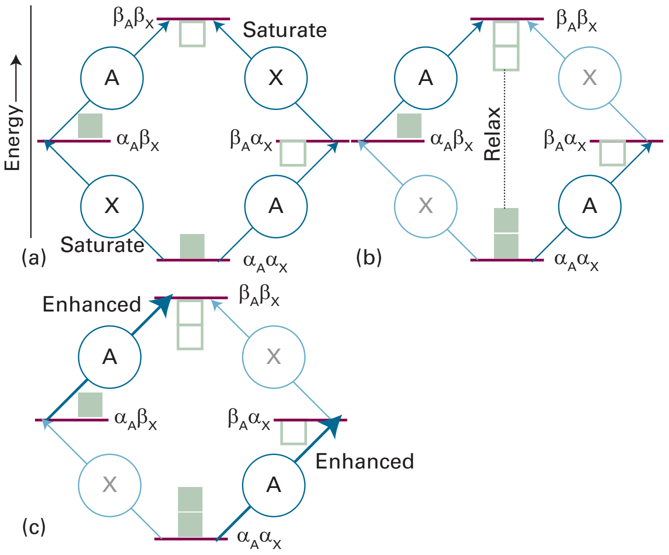


Figure 49.13 (a) When the X transition is saturated, the populations of its two states are equalized and the population excess and deficit become as shown (using the same symbols as in Fig. 49.12). (b) Dipole–dipole relaxation relaxes the populations of the highest and lowest states, and they regain their original populations. (c) The A transitions reflect the difference in populations resulting from the preceding changes, and are enhanced compared with those shown in Fig. 49.12.

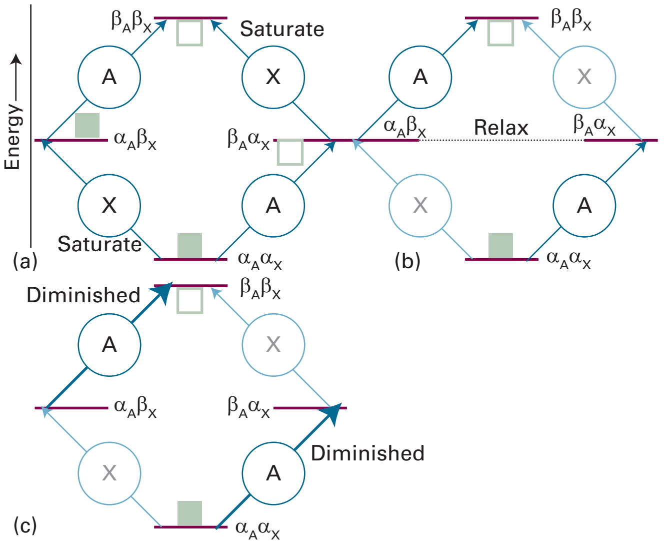


Figure 49.14 (a) When the X transition is saturated, just as in Fig. 49.13 the populations of its two states are equalized and the population excess and deficit become as shown. (b) Dipole–dipole relaxation relaxes the populations of the two intermediate states, and they regain their original populations. (c) The A transitions reflect the difference in populations resulting from the preceding changes, and are diminished compared with those shown in Fig. 49.12.

ratios of A and X. In the case of maximal enhancement it is possible to show that

$$\eta=\frac{\gamma_X}{2\gamma_A} \tag{49.9}$$

where γ_A and γ_X are the magnetogyric ratios of nuclei A and X, respectively.

Brief illustration 49.4 NOE enhancement

From eqn 49.9 and the data in Table 47.2, the NOE enhancement parameter for ^{13}C close to a saturated proton is

$$\eta=\frac{\overbrace{2.675\times10^{8}\ \mathrm{T^{-1}\,s^{-1}}}^{\gamma_{^{1}\mathrm{H}}}}{2\times\underbrace{(6.73\times10^{7}\ \mathrm{T^{-1}\,s^{-1}})}_{\gamma_{^{13}\mathrm{C}}}}=1.99$$

which shows that an enhancement of about a factor of 2 can be achieved.

Self-test 49.4 Interpret the following features of the NMR spectra of a protein: (a) saturation of a proton resonance assigned to the side chain of a methionine residue changes the intensities of proton resonances assigned to the side chains of a tryptophan and a tyrosine residue; (b) saturation of proton resonances assigned to the tryptophan residue did not affect the spectrum of the tyrosine residue.

Answer: The tryptophan and tyrosine residues are close to the methionine residue, but are far from each other

The NOE is also used to determine interproton distances. The Overhauser enhancement of a proton A generated by saturating a spin X depends on the fraction of A's spin–lattice relaxation that is caused by its dipolar interaction with X. Because the dipolar field is proportional to r^{-3}, where r is the internuclear distance, and the relaxation effect is proportional to the square of the field, and therefore to r^{-6}, the NOE may be used to determine the geometries of molecules in solution. The determination of the structure of a small protein in solution involves the use of several hundred NOE measurements, effectively casting a net over the protons present. The enormous importance of this procedure is that we can determine the conformation of biological macromolecules in an aqueous environment and do not need to try to make the single crystals that are essential for an X-ray diffraction investigation (Topic 37).

49.4 Two-dimensional NMR

An NMR spectrum contains a great deal of information and, if many protons are present, is very complex when the fine structures of different groups of lines overlap. The complexity would be reduced if we could use two axes to display the data, with resonances belonging to different groups lying at different locations on the second axis. This separation is essentially what is achieved in **two-dimensional NMR**.

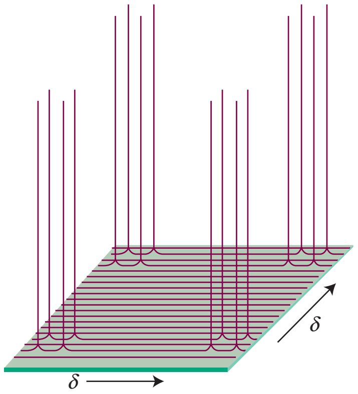


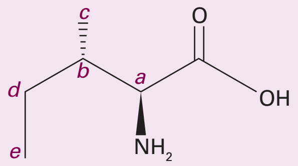
Figure 49.15 An idealization of the COSY spectrum of an AX spin system.

Much modern NMR work makes use of **correlation spectroscopy** (COSY), in which a clever choice of pulses and Fourier transformation techniques makes it possible to determine all spin–spin couplings in a molecule. A typical outcome for an AX system is shown in Fig. 49.15. The diagram shows contours of equal signal intensity on a plot of intensity against the frequency coordinates ν_1 and ν_2. The **diagonal peaks** are signals centred on (δ_A,δ_A) and (δ_X,δ_X) and lie along the diagonal where $\nu_1=\nu_2$. That is, the spectrum along the diagonal is equivalent to the one-dimensional spectrum obtained with the conventional NMR technique (as in Fig. 48.10). The **cross-peaks** (or *off-diagonal peaks*) are signals centred on (δ_A,δ_X) and (δ_X,δ_A) and owe their existence to the coupling between the A and X nuclei.

Although information from two-dimensional NMR spectroscopy is trivial in an AX system, it can be of enormous help in the interpretation of more complex spectra, leading to a map of the couplings between spins and to the determination of the bonding network in complex molecules. Indeed, the spectrum of a synthetic or biological polymer that would be impossible to interpret in one-dimensional NMR can often be interpreted reasonably rapidly by two-dimensional NMR.

Example 49.1 Interpreting a two-dimensional NMR spectrum

Figure 49.16 is a portion of the COSY spectrum of the amino acid isoleucine (**1**), showing the resonances associated with the protons bound to the carbon atoms.



1 Isoleucine

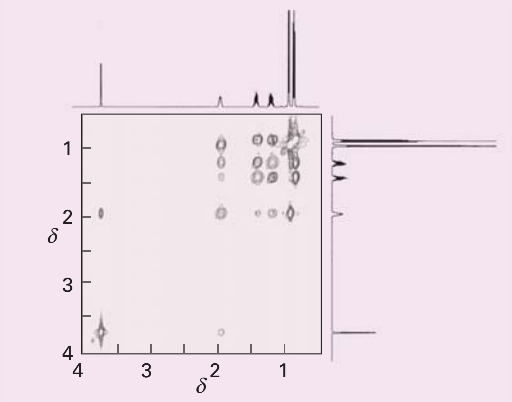


Figure 49.16 Proton COSY spectrum of isoleucine. (Example 49.1 and the corresponding spectrum are adapted from K.E. van Holde, et al., *Principles of physical biochemistry*, Prentice Hall (1998).)

Method From the molecular structure, we expect that: (i) the C_a—H proton is coupled only to the C_b—H proton; (ii) the C_b—H protons are coupled to the C_a—H, C_c—H, and C_d—H protons; and (iii) the inequivalent C_d—H protons are coupled to the C_b—H and C_e—H protons.

Answer We note that:

- The resonance with $\delta = 3.6$ shares a cross-peak with only one other resonance at $\delta = 1.9$, which in turn shares cross-peaks with resonances at $\delta = 1.4$, 1.2, and 0.9. We conclude that the resonances at $\delta = 3.6$ and 1.9 correspond to the C_a—H and C_b—H protons, respectively.
- The proton with resonance at $\delta = 0.8$ is not coupled to the C_b—H protons, so we assign the resonance at $\delta = 0.8$ to the C_e—H protons.
- The resonances at $\delta = 1.4$ and 1.2 do not share cross-peaks with the resonance at $\delta = 0.9$.
- In the light of the expected couplings, we assign the resonance at $\delta = 0.9$ to the C_c—H protons and the resonances at $\delta = 1.4$ and 1.2 to the inequivalent C_d—H protons.

Self-test 49.5 The proton chemical shifts for the NH, C_αH, and C_βH groups of alanine ($H_2NCH(CH_3)COOH$) are 8.25, 4.35, and 1.39, respectively. Describe the COSY spectrum of alanine between $\delta = 1.00$ and 8.50.

Answer: Only the NH and C_αH protons and the C_αH and C_βH protons are expected to show coupling, so the spectrum has only two off-diagonal peaks, one at (8.25, 4.35) and the other at (4.35, 1.39)

We have seen that the nuclear Overhauser effect can provide information about internuclear distances through analysis of enhancement patterns in the NMR spectrum before and after saturation of selected resonances. In **nuclear Overhauser effect spectroscopy** (NOESY) a map of all possible NOE interactions is obtained by again using a proper choice of radiofrequency pulses and Fourier transformation techniques. Like a COSY spectrum, a NOESY spectrum consists of a series of diagonal peaks that correspond to the one-dimensional NMR spectrum of the sample. The off-diagonal peaks indicate which nuclei are close enough to each other to give rise to a nuclear Overhauser effect. NOESY data reveal internuclear distances up to about 0.5 nm.

49.5 Solid-state NMR

The principal difficulty with the application of NMR to solids is the low resolution characteristic of solid samples. Nevertheless, there are good reasons for seeking to overcome these difficulties. They include the possibility that a compound of interest is unstable in solution or that it is insoluble, so conventional solution NMR cannot be employed. Moreover, many species, such as polymers and nanomaterials, are intrinsically interesting as solids, and it is important to determine their structures and dynamics when X-ray diffraction techniques fail.

There are three principal contributions to the linewidths of solids. One is the direct magnetic dipolar interaction between nuclear spins. As we saw in the discussion of spin–spin coupling, a nuclear magnetic moment will give rise to a local magnetic field, which points in different directions at different locations around the nucleus. If we are interested only in the component parallel to the direction of the applied magnetic field (because only this component has a significant effect), then, provided certain subtle effects arising from transformation from the static to the rotating frame are neglected, we can use a classical expression in *The chemist's toolkit* 48.1 to write the magnitude of the local magnetic field as

$$\mathcal{B}_{\mathrm{loc}} = -\frac{\gamma_{\mathrm{N}}\hbar\mu_0 m_I}{4\pi R^3}(1-3\cos^2\theta) \tag{49.10}$$

Unlike in solution, in a solid this field is not motionally averaged to zero. Many nuclei may contribute to the total local field experienced by a nucleus of interest, and different nuclei in a sample may experience a wide range of fields. Typical dipole fields are of the order of 1 mT, which corresponds to splittings and linewidths of the order of 10 kHz.

Brief illustration 49.5 Dipolar fields in solids

When the angle θ can vary only between 0 and $\theta_{\max}$, eqn 49.10 becomes

$$\mathcal{B}_{\text{loc}} = \frac{\gamma_{\text{N}}\hbar\mu_0 m_I}{4\pi R^3}(\cos^2\theta_{\max} + \cos\theta_{\max})$$

When $\theta_{\max} = 30°$ and $R = 160\,\text{pm}$, the local field generated by a proton is

$$\mathcal{B}_{\text{loc}} = \frac{\overbrace{2.675\times10^{8}\,\text{T}^{-1}\,\text{s}^{-1}}^{\gamma_{\text{N}}}\times\overbrace{(1.055\times10^{-34}\,\text{J s})}^{\hbar} \times\overbrace{(4\pi\times10^{-7}\,\text{T}^2\,\text{J}^{-1}\,\text{m}^3)}^{\mu_0}\times\overbrace{\left(\frac{1}{2}\right)}^{m_I}\times\overbrace{(1.616)}^{\substack{\cos^2\theta_{\max}+\\ \cos\theta_{\max}}}}{4\pi\times(\underbrace{1.60\times10^{-10}\,\text{m}}_{R})}$$

$$= 5.57\times10^{-4}\,\text{T} = 0.557\,\text{mT}$$

Self-test 49.6 Calculate the distance at which the local field from a ^{13}C nucleus is 0.50 mT, with $\theta_{\max} = 40°$.

Answer: $R = 99\,\text{pm}$

A second source of linewidth is the anisotropy of the chemical shift. Chemical shifts arise from the ability of the applied field to generate electron currents in molecules. In general, this ability depends on the orientation of the molecule relative to the applied field. In solution, when the molecule is tumbling rapidly, only the average value of the chemical shift is relevant. However, the anisotropy is not averaged to zero for stationary molecules in a solid, and molecules in different orientations have resonances at different frequencies. The chemical-shift anisotropy also varies with the angle between the applied field and the principal axis of the molecule, as $1 - 3\cos^2\theta$.

The third contribution is the electric quadrupole interaction. Nuclei with $I > \frac{1}{2}$ have a distribution of charge that gives rise to an electric quadrupole moment, a measure of the non-spherical distribution of charge over the nucleus (for instance, the positive charge may be concentrated around the equator or at the poles). An electric quadrupole interacts with an electric field gradient, such as may arise from a non-spherical distribution of charge around the nucleus. This interaction also varies as $1 - 3\cos^2\theta$.

Fortunately, there are techniques available for reducing the linewidths of solid samples. One technique, **magic-angle spinning** (MAS), takes note of the $1 - 3\cos^2\theta$ dependence of the dipole–dipole interaction, the chemical shift anisotropy, and the electric quadrupole interaction. The 'magic angle' is the angle at which $1 - 3\cos^2\theta = 0$, and corresponds to 54.74°. In the technique, the sample is spun at high speed at the magic angle to the applied field (Fig. 49.17). All the dipolar interactions and the anisotropies average to the value they would have at the magic angle, but at that angle they are zero. The difficulty with MAS is that the spinning frequency must not be less than the width of the spectrum, which is of the order of kilohertz. However, gas-driven sample spinners that can be rotated at 25 kHz or higher frequencies are now routinely available, and a considerable body of work has been done.

Pulsed techniques similar to those described in the previous section may also be used to reduce linewidths. Elaborate pulse sequences have also been devised that reduce linewidths by averaging procedures that make use of twisting the magnetization vector through a series of angles.

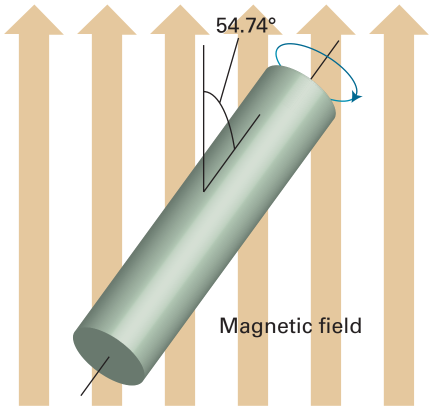


Figure 49.17 In magic-angle spinning, the sample spins at 54.74° (that is, arccos $1/3^{1/2}$) to the applied magnetic field. Rapid motion at this angle averages dipole–dipole interactions and chemical-shift anisotropies to zero.

Checklist of concepts

☐ 1. **Free-induction decay** (FID) is the decay of the magnetization after the application of a radiofrequency pulse.
☐ 2. Fourier transformation of the FID curve gives the NMR spectrum.
☐ 3. During **longitudinal** (or **spin–lattice**) **relaxation**, β spins revert to α spins.
☐ 4. **Transverse** (or **spin–spin**) **relaxation** is the randomization of spin directions around the z-axis.

☐ 5. The **nuclear Overhauser effect** is the modification of the intensity of one resonance by the saturation of another.

☐ 6. In **two-dimensional NMR**, spectra are displayed in two axes, with resonances belonging to different groups lying at different locations on the second axis.

☐ 7. **Magic-angle spinning** (MAS) is technique in which the NMR linewidths in a solid sample are reduced by spinning at an angle of 54.74° to the applied magnetic field.

Checklist of equations

Property	Equation	Comment	Equation number
Free-induction decay	$M_y(t)=M_0\cos(2\pi\nu_{\mathrm{L}}t)\mathrm{e}^{-t/T_2}$	T_2 is the transverse relaxation time	49.1
Longitudinal relaxation	$M_z(t)-M_0\propto \mathrm{e}^{-t/T_1}$	T_1 is the spin–lattice relaxation time	49.4
Transverse relaxation	$M_y(t)\propto \mathrm{e}^{-t/T_2}$		49.5
Width at half-height of an NMR line	$\Delta\nu_{1/2}=1/\pi T_2$	Inhomogeneous broadening is treated by using T_2^*	49.6
NOE enhancement parameter	$\eta=(I_{\mathrm{A}}-I_A^\circ)/I_A^\circ$	Definition	49.8

TOPIC 50

Electron paramagnetic resonance

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➤ Why do you need to know this material?

Some chemical reactions generate intermediates or products containing unpaired electrons, and you need to know how to characterize the structures of such species with special spectroscopic techniques.

➤ What is the key idea?

The electron paramagnetic resonance spectrum of a radical arises from the ability of the applied magnetic field to induce local electron currents and the magnetic interaction between the unpaired electron and nuclei with spin.

➤ What do you need to know already?

You need to be familiar with the concepts of electron spin (Topic 19), the general principles of magnetic resonance (Topic 47), and the magnetic properties of molecules (Topic 39). The discussion refers to spin–orbit coupling in atoms (Topic 21) and the Fermi contact interaction in molecules (Topic 48).

Electron paramagnetic resonance (EPR), which is also known as electron spin resonance (ESR), is used to study radicals formed during chemical reactions or by radiation, radicals that act as probes of biological structure, many d-metal complexes, and molecules in triplet states (such as those involved in phosphorescence, Topic 46). The sample may be a gas, a liquid, or a solid, but the free rotation of molecules in the gas phase gives rise to complications.

50.1 The *g*-value

The resonance frequency for a transition between the $m_s = -\frac{1}{2}$ and the $m_s = +\frac{1}{2}$ levels of an electron is

$$h\nu = g_e \mu_B \mathcal{B}_0 \qquad \textit{Free electron} \quad \text{Resonance condition} \qquad (50.1)$$

where $g_e \approx 2.0023$ (Topic 47). The magnetic moment of an unpaired electron in a radical also interacts with an external field, but the field it experiences differs from the applied field due to the presence of local magnetic fields arising from electron currents induced in the molecular framework. This difference is taken into account by replacing g_e by g and expressing the resonance condition as

$$h\nu = g \mu_B \mathcal{B}_0 \qquad \text{EPR resonance condition} \qquad (50.2)$$

where g is the ***g*-value** of the radical.

Brief illustration 50.1 The *g*-value of a radical

The centre of the EPR spectrum of the methyl radical occurred at 329.40 mT in a spectrometer operating at 9.2330 GHz (radiation belonging to the X band of the microwave region). Its *g*-value is therefore

$$g = \frac{\overbrace{(6.626\,08\times10^{-34}\,\mathrm{J\,s})}^{h} \times \overbrace{(9.2330\times10^{9}\,\mathrm{s}^{-1})}^{\nu}}{\underbrace{(9.2740\times10^{-24}\,\mathrm{J\,T}^{-1})}_{\mu_B} \times \underbrace{(0.329\,40\,\mathrm{T})}_{\mathcal{B}_0}} = 2.0027$$

Self-test 50.1 At what magnetic field would the methyl radical come into resonance in a spectrometer operating at 34.000 GHz (radiation belonging to the Q band of the microwave region)?

Answer: 1.213 T

The g-value is related to the ease with which the applied field can stir up currents through the molecular framework, and the strength of the magnetic field the currents generate. Therefore, the g-value gives some information about electronic structure and plays a similar role in EPR to that played by shielding constants in NMR.

Two factors are responsible for the difference of the g-value from g_e. Electrons migrate through the molecular framework by making use of excited states (Fig. 50.1). This circulation gives rise to a local magnetic field that adds to the applied field. The extent to which these currents are induced is inversely proportional to the separation of energy levels, ΔE, in the radical or complex. Secondly, the strength of the field experienced by the electron spin as a result of these electronic currents is proportional to the spin–orbit coupling constant, ξ (Topic 21). We can conclude that the g-value differs from g_e by an amount that is proportional to $\xi/\Delta E$. This proportionality is widely observed. Many organic radicals, for which ΔE is large and ξ (for carbon) is small, have g-values close to 2.0027, not far removed from g_e itself. Inorganic radicals, which commonly are built from heavier atoms and therefore have larger spin–orbit coupling constants, have g-values typically in the range 1.9 to 2.1. The g-values of paramagnetic d-metal complexes often differ considerably from g_e, varying from 0 to 6, because in them ΔE is small on account of the small splitting of d orbitals brought about by interactions with ligands (Topic 45).

The g-value is anisotropic: that is, its magnitude depends on the orientation of the radical with respect to the applied field. The anisotropy arises from the fact that the extent to which an applied field induces currents in the molecule, and therefore the magnitude of the local field, depends on the relative orientation of the molecules and the field. In solution, when the molecule is tumbling rapidly, only the average value of the g-value is observed. Therefore, anisotropy of the g-value is observed only for radicals trapped in solids.

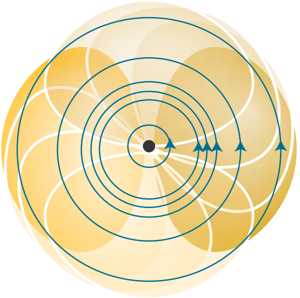


Figure 50.1 An applied magnetic field can induce circulation of electrons that makes use of excited-state orbitals (shown with a white line).

50.2 Hyperfine structure

The most important feature of an EPR spectrum is its **hyperfine structure**, the splitting of individual resonance lines into components. In general in spectroscopy, the term 'hyperfine structure' means the structure of a spectrum that can be traced to interactions of the electrons with nuclei other than as a result of the latter's point electric charge. The source of the hyperfine structure in EPR is the magnetic interaction between the electron spin and the magnetic dipole moments of the nuclei present in the radical which give rise to local magnetic fields.

(a) The effects of nuclear spin

Consider the effect on the EPR spectrum of a single H nucleus located somewhere in a radical. The proton spin is a source of magnetic field and, depending on the orientation of the nuclear spin, the field it generates adds to or subtracts from the applied field. The total local field is therefore

$$\mathcal{B}_{\text{loc}} = \mathcal{B}_0 + am_I \qquad m_I = \pm\tfrac{1}{2} \tag{50.3}$$

where a is the **hyperfine coupling constant**. Half the radicals in a sample have $m_I = +\frac{1}{2}$, so half resonate when the applied field satisfies the condition

$$h\nu = g\mu_{\text{B}}\left(\mathcal{B}_0 + \tfrac{1}{2}a\right), \quad \text{or} \quad \mathcal{B}_0 = \frac{h\nu}{g\mu_{\text{B}}} - \tfrac{1}{2}a \tag{50.4a}$$

The other half (which have $m_I = -\frac{1}{2}$) resonate when

$$h\nu = g\mu_{\text{B}}\left(\mathcal{B}_0 - \tfrac{1}{2}a\right), \quad \text{or} \quad \mathcal{B}_0 = \frac{h\nu}{g\mu_{\text{B}}} + \tfrac{1}{2}a \tag{50.4b}$$

Therefore, instead of a single line, the spectrum shows two lines of half the original intensity separated by a and centred on the field determined by g (Fig. 50.2).

If the radical contains an ^{14}N atom ($I = 1$), its EPR spectrum consists of three lines of equal intensity, because the ^{14}N nucleus has three possible spin orientations, and each spin orientation is possessed by one-third of all the radicals in the sample. In general, a spin-I nucleus splits the spectrum into $2I + 1$ hyperfine lines of equal intensity.

When there are several magnetic nuclei present in the radical, each one contributes to the hyperfine structure. In the case of equivalent protons (for example, the two CH_2 protons in the

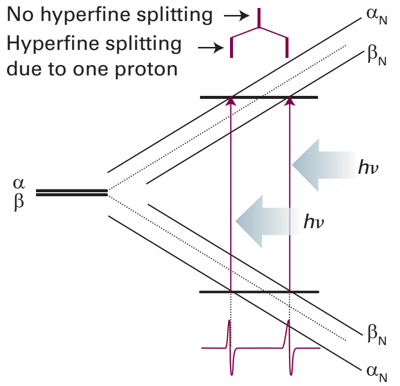


Figure 50.2 The hyperfine interaction between an electron and a spin-$\frac{1}{2}$ nucleus results in four energy levels in place of the original two. As a result, the spectrum consists of two lines (of equal intensity) instead of one. The intensity distribution can be summarized by a simple stick diagram. The diagonal lines show the energies of the states as the applied field is increased, and resonance occurs when the separation of states matches the fixed energy of the microwave photon.

radical CH_3CH_2) some of the hyperfine lines are coincident. If the radical contains N equivalent protons, then there are $N+1$ hyperfine lines with an intensity distribution given by Pascal's triangle (Topic 48, reproduced here as **1**). The spectrum of the benzene radical anion in Fig. 50.3, which has seven lines with intensity ratio 1:6:15:20:15:6:1, is consistent with a radical containing six equivalent protons. More generally, if the radical contains N equivalent nuclei with spin quantum number I, then there are $2NI+1$ hyperfine lines with an intensity distribution based on a modified version of Pascal's triangle, as shown in Example 50.1.

1
1 1
1 2 1
1 3 3 1
1 4 6 4 1
1 5 10 10 5 1

1

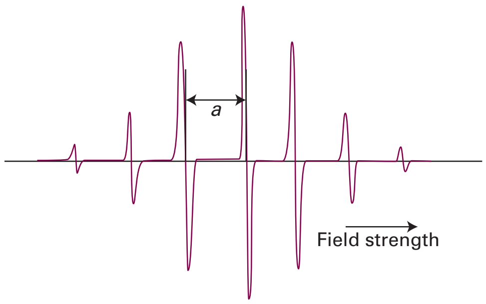


Figure 50.3 The EPR spectrum of the benzene radical anion, $C_6H_6^-$, in fluid solution, with a the hyperfine splitting of the spectrum. The centre of the spectrum is determined by the g-value of the radical.

Example 50.1 Predicting the hyperfine structure of an EPR spectrum

A radical contains one ^{14}N nucleus ($I=1$) with hyperfine constant 1.61 mT and two equivalent protons ($I=\frac{1}{2}$) with hyperfine constant 0.35 mT. Predict the form of the EPR spectrum.

Method Consider the hyperfine structure that arises from each type of nucleus or group of equivalent nuclei in succession. So, split a line with one nucleus, then each of those lines is split by a second nucleus (or group of nuclei), and so on. It is best to start with the nucleus with the largest hyperfine splitting; however, any choice could be made, and the order in which nuclei are considered does not affect the conclusion.

Answer The ^{14}N nucleus gives three hyperfine lines of equal intensity separated by 1.61 mT. Each line is split into doublets of spacing 0.35 mT by the first proton, and each line of these doublets is split into doublets with the same 0.35 mT splitting (Fig. 50.4). The central lines of each split doublet coincide, so the proton splitting gives 1:2:1 triplets of internal splitting 0.35 mT. Therefore, the spectrum consists of three equivalent 1:2:1 triplets.

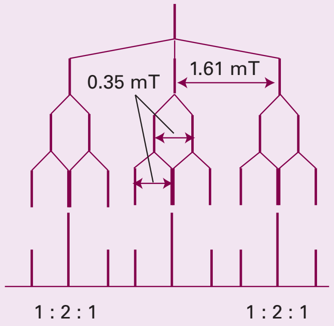


Figure 50.4 The analysis of the hyperfine structure of radicals containing one ^{14}N nucleus ($I=1$) and two equivalent protons.

Self-test 50.2 Predict the form of the EPR spectrum of a radical containing three equivalent ^{14}N nuclei.

Answer: See Fig. 50.5

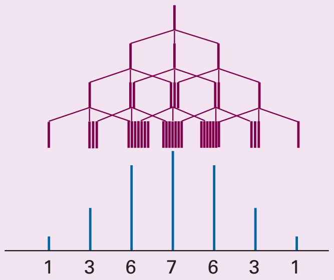


Figure 50.5 The analysis of the hyperfine structure of radicals containing three equivalent ^{14}N nuclei.

(b) The McConnell equation

The hyperfine structure of an EPR spectrum is a kind of fingerprint that helps to identify the radicals present in a sample. Moreover, because the magnitude of the splitting depends on the distribution of the unpaired electron in the vicinity of the magnetic nuclei, the spectrum can be used to map the molecular orbital occupied by the unpaired electron. For example, because the hyperfine splitting in $C_6H_6^-$ is 0.375 mT, and one proton is close to a C atom that has one-sixth the unpaired electron spin density (because the electron is spread uniformly around the ring), the hyperfine splitting caused by a proton in the electron spin entirely confined to a single adjacent C atom should be $6 \times 0.375\,\text{mT} = 2.25\,\text{mT}$. If in another aromatic radical we find a hyperfine splitting constant a, then the **spin density**, ρ, the probability that an unpaired electron is on the atom, can be calculated from the **McConnell equation**:

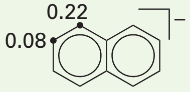
$$a = Q\rho \qquad \text{McConnell equation} \qquad (50.5)$$

with $Q = 2.25\,\text{mT}$. In this equation, ρ is the spin density on a C atom and a is the hyperfine splitting observed for the H atom to which it is attached.

Brief illustration 50.2 The McConnell equation

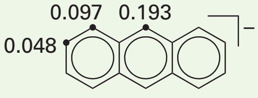
The hyperfine structure of the EPR spectrum of the radical anion $C_{10}H_8^-$, the naphthalene radical anion, can be interpreted as arising from two groups of four equivalent protons. Those at the 1, 4, 5, and 8 positions in the ring have $a = 0.490\,\text{mT}$ and those in the 2, 3, 6, and 7 positions have $a = 0.183\,\text{mT}$. The densities obtained by using the McConnell equation are, respectively (**2**),

$$\rho = \frac{\overbrace{0.490\,\text{mT}}^{a}}{\underbrace{2.25\,\text{mT}}_{Q}} = 0.218 \quad \text{and} \quad \rho = \frac{0.183\,\text{mT}}{2.25\,\text{mT}} = 0.0813$$



2

Self-test 50.3 The spin density in $C_{14}H_{10}^-$, the anthracene radical anion, is shown in **3**. Predict the form of its EPR spectrum.



3

Answer: A 1:2:1 triplet of splitting 0.43 mT split into a 1:4:6:4:1 quintet of splitting 0.22 mT, split into a 1:4:6:4:1 quintet of splitting 0.11 mT, $3 \times 5 \times 5 = 75$ lines in all

(c) The origin of the hyperfine interaction

The hyperfine interaction is an interaction between the magnetic moments of the unpaired electron and the nuclei. There are two contributions to the interaction.

An electron in a p orbital centred on a nucleus does not approach the nucleus very closely, so it experiences a field that appears to arise from a point magnetic dipole. The resulting interaction is called the **dipole–dipole interaction**. The contribution of a magnetic nucleus to the local field experienced by the unpaired electron is given by an expression like that in eqn 48.10 (a dependence proportional to $(1 - 3\cos^2\theta)/r^3$). A characteristic of this type of interaction is that it is anisotropic and averages to zero when the radical is free to tumble. Therefore, hyperfine structure due to the dipole–dipole interaction is observed only for radicals trapped in solids.

An s electron is spherically distributed around a nucleus and so has zero average dipole–dipole interaction with the nucleus even in a solid sample. However, because it has a nonzero probability of being at the nucleus (Topic 17), it is incorrect to treat the interaction as one between two point dipoles. As explained in Topic 48, an s electron has a Fermi contact interaction with the nucleus, a magnetic interaction that occurs when the point dipole approximation fails. The contact interaction is isotropic (that is, independent of the radical's orientation), and consequently is shown even by rapidly tumbling molecules in fluids (provided the spin density has some s character).

The dipole–dipole interactions of p electrons and the Fermi contact interaction of s electrons can be quite large. For example, a 2p electron in a nitrogen atom experiences an average field of about 3.4 mT from the ^{14}N nucleus. A 1s electron in a hydrogen atom experiences a field of about 50 mT as a result of its Fermi contact interaction with the central proton. More values are listed in Table 50.1. The magnitudes of the contact interactions in radicals can be interpreted in terms of the s orbital character of the molecular orbital occupied by the unpaired electron, and the dipole–dipole interaction can be interpreted in terms of the p character. The analysis of hyperfine structure therefore gives information about the composition of the orbital, and especially the hybridization of the atomic orbitals.

Table 50.1* Hyperfine coupling constants for atoms, a/mT

Nuclide	Isotropic coupling	Anisotropic coupling
^{1}H	50.8 (1s)	
^{2}H	7.8 (1s)	
^{14}N	55.2 (2s)	4.8 (2p)
^{19}F	1720 (2s)	108.4 (2p)

*More values are given in the *Resource section*.

Brief illustration 50.3 The composition of a molecular orbital from analysis of the hyperfine structure

From Table 50.1, the hyperfine interaction between a 2s electron and the nucleus of a nitrogen atom is 55.2 mT. The EPR spectrum of NO_2 shows an isotropic hyperfine interaction of 5.7 mT. The s character of the molecular orbital occupied by the unpaired electron is the ratio 5.7/55.2 = 0.10. For a continuation of this story, see Problem 50.6.

Self-test 50.4 In NO_2 the anisotropic part of the hyperfine coupling is 1.3 mT. What is the p character of the molecular orbital occupied by the unpaired electron?

Answer: 0.38

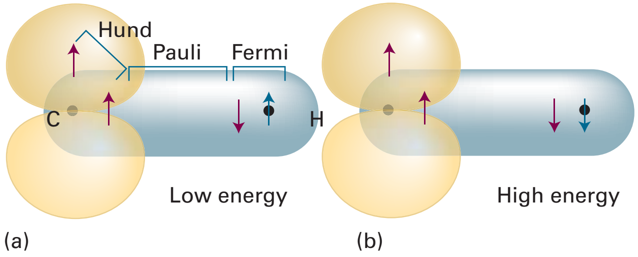


Figure 50.6 The polarization mechanism for the hyperfine interaction in π-electron radicals. The arrangement in (a) is lower in energy than that in (b), so there is an effective coupling between the unpaired electron and the proton.

We still have to explain the source of the hyperfine structure of the $C_6H_6^-$ anion and other aromatic radical anions. The sample is fluid, and as the radicals are tumbling the hyperfine structure cannot be due to the dipole–dipole interaction. Moreover, the protons lie in the nodal plane of the π orbital occupied by the unpaired electron, so the structure cannot be due to a Fermi contact interaction. The explanation lies in a **polarization mechanism** similar to the one responsible for spin–spin coupling in NMR. There is a magnetic interaction between a proton and the α electrons ($m_s = +\frac{1}{2}$) which results in one of the electrons tending to be found with a greater probability nearby (Fig. 50.6). The electron with opposite spin is therefore more likely to be close to the C atom at the other end of the bond. The unpaired electron on the C atom has a lower energy if it is parallel to that electron (Hund's rule favours parallel electrons on atoms), so the unpaired electron can detect the spin of the proton indirectly. Calculation using this model leads to a hyperfine interaction in agreement with the observed value of 2.25 mT.

Checklist of concepts

- ☐ 1. The EPR resonance condition is written in terms of the ***g*-value** of the radical.
- ☐ 2. The value of *g* depends on the ability of the applied field to induce local electron currents in the radical.
- ☐ 3. The **hyperfine structure** of an EPR spectrum is its splitting of individual resonance lines into components by the magnetic interaction between the electron and nuclei with spin.
- ☐ 4. If a radical contains N equivalent nuclei with spin quantum number I, then there are $2NI + 1$ hyperfine lines, with an intensity distribution given by a modified version of Pascal's triangle.
- ☐ 5. Hyperfine structure can be explained by **dipole–dipole interactions**, **Fermi contact interactions**, and the **polarization mechanism**.
- ☐ 6. The **spin density** is the probability that an unpaired electron is on the atom.

Checklist of equations

Property	Equation	Comment	Equation number
EPR resonance condition	$h\nu = g\mu_B\mathcal{B}_0$	No hyperfine interaction	50.2
	$h\nu = g\mu_B(\mathcal{B}_0 \pm \frac{1}{2}a)$	Hyperfine interaction between an electron and a proton	50.4
McConnell equation	$a = Q\rho$	$Q = 2.25$ mT	50.5

Focus 10 on Magnetic resonance

Topic 47 General principles

Discussion questions

47.1 To determine the structures of macromolecules by NMR spectroscopy, chemists use spectrometers that operate at the highest available fields and frequencies. Justify this choice.

47.2 Compare the effects of magnetic fields on the energies of nuclei and the energies of electrons.

47.3 What is the Larmor frequency?

Exercises

47.1(a) Given that g is a dimensionless number, what are the units of γ_N expressed in tesla and hertz?
47.1(b) Given that g is a dimensionless number, what are the units of γ_N expressed in SI base units?

47.2(a) For a proton, what are the magnitude of the spin angular momentum and its allowed components along the z-axis? What are the possible orientations of the angular momentum in terms of the angle it makes with the z-axis?
47.2(b) For a ^{14}N nucleus, what are the magnitude of the spin angular momentum and its allowed components along the z-axis? What are the possible orientations of the angular momentum in terms of the angle it makes with the z-axis?

47.3(a) What is the resonance frequency of a proton in a magnetic field of 13.5 T?
47.3(b) What is the resonance frequency of a ^{19}F nucleus in a magnetic field of 17.1 T?

47.4(a) ^{33}S has a nuclear spin of $\frac{3}{2}$ and a nuclear g-factor of 0.4289. Calculate the energies of the nuclear spin states in a magnetic field of 6.800 T.
47.4(b) ^{14}N has a nuclear spin of 1 and a nuclear g-factor of 0.404. Calculate the energies of the nuclear spin states in a magnetic field of 10.50 T.

47.5(a) Calculate the frequency separation of the nuclear spin levels of a ^{13}C nucleus in a magnetic field of 15.4 T given that the magnetogyric ratio is 6.73×10^{-7} T^{-1} s^{-1}.
47.5(b) Calculate the frequency separation of the nuclear spin levels of a ^{14}N nucleus in a magnetic field of 14.4 T given that the magnetogyric ratio is 1.93×10^{-7} T^{-1} s^{-1}.

47.6(a) In which of the following systems is the energy level separation larger? (a) A proton in a 600 MHz NMR spectrometer, (b) a deuteron in the same spectrometer.
47.6(b) In which of the following systems is the energy level separation larger? (a) A ^{14}N nucleus in (for protons) a 600 MHz NMR spectrometer, (b) an electron in a radical in a field of 0.300 T.

47.7(a) Calculate the magnetic field needed to satisfy the resonance condition for unshielded ^{14}N nuclei in a 50.0 MHz radiofrequency field.
47.7(b) Calculate the magnetic field needed to satisfy the resonance condition for unshielded protons in a 400.0 MHz radiofrequency field.

47.8(a) Use the information in Table 47.2 to predict the magnetic fields at which (a) ^{1}H, (b) ^{2}H, (c) ^{13}C come into resonance at (i) 500 MHz, (ii) 800 MHz.
47.8(b) Use the information in Table 47.2 to predict the magnetic fields at which (a) ^{14}N, (b) ^{19}F, and (c) ^{31}P come into resonance at (i) 400 MHz, (ii) 750 MHz.

47.9(a) Calculate the relative population differences ($\delta N/N$, where δN denotes a small difference $N_\alpha - N_\beta$) for protons in fields of (a) 0.30 T, (b) 1.5 T, and (c) 10 T at 25 °C.
47.9(b) Calculate the relative population differences ($\delta N/N$, where δN denotes a small difference $N_\alpha - N_\beta$) for ^{13}C nuclei in fields of (a) 0.50 T, (b) 2.5 T, and (c) 15.5 T at 25 °C.

47.10(a) The first generally available NMR spectrometers operated at a frequency of 60 MHz; today it is not uncommon to use a spectrometer that operates at 800 MHz. What are the relative population differences of ^{13}C spin states in these two spectrometers at 25 °C?
47.10(b) What are the relative population differences of ^{19}F spin states in spectrometers operating at 60 MHz and 450 MHz at 25 °C?

47.11(a) What magnetic field would be required in order to use an EPR X-band spectrometer (9 GHz) to observe ^{1}H-NMR and a 300 MHz spectrometer to observe EPR?
47.11(b) Some commercial EPR spectrometers use 8 mm microwave radiation (the Q band). What magnetic field is needed to satisfy the resonance condition?

Problems

47.1[‡] The relative sensitivity of NMR lines for equal numbers of different nuclei at constant temperature for a given frequency is $R_\nu \propto (I+1)\mu^3$, whereas for a given field it is $R_{\mathcal{B}} \propto \{(I+1)/I^2\}\mu^3$. (a) From the data in Table 47.2, calculate these sensitivities for the deuteron, ^{13}C, ^{14}N, ^{19}F, and ^{31}P relative to the proton. (b) Derive the equation for $R_{\mathcal{B}}$ from the equation for R_ν.

47.2 With special techniques, known collectively as magnetic resonance imaging (MRI), it is possible to obtain NMR spectra of entire organisms. A key to MRI is the application of a magnetic field that varies linearly

---

[‡] These problems were supplied by Charles Trapp and Carmen Giunta.

across the specimen. Consider a flask of water held in a field that varies in the z-direction according to $\mathcal{B}_0 + \mathcal{G}_z z$, where $\mathcal{G}_z$ is the field gradient along the z-direction. Then the water protons will be resonant at the frequencies

$$\nu_{\mathrm{L}}(z) = \frac{\gamma_{\mathrm{N}}}{2\pi}(\mathcal{B}_0 + \mathcal{G}_z z)$$

(Similar equations may be written for gradients along the x- and y-directions.) Application of a 90° radiofrequency pulse with $\nu = \nu_{\mathrm{L}}(z)$ will result in a signal with an intensity that is proportional to the number of protons at the position z. Now suppose a uniform disk-shaped organ is in a linear field gradient, and that the MRI signal is proportional to the number of protons in a slice of width δz at each horizontal distance z from the centre of the disk. Sketch the shape of the absorption intensity for the MRI image of the disk before any computer manipulation has been carried out.

Topic 48 Features of NMR spectra

Discussion questions

48.1 Discuss in detail the origins of the local, neighbouring group, and solvent contributions to the shielding constant.

48.2 Discuss how the Fermi contact interaction and the polarization mechanism contribute to spin–spin couplings in NMR.

Exercises

48.1(a) What are the relative values of the chemical shifts observed for nuclei in the spectrometers mentioned in Exercise 47.10(a) in terms of (a) δ values, (b) frequencies?

48.1(b) What are the relative values of the chemical shifts observed for nuclei in the spectrometers mentioned in Exercise 47.10(b) in terms of (a) δ values, (b) frequencies?

48.2(a) The chemical shift of the CH_3 protons in acetaldehyde (ethanal) is $\delta = 2.20$ and that of the CHO proton is 9.80. What is the difference in local magnetic field between the two regions of the molecule when the applied field is (a) 1.5 T, (b) 15 T?

48.2(b) The chemical shift of the CH_3 protons in diethyl ether is $\delta = 1.16$ and that of the CH_2 protons is 3.36. What is the difference in local magnetic field between the two regions of the molecule when the applied field is (a) 1.9 T, (b) 16.5 T?

48.3(a) Sketch the appearance of the ^{1}H-NMR spectrum of acetaldehyde (ethanal) using $J = 2.90$ Hz and the data in Exercise 48.2a in a spectrometer operating at (a) 250 MHz, (b) 800 MHz.

48.3(b) Sketch the appearance of the ^{1}H-NMR spectrum of diethyl ether using $J = 6.97$ Hz and the data in Exercise 48.2b in a spectrometer operating at (a) 400 MHz, (b) 650 MHz.

48.4(a) Sketch the form of the ^{19}F-NMR spectra of a natural sample of $^{10}BF_4^-$ and $^{11}BF_4^-$.

48.4(b) Sketch the form of the ^{31}P-NMR spectra of a sample of $^{31}PF_6^-$.

48.5(a) From the data in Table 47.2, predict the frequency needed for ^{19}F-NMR in an NMR spectrometer designed to observe proton resonance at 800 MHz. Sketch the proton and ^{19}F resonances in the NMR spectrum of FH_2^+.

48.5(b) From the data in Table 47.2, predict the frequency needed for ^{31}P-NMR in an NMR spectrometer designed to observe proton resonance at 500 MHz. Sketch the proton and ^{31}P resonances in the NMR spectrum of PH_4^+.

48.6(a) Sketch the form of an $A_3M_2X_4$ spectrum, where A, M, and X are protons with distinctly different chemical shifts and $J_{\mathrm{AM}} > J_{\mathrm{AX}} > J_{\mathrm{MX}}$.

48.6(b) Sketch the form of an $A_2M_2X_5$ spectrum, where A, M, and X are protons with distinctly different chemical shifts and $J_{\mathrm{AM}} > J_{\mathrm{AX}} > J_{\mathrm{MX}}$.

48.7(a) A proton jumps between two sites with $\delta = 2.7$ and $\delta = 4.8$. At what rate of interconversion will the two signals collapse to a single line in a spectrometer operating at 550 MHz?

48.7(b) A proton jumps between two sites with $\delta = 4.2$ and $\delta = 5.5$. At what rate of interconversion will the two signals collapse to a single line in a spectrometer operating at 350 MHz?

Problems

48.1 You are designing an MRI spectrometer (see Problem 47.2). What field gradient (in microtesla per metre, $\mu\mathrm{T\,m^{-1}}$) is required to produce a separation of 100 Hz between two protons separated by the long diameter of a human kidney (taken as 8 cm), given that they are in environments with $\delta = 3.4$? The radiofrequency field of the spectrometer is at 400 MHz and the applied field is 9.4 T.

48.2$^{\mathrm{LG}}$ Refer to Fig. 48.14 and use mathematical software, a spreadsheet, or the *Living graphs* (labelled $^{\mathrm{LG}}$) on the website of this book to draw a family of curves showing the variation of $^3J_{\mathrm{HH}}$ with ϕ for which $A = +7.0$ Hz, $B = -1.0$ Hz, and C varies slightly from a typical value of +5.0 Hz. What is the effect of changing the value of the parameter C on the shape of the curve? In a similar fashion, explore the effect of the values of A and B on the shape of the curve.

48.3‡ Various versions of the Karplus equation (eqn 48.14) have been used to correlate data on vicinal proton coupling constants in systems of the type $R_1R_2CHCHR_3R_4$. The original version (M. Karplus, *J. Am. Chem.* Soc. **85**, 2870 (1963)) is $^3J_{\mathrm{HH}} = A\cos^2\phi_{\mathrm{HH}} + B$. When $R_3 = R_4 = H$, $^3J_{\mathrm{HH}} = 7.3$ Hz; when $R_3 = CH_3$ and $R_4 = H$, $^3J_{\mathrm{HH}} = 8.0$ Hz; when $R_3 = R_4 = CH_3$, $^3J_{\mathrm{HH}} = 11.2$ Hz. Assume that only staggered conformations are important and determine which version of the Karplus equation fits the data better.

48.4‡ It might be unexpected that the Karplus equation, which was first derived for $^3J_{\mathrm{HH}}$ coupling constants, should also apply to vicinal coupling between the nuclei of metals such as tin. T.N. Mitchell and B. Kowall (*Magn. Reson. Chem.* **33**, 325 (1995)) studied the relation between $^3J_{\mathrm{HH}}$ and $^3J_{\mathrm{SnSn}}$ in compounds of the type $Me_3SnCH_2CHRSnMe_3$ and found that $^3J_{\mathrm{SnSn}} = 78.86\,{}^3J_{\mathrm{HH}} + 27.84$ Hz. (a) Does this result support a Karplus-type equation for tin? Explain your reasoning. (b) Obtain the Karplus equation for $^{3}J_{\mathrm{SnSn}}$ and plot it as a function of the dihedral angle. (c) Draw the preferred conformation.

48.5 Show that the coupling constant as expressed by the Karplus equation passes through a minimum when $\cos\phi = B/4C$.

48.6 In a liquid, the dipolar magnetic field averages to zero. Show this result by evaluating the average of the field given in eqn 48.15. *Hint*: The surface area element is $\sin\theta\,\mathrm{d}\theta\mathrm{d}\phi$ in polar coordinates.

Topic 49 Pulse techniques in NMR

Discussion questions

49.1 Discuss in detail the effects of a 90° pulse and of a 180° pulse on a system of spin-$\frac{1}{2}$ nuclei in a static magnetic field.

49.2 Suggest a reason why the relaxation times of ^{13}C nuclei are typically much longer than those of ^{1}H nuclei.

49.3 Suggest a reason why the spin–lattice relaxation time of a small molecule (like benzene) in a mobile, deuterated hydrocarbon solvent increases, whereas that of a large molecule (like a polymer) decreases.

49.4 Discuss the origin of the nuclear Overhauser effect and how it can be used to measure distances between protons in a biopolymer.

49.5 Discuss the origins of diagonal and cross-peaks in the COSY spectrum of an AX system.

Exercises

49.1(a) The duration of a 90° or 180° pulse depends on the strength of the $\mathcal{B}_1$ field. If a 180° pulse requires 12.5 μs, what is the strength of the $\mathcal{B}_1$ field? How long would the corresponding 90° pulse require?
49.1(b) The duration of a 90° or 180° pulse depends on the strength of the $\mathcal{B}_1$ field. If a 90° pulse requires 5 μs, what is the strength of the $\mathcal{B}_1$ field? How long would the corresponding 180° pulse require?

49.2(a) Figure F10.1 shows the proton COSY spectrum of 1-nitropropane. Account for the appearance of off-diagonal peaks in the spectrum.
49.2(b) Account for the observation that the COSY spectrum of alanine has only two off-diagonal peaks between $\Delta = 1.00$ and 8.50.

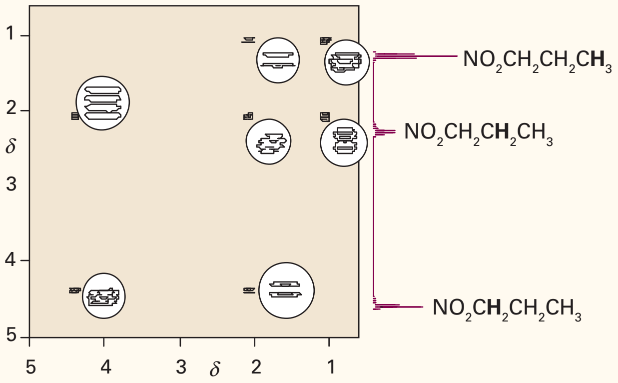


Figure F10.1 The COSY spectrum of 1-nitropropane (NO$_2$CH$_2$CH$_2$CH$_3$). The circles show enhanced views of the spectral features. (Spectrum provided by Prof. G. Morris.)

Problems

49.1‡ Suppose that the FID in Fig. 49.5 was recorded in a 400 MHz spectrometer, and that the interval between maxima in the oscillations in the FID is 0.12 s. What is the Larmor frequency of the nuclei and the spin–spin relaxation time?

49.2 To gain some appreciation for the numerical work done by computers interfaced to NMR spectrometers, perform the following calculations.

(a) The total FID $F(t)$ of a signal containing many frequencies, each corresponding to a different nucleus, is given by

$$F(t) = \sum_j S_{0j}\cos(2\pi\nu_{\mathrm{L}j}t)\mathrm{e}^{-t/T_{2j}}$$

where, for each nucleus j, S_{0j} is the maximum intensity of the signal, $\nu_{\mathrm{L}j}$ is the Larmor frequency, and T_{2j} is the spin–spin relaxation time. Plot the FID for the case

$$S_{01} = 1.0 \qquad \nu_{\mathrm{L}1} = 50\,\mathrm{MHz} \qquad T_{21} = 0.50\,\mu\mathrm{s}$$
$$S_{02} = 3.0 \qquad \nu_{\mathrm{L}2} = 10\,\mathrm{MHz} \qquad T_{22} = 1.0\,\mu\mathrm{s}$$

(b) Explore how the shape of the FID curve changes with changes in the Larmor frequency and the spin–spin relaxation time. (c) Use mathematical software to calculate and plot the Fourier transforms of the FID curves you calculated in parts (a) and (b). How do spectral linewidths vary with the value of T_2? *Hint*: This operation can be performed with the 'fast Fourier transform' routine available in most mathematical software packages. Please consult the package's user manual for details.

49.3 (a) In many instances it is possible to approximate the NMR lineshape by using a *Lorentzian function* of the form

$$I_{\mathrm{Lorentzian}}(\omega) = \frac{S_0 T_2}{1 + T_2^2(\omega - \omega_0)^2}$$

where $I(\omega)$ is the intensity as a function of the angular frequency $\omega = 2\pi\nu$, ω_0 is the resonance frequency, S_0 is a constant, and T_2 is the spin–spin relaxation time. Confirm that for this lineshape the width at half-height is $1/\pi T_2$. (b) Under certain circumstances, NMR lines are Gaussian functions of the frequency, given by

$$I_{\mathrm{Gaussian}}(\omega) = S_0 T_2 \mathrm{e}^{-T_2^2(\omega-\omega_0)^2}$$

Confirm that for the Gaussian lineshape the width at half-height is equal to $2(\ln 2)^{1/2}/T_2$. (c) Compare and contrast the shapes of Lorentzian and Gaussian lines by plotting two lines with the same values of S_0, T_2, and ω_0.

49.4 The shape of a spectral line, $I(\omega)$, is related to the free-induction decay signal $G(t)$ by

$$I(\omega)=a\,\mathrm{Re}\int_0^\infty G(t)\mathrm{e}^{\mathrm{i}\omega t}\,\mathrm{d}t$$

where a is a constant and 'Re' means take the real part of what follows. Calculate the lineshape corresponding to an oscillating, decaying function $G(t)=\cos\omega t\,\mathrm{e}^{-t/\tau}$.

49.5 In the language of Problem 49.4, show that, if $G(t)=(a\cos\omega t+b\cos\omega t)\mathrm{e}^{-t/\tau}$, then the spectrum consists of two lines with intensities proportional to a and b and located at $\omega=\omega_1$ and ω_2, respectively.

49.6 The z-component of the magnetic field at a distance R from a magnetic moment parallel to the z-axis is given by eqn 49.10. In a solid, a proton at a distance R from another can experience such a field and the measurement of the splitting it causes in the spectrum can be used to calculate R. In gypsum, for instance, the splitting in the H_2O resonance can be interpreted in terms of a magnetic field of 0.715 mT generated by one proton and experienced by the other. What is the separation of the protons in the H_2O molecule?

49.7 In a liquid crystal a molecule might not rotate freely in all directions and the dipolar interaction might not average to zero. Suppose a molecule is trapped so that, although the vector separating two protons may rotate freely around the z-axis, the colatitude may vary only between 0 and θ'. Use mathematical software to average the dipolar field over this restricted range of orientation and confirm that the average vanishes when θ' is equal to π (corresponding to free rotation over a sphere). What is the average value of the local dipolar field for the H_2O molecule in Problem 49.6 if it is dissolved in a liquid crystal that enables it to rotate up to $\theta'=30°$?

Topic 50 Electron paramagnetic resonance

Discussion questions

50.1 Discuss how the Fermi contact interaction and the polarization mechanism contribute to hyperfine interactions in EPR.

50.2 Explain how the EPR spectrum of an organic radical can be used to identify and map the molecular orbital occupied by the unpaired electron.

Exercises

50.1(a) The centre of the EPR spectrum of atomic hydrogen lies at 329.12 mT in a spectrometer operating at 9.2231 GHz. What is the g-value of the electron in the atom?
50.1(b) The centre of the EPR spectrum of atomic deuterium lies at 330.02 mT in a spectrometer operating at 9.2482 GHz. What is the g-value of the electron in the atom?

50.2(a) A radical containing two equivalent protons shows a three-line spectrum with an intensity distribution 1:2:1. The lines occur at 330.2 mT, 332.5 mT, and 334.8 mT. What is the hyperfine coupling constant for each proton? What is the g-value of the radical given that the spectrometer is operating at 9.319 GHz?
50.2(b) A radical containing three equivalent protons shows a four-line spectrum with an intensity distribution 1:3:3:1. The lines occur at 331.4 mT, 333.6 mT, 335.8 mT, and 338.0 mT. What is the hyperfine coupling constant for each proton? What is the g-value of the radical given that the spectrometer is operating at 9.332 GHz?

50.3(a) A radical containing two inequivalent protons with hyperfine constants 2.0 mT and 2.6 mT gives a spectrum centred on 332.5 mT. At what fields do the hyperfine lines occur and what are their relative intensities?
50.3(b) A radical containing three inequivalent protons with hyperfine constants 2.11 mT, 2.87 mT, and 2.89 mT gives a spectrum centred on 332.8 mT. At what fields do the hyperfine lines occur and what are their relative intensities?

50.4(a) Predict the intensity distribution in the hyperfine lines of the EPR spectra of (a) $\cdot CH_3$, (b) $\cdot CD_3$.
50.4(b) Predict the intensity distribution in the hyperfine lines of the EPR spectra of (a) $\cdot CH_2CH_3$, (b) $\cdot CD_2CD_3$.

50.5(a) The benzene radical anion has $g=2.0025$. At what field should you search for resonance in a spectrometer operating at (a) 9.313 GHz, (b) 33.80 GHz?
50.5(b) The naphthalene radical anion has $g=2.0024$. At what field should you search for resonance in a spectrometer operating at (a) 9.501 GHz, (b) 34.77 GHz?

50.6(a) The EPR spectrum of a radical with a single magnetic nucleus is split into four lines of equal intensity. What is the nuclear spin of the nucleus?
50.6(b) The EPR spectrum of a radical with two equivalent nuclei of a particular kind is split into five lines of intensity ratio 1:2:3:2:1. What is the spin of the nuclei?

50.7(a) Sketch the form of the hyperfine structures of radicals XH_2 and XD_2, where the nucleus X has $I=\frac{5}{2}$.
50.7(b) Sketch the form of the hyperfine structures of radicals XH_3 and XD_3, where the nucleus X has $I=\frac{3}{2}$.

Problems

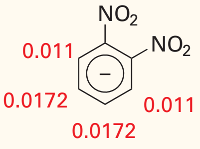
50.1 It is possible to produce very high magnetic fields over small volumes by special techniques. What would be the resonance frequency of an electron spin in an organic radical in a field of 1.0 kT? How does this frequency compare to typical molecular rotational, vibrational, and electronic energy level separations?

50.2 The angular NO_2 molecule has a single unpaired electron and can be trapped in a solid matrix or prepared inside a nitrite crystal by radiation damage of NO_2^- ions. When the applied field is parallel to the OO direction the centre of the spectrum lies at 333.64 mT in a spectrometer operating at 9.302 GHz. When the field lies along the bisector of the ONO angle, the resonance lies at 331.94 mT. What are the g-values in the two orientations?

50.3 The hyperfine coupling constant in $\cdot CH_3$ is 2.3 mT. Use the information in Table 50.1 to predict the splitting between the hyperfine lines of the spectrum of $\cdot CD_3$. What are the overall widths of the hyperfine spectra in each case?

50.4 The *p*-dinitrobenzene radical anion can be prepared by reduction of *p*-dinitrobenzene. The radical anion has two equivalent N nuclei ($I = 1$) and four equivalent protons. Predict the form of the EPR spectrum using $a(N) = 0.148$ mT and $a(H) = 0.112$ mT.

50.5 The hyperfine coupling constants observed in the radical anions **1**, **2**, and **3** are shown (in millitesla, mT). Use the value for the benzene radical anion to map the probability of finding the unpaired electron in the π orbital on each C atom.



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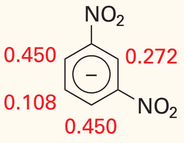

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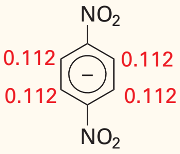
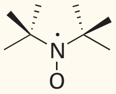


3

50.6 When an electron occupies a 2s orbital on an N atom it has a hyperfine interaction of 55.2 mT with the nucleus. The spectrum of NO_2 shows an isotropic hyperfine interaction of 5.7 mT. For what proportion of its time is the unpaired electron of NO_2 occupying a 2s orbital? The hyperfine coupling constant for an electron in a 2p orbital of an N atom is 3.4 mT. In NO_2 the anisotropic part of the hyperfine coupling is 1.3 mT. What proportion of its time does the unpaired electron spend in the 2p orbital of the N atom in NO_2? What is the total probability that the electron will be found on (a) the N atom, (b) the O atoms? What is the hybridization ratio of the N atom? Does the hybridization support the view that NO_2 is angular?

50.7 Sketch the EPR spectra of the di-*tert*-butyl nitroxide radical (**4**) at 292 K in the limits of very low concentration (at which electron exchange is negligible), moderate concentration (at which electron exchange effects begin to be observed), and high concentration (at which electron exchange effects predominate).



4 di-*tert*-Butyl nitroxide

Integrated activities

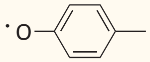
F10.1 In Problem F6.15 you are asked to use molecular electronic structure methods to investigate the hypothesis that the magnitude of the ^{13}C chemical shift correlates with the net charge on a ^{13}C atom by calculating the net charge at the C atom *para* to the substituents in the following series of molecules: methylbenzene, benzene, trifluoromethylbenzene, benzonitrile, nitrobenzene. The ^{13}C chemical shifts of the *para* C atoms in each of the molecules that you examined are given below:

Substituent	CH_3	H	CF_3	CN	NO_2
δ	128.4	128.5	128.9	129.1	129.4

(a) Is there a linear correlation between net charge and ^{13}C chemical shift of the *para* C atom in this series of molecules?
(b) If you did find a correlation in part (a), use the concepts developed in Topic 48 to explain the physical origins of the correlation.

F10.2 EPR spectra are commonly discussed in terms of the parameters that occur in the *spin-hamiltonian*, a hamiltonian operator that incorporates various effects involving spatial operators (like the orbital angular momentum) into operators that depend on the spin alone. Show that if you use $\hat{H} = -g_e\gamma_e\mathcal{B}_0\hat{s}_z - \gamma_e\mathcal{B}_0\hat{l}_z$ as the true hamiltonian, then from second-order perturbation theory, the eigenvalues of the spin are the same as those of the spin-hamiltonian $\hat{H} = -g\gamma_e\mathcal{B}_0\hat{s}_z$ (note the g in place of g_e) and find an expression for g.

F10.3 The computational techniques described in Topics 28–30 have shown that the amino acid tyrosine participates in a number of biological electron transfer reactions, including the processes of water oxidation to O_2 in plant photosystem II and of O_2 reduction to water in cytochrome *c* oxidase. During the course of these electron transfer reactions, a tyrosine radical forms, with spin density delocalized over the side chain of the amino acid. (a) The phenoxy radical shown in **5** is a suitable model of the tyrosine radical. Using molecular modelling software and the computational method of your choice (semi-empirical or *ab initio* method), calculate the spin densities at the O atom and at all of the C atoms in **5**. (b) Predict the form of the EPR spectrum of **5**.



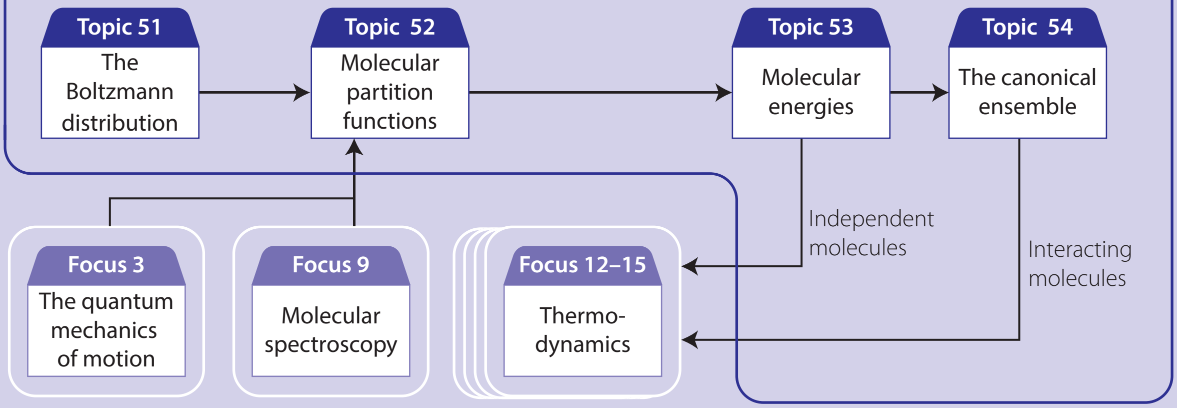
5 Phenoxy radical

F10.4 NMR spectroscopy may be used to determine the equilibrium constant for dissociation of a complex between a small molecule, such as an enzyme inhibitor I, and a protein, such as an enzyme E:

$$\mathrm{EI} \rightleftharpoons \mathrm{E} + \mathrm{I} \quad K_I = [\mathrm{E}][\mathrm{I}]/[\mathrm{EI}]$$

In the limit of slow chemical exchange, the NMR spectrum of a proton in I would consist of two resonances: one at ν_I for free I and another at ν_{EI} for bound I. When chemical exchange is fast, the NMR spectrum of the same proton in I consists of a single peak with a resonance frequency ν given by $\nu = f_I\nu_I + f_{EI}\nu_{EI}$, where $f_I = [\mathrm{I}]/([\mathrm{I}] + [\mathrm{EI}])$ and $f_{EI} = [\mathrm{EI}]/([\mathrm{I}] + [\mathrm{EI}])$ are, respectively, the fractions of free I and bound I. For the purposes of analysing the data, it is also useful to define the frequency differences $\delta\nu = \nu - \nu_I$ and $\Delta\nu = \nu_{EI} - \nu_I$. Show that when the initial concentration of I, $[\mathrm{I}]_0$, is much greater than the initial concentration of E, $[\mathrm{E}]_0$, a plot of $[\mathrm{I}]_0$ against $\delta\nu^{-1}$ is a straight line with slope $[\mathrm{E}]_0\Delta\nu$ and y-intercept $-K_I$.

FOCUS 11 ON Statistical thermodynamics



One of the most important equations linking the properties of molecules to the properties of the bulk matter to which the molecules contribute is the 'Boltzmann distribution', which is established and developed in this group of Topics. The derivation of the distribution (**Topic 51**) is based on the supposition that molecules are distributed over the available energy levels in the most probable way subject to the total energy and the total number of particles of the system having particular values. It can then be used to predict the population of each level for a system at a given temperature. Indeed, the Boltzmann distribution provides insight into the nature of temperature as the single parameter that determines the population of levels of a collection of molecules. As is demonstrated in other Topics, the Boltzmann distribution lies at the heart of molecular interpretations of thermodynamics.

The Boltzmann distribution introduces the concept of 'partition function' (**Topic 52**), which is a kind of 'thermodynamic wavefunction' of the system in the sense that it can be used to calculate all its thermodynamic properties, as explained in the groups of Topics on *The First Law of thermodynamics*, *The Second and Third Laws of thermodynamics*, *Physical equilibria*, and *Chemical equilibria*. A 'molecular partition function', which is appropriate when molecules can be treated as not interacting with one another, can be calculated from molecular properties, such as the mass (for the translational contribution), the moment of inertia (for the rotational contribution), and from the force constant (for the vibrational contribution). Because parameters such as these can be determined from *Molecular spectroscopy*, the partition function provides a very important link between spectroscopy and thermodynamics. When molecular interactions cannot be ignored, it is necessary to make use of the concept and techniques related to a 'canonical ensemble' and the 'canonical partition function', as explained in **Topic 54**.

The most straightforward application of the molecular partition function is to the calculation of the contribution of the various modes of motion (translation, rotation, and vibration as introduced in *The quantum mechanics of motion*) to the mean energy of a collection of independent molecules (**Topic 53**). That is a basis for the calculation and interpretation of the internal energy of a system, as used in the *First Law of thermodynamics*.

TOPIC 51

The Boltzmann distribution

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➤ Why do you need to know this material?

The Boltzmann distribution is the key to understanding a great deal of chemistry. All thermodynamic properties can be interpreted in its terms, as can the temperature dependence of equilibrium constants and the rates of chemical reactions. It also illuminates the meaning of 'temperature'. There is, perhaps, no more important unifying concept in chemistry.

➤ What is the key idea?

The most probable distribution of molecules over the available energy levels subject to certain constraints depends on a single parameter, the temperature.

➤ What do you need to know already?

You need to be aware that molecules can exist only in certain discrete energy levels (Topics 9–14) and that in some cases more than one state has the same energy.

The crucial step in going from the quantum mechanical properties of individual molecules to the properties of bulk samples, the province of **statistical thermodynamics**, is to recognize that the latter deals with the *average* behaviour of large numbers of molecules. For example, the pressure of a gas depends on the average force exerted by its molecules and there is no need to specify which molecules happen to be striking the wall at any instant. Nor is it necessary to consider the fluctuations in the pressure as different numbers of molecules collide with the wall at different moments. The fluctuations in pressure are very small compared with the steady pressure: it is highly improbable that there will be a sudden lull in the number of collisions, or a sudden surge. Fluctuations in other bulk properties also occur, but for large numbers of particles they are very much smaller than the mean values.

We consider a system composed of N molecules, with N a large number (of the order of 10^{23} for systems typical of chemistry). Although the total energy is constant at E, it is not possible to be definite about how that energy is shared between the molecules. Collisions result in the ceaseless redistribution of energy not only between the molecules but also between the quantum states that each molecule occupies. The closest we can come to a description of the distribution of energy is to report the **population** of a state, the average number of molecules that occupy it, and to say that on average there are N_i molecules in a state of energy ε_i. The populations of the states remain almost constant, but the precise identities of the molecules in each state may change at every collision.

The problem we address in this Topic is the calculation of the populations of states for any type of molecule in any mode of motion at any temperature. The only restriction is that the molecules should be independent, in the sense that the total energy of the system is a sum of their individual energies. We are discounting (at this stage) the possibility that in a real system a contribution to the total energy may arise from interactions between molecules. We also adopt the **principle of equal *a priori* probabilities**, the assumption that all possibilities for the distribution of energy are equally probable. '*A priori*' in this context loosely means 'as far as one knows'. We have no reason to presume otherwise than that for a collection of molecules at thermal equilibrium, a vibrational state of a certain energy, for instance, is as likely to be populated as a rotational state of the same energy.

One very important conclusion that will emerge from the following analysis is that the overwhelmingly most probable populations of the available states depend on a single parameter, the 'temperature'. That is, the work we do here provides a molecular justification for the concept of temperature and some insight into this crucially important quantity.

51.1 Configurations and weights

Any individual molecule may exist in states with energies ε_0, ε_1, …. For reasons that will become clear, we shall always take the lowest available state as the zero of energy (that is, we set $\varepsilon_0=0$), and measure all other energies relative to that state. To obtain the actual energy of the system we may have to add a constant to the energy calculated on this basis. For example, if we are considering the vibrational contribution to the energy, then we must add the total zero-point energy of any oscillators in the system.

(a) Instantaneous configurations

At any instant there will be N_0 molecules in the state 0 with energy ε_0, N_1 in the state 1 with ε_1, and so on, with $N_0+N_1+\ldots=N$, the total number of molecules in the system. Initially we shall suppose that all the states have exactly the same energy. The specification of the set of populations N_0, N_1, … in the form $\{N_0,N_1,\ldots\}$ is a statement of the instantaneous **configuration** of the system. The instantaneous configuration fluctuates with time because the populations change, perhaps as a result of collisions. At this stage the energies of all the configurations are identical so there is no restriction on how many of the N molecules are in each state.

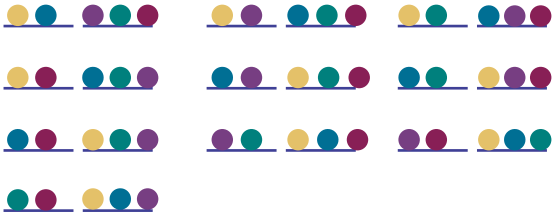

Figure 51.1 Whereas a configuration {5,0,0,…} can be achieved in only one way, a configuration {3,2,0,…} can be achieved in the ten different ways shown here, where the tinted circles represent different molecules.

We can picture a large number of different instantaneous configurations. One, for example, might be $\{N,0,0,\ldots\}$, corresponding to every molecule being in state 0. Another might be $\{N-2,2,0,0,\ldots\}$, in which two molecules are in state 1. The latter configuration is intrinsically more likely to be found than the former because it can be achieved in more ways: $\{N,0,0,\ldots\}$ can be achieved in only one way, but $\{N-2,2,0,\ldots\}$ can be achieved in $\frac{1}{2}N(N-1)$ different ways (Fig. 51.1; see the following *Justification*). If, as a result of collisions, the system were to fluctuate between the configurations $\{N,0,0,\ldots\}$ and $\{N-2,2,0,\ldots\}$, it would almost always be found in the second, more likely configuration (especially if N were large). In other words, a system free to switch between the two configurations would show properties characteristic almost exclusively of the second configuration. A general configuration $\{N_0,N_1,\ldots\}$ can be achieved in W different ways, where W is called the **weight** of the configuration. The weight of the configuration $\{N_0,N_1,\ldots\}$ is given by the expression

$$W=\frac{N!}{N_0!N_1!N_2!\cdots} \qquad (51.1)$$

Weight of a configuration

with $x!=x(x-1)\ldots1$ and by definition $0!=1$. Equation 51.1 is a generalization of the formula $W=\frac{1}{2}N(N-1)$, and reduces to it for the configuration $\{N-2,2,0,\ldots\}$.

Brief illustration 51.1 The weight of a configuration

To calculate the number of ways of distributing 20 identical objects with the arrangement 1, 0, 3, 5, 10, 1, we note that the configuration is {1,0,3,5,10,1} with $N=20$; therefore the weight is

$$W=\frac{20!}{1!0!3!5!10!1!}=9.31\times10^{8}$$

Self-test 51.1 Calculate the weight of the configuration in which 20 objects are distributed in the arrangement 0, 1, 5, 0, 8, 0, 3, 2, 0, 1.

Answer: 4.19×10^{10}

Justification 51.1 The weight of a configuration

First, consider the weight of the configuration $\{N-2,2,0,0,\ldots\}$, which is prepared from the configuration $\{N,0,0,0,\ldots\}$ by the migration of two molecules from state 0 into state 2. One candidate for migration to state 1 can be selected in N ways. There are $N-1$ candidates for the second choice, so the total number of choices is $N(N-1)$. However, we should not distinguish the choice (Jack, Jill) from the choice (Jill, Jack) because they lead to the same configurations. Therefore, only half the choices lead to distinguishable configurations, and the total number of distinguishable choices is $\frac{1}{2}N(N-1)$.

Now we generalize this remark. Consider the number of ways of distributing N balls into bins. The first ball can be selected in N different ways, the next ball in $N-1$ different ways for the balls remaining, and so on. Therefore, there are $N(N-1)\ldots 1 = N!$ ways of selecting the balls for distribution over the bins. However, if there are N_0 balls in the bin labelled 0, there would be $N_0!$ different ways in which the same balls could have been chosen (Fig. 51.2). Similarly, there are $N_1!$ ways in which the N_1 balls in the bin labelled 1 can be chosen, and so on. Therefore, the total number of distinguishable ways of distributing the balls so that there are N_0 in bin 0, N_1 in bin 1, etc. regardless of the order in which the balls were chosen is $N!/N_0!N_1!\ldots$, which is the content of eqn 51.1.

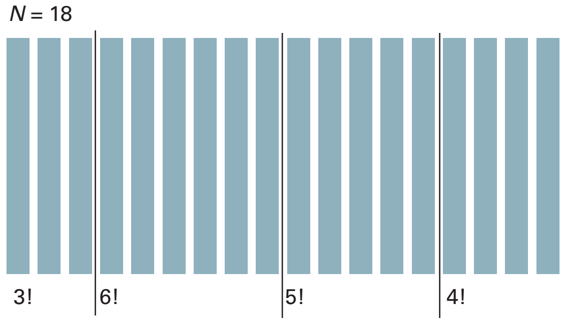

Figure 51.2 The 18 molecules shown here can be distributed into four receptacles (distinguished by the three vertical lines) in 18! different ways. However, 3! of the selections that put three molecules in the first receptacle are equivalent, 6! that put six molecules into the second receptacle are equivalent, and so on. Hence the number of distinguishable arrangements is 18!/3!6!5!4!.

It will turn out to be more convenient to deal with the natural logarithm of the weight, ln $\mathcal{W}$, rather than with the weight itself. We shall therefore need the expression

$$\begin{aligned}\ln \mathcal{W} &= \ln \frac{N!}{N_0!N_1!N_2!\cdots} = \ln N! - \ln N_0!N_1!N_2!\cdots \\ &= \ln N! - \ln N_0! - \ln N_1! - \ln N_2! - \cdots \\ &= \ln N! - \sum_i \ln N_i!\end{aligned}$$

where in the first line we have used $\ln(x/y) = \ln x - \ln y$ and in the second $\ln xy = \ln x + \ln y$. One reason for introducing ln $\mathcal{W}$ is that it is easier to make approximations. In particular, we can simplify the factorials by using *Stirling's approximation*

$$\ln x! \approx \left(x+\tfrac{1}{2}\right)\ln x - x + \tfrac{1}{2}\ln 2\pi \quad x \gg 1 \qquad (51.2a)$$

Stirling's approximation

This approximation is in error by less than 1 per cent when x is greater than about 10. We deal with far larger values of x, and the simplified version

$$\ln x! \approx x \ln x - x \quad x \gg 1 \qquad (51.2b)$$

Stirling's approximation (for large *x*)

is adequate. Then the approximate expression for the weight is

$$\begin{aligned}\ln \mathcal{W} &= \{N\ln N - N\} - \sum_i \{N_i \ln N_i - N_i\} \\ &= N\ln N - N - \sum_i N_i \ln N_i + N \quad \left[\text{because} \sum_i N_i = N\right] \\ &= N\ln N - \sum_i N_i \ln N_i \end{aligned} \qquad (51.3)$$

(b) The most probable distribution

We have seen that the configuration $\{N-2,2,0,\ldots\}$ dominates $\{N,0,0,\ldots\}$, and it should be easy to believe that there may be other configurations that have a much greater weight than both. We shall see, in fact, that there is a configuration with so great a weight that it overwhelms all the rest in importance to such an extent that the system will almost always be found in it. The properties of the system will therefore be characteristic of that particular dominating configuration. This dominating configuration can be found by looking for the values of N_i that lead to a maximum value of $\mathcal{W}$. Because $\mathcal{W}$ is a function of all the N_i, we can do this search by varying the N_i and looking for the values that correspond to $\mathrm{d}\mathcal{W} = 0$ (just as in the search for the maximum of any function), or equivalently a maximum value of ln $\mathcal{W}$. However, there are two difficulties with this procedure.

At this point we allow the states to have different energies. The first difficulty that results from this change is the need to take into account the fact that the only permitted configurations are those corresponding to the specified, constant, total energy of the system. This requirement rules out many configurations; $\{N,0,0,\ldots\}$ and $\{N-2,2,0,\ldots\}$, for instance, have different energies (unless the states 0 and 1 happen to be degenerate), so both cannot occur in the same isolated system. It follows that in looking for the configuration with the greatest weight, we must ensure that the configuration also satisfies the condition

$$\sum_i N_i \varepsilon_i = E \qquad (51.4)$$

Energy constraint Constant total energy

where E is the total energy of the system.

The second constraint is that, because the total number of molecules present is also fixed (at N), we cannot arbitrarily vary all the populations simultaneously. Thus, increasing the population of one state by 1 demands that the population of another state must be reduced by 1. Therefore, the search for the maximum value of $\mathcal{W}$ is also subject to the condition

$$\sum_i N_i = N \qquad (51.5)$$

Constant total number of molecules Number constraint

We show in the next section that the populations in the configuration of greatest weight, subject to the two constraints in eqns 51.4 and 51.5, depend on the energy of the state according to the **Boltzmann distribution**:

$$\frac{N_i}{N}=\frac{\mathrm{e}^{-\beta\varepsilon_i}}{\sum_i \mathrm{e}^{-\beta\varepsilon_i}} \qquad \text{Boltzmann distribution} \qquad (51.6a)$$

The denominator in eqn 51.6a is denoted q and called the **partition function**:

$$q=\sum_i \mathrm{e}^{-\beta\varepsilon_i} \qquad \textit{Definition} \qquad \text{Partition function} \qquad (51.6b)$$

In this Topic, the partition function is no more than a convenient abbreviation for the sum; but in Topic 52 we see that it is central to the statistical interpretation of thermodynamic properties.

Equation 51.6a is the justification of the remark that a single parameter, here denoted β, determines the most probable populations of the states of the system. We shall confirm in Topic 54 and anticipate throughout this Topic that

$$\beta=\frac{1}{kT} \qquad (51.7)$$

where T is the thermodynamic temperature and k is Boltzmann's constant. In other words:

> The temperature is the unique parameter that governs the most probable populations of states of a system at thermal equilibrium.

Brief illustration 51.2 The Boltzmann distribution

Suppose that two conformations of an organic molecule differ in energy by 5.0 kJ mol^{-1} (corresponding to 8.3×10^{-21} J for a single molecule), so conformation A lies at energy 0 and conformation B lies at $\varepsilon=8.3\times10^{-21}$ J. At 20 °C (293 K) the denominator in eqn 51.6a is

$$\sum_i \mathrm{e}^{-\beta\varepsilon_i}=1+\mathrm{e}^{-\varepsilon/kT}=1+\mathrm{e}^{-(8.3\times10^{-21}\,\mathrm{J})/(1.381\times10^{-23}\,\mathrm{J})\times(293\,\mathrm{K})}=1.13$$

The proportion of molecules in conformation B at this temperature is therefore

$$\frac{N_\mathrm{B}}{N}=\frac{\mathrm{e}^{-(8.3\times10^{-21}\,\mathrm{J})/(1.381\times10^{-23}\,\mathrm{J})\times(293\,\mathrm{K})}}{1.13}=0.11$$

or 11 per cent of the molecules. The remaining 89 per cent of the molecules are in conformation A.

Self-Test 51.2 Suppose that there is a third conformation a further 0.50 kJ mol^{-1} above B. What proportion of molecules will now be in conformation B?

Answer: 0.10, 10 per cent

(c) The relative population of states

If we are interested only in the relative populations of states, the sum in the denominator of the Boltzmann distribution need not be evaluated, because it cancels when the ratio is taken:

$$\frac{N_i}{N_j}=\frac{\mathrm{e}^{-\beta\varepsilon_i}}{\mathrm{e}^{-\beta\varepsilon_j}}=\mathrm{e}^{-\beta(\varepsilon_i-\varepsilon_j)} \qquad \textit{Thermal equilibrium} \qquad \text{Boltzmann population ratio} \qquad (51.8a)$$

That $\beta\propto 1/T$ is plausible is demonstrated by noting from eqn 51.8a that for a given energy separation the ratio of populations N_1/N_0 decreases as β increases, which is what is expected as the temperature decreases. At $T=0$ ($\beta=\infty$) all the population is in the ground state and the ratio is zero. Equation 51.8a is enormously important for understanding a wide range of chemical phenomena and is the form in which the Boltzmann distribution is commonly employed (for instance, in the discussion of the intensities of spectral transitions, Topic 16). It tells us that the relative population of two states falls off exponentially with their difference in energy.

A very important point to note is that the Boltzmann distribution gives the relative populations of *states*, not energy *levels*. Several states might correspond to the same energy, and each state has a population given by eqn 51.6. If we want to consider the relative populations of energy levels rather than states, then we need to take into account this degeneracy. Thus, if the level of energy ε_i is g_i-fold degenerate (in the sense that there are g_i states with that energy), and the level of energy ε_j is g_j-fold degenerate, then the relative total populations of the levels are given by

$$\frac{N_i}{N_j}=\frac{g_i\mathrm{e}^{-\beta\varepsilon_i}}{g_j\mathrm{e}^{-\beta\varepsilon_j}}=\frac{g_i}{g_j}\mathrm{e}^{-\beta(\varepsilon_i-\varepsilon_j)} \qquad \textit{Thermal equilibrium, degeneracies} \qquad \text{Boltzmann population ratio} \qquad (51.8b)$$

Example 51.1 Calculating the relative populations of rotational states

Calculate the relative populations of the $J=1$ and $J=0$ rotational states of HCl at 25 °C.

Method Although the ground state is non-degenerate, the level with $J=1$ is triply degenerate ($M_J=0,\pm1$); see Topic 41. From that Topic, the energy of state with quantum number J is $\varepsilon_J=hc\tilde{B}J(J+1)$. Use $\tilde{B}=10.591\ \mathrm{cm}^{-1}$. A useful relation is $kT/hc=207.22\ \mathrm{cm}^{-1}$ at 298.15 K.

Answer The energy separation of states with $J=1$ and $J=0$ is

$$\varepsilon_1-\varepsilon_0=2hc\tilde{B}$$

The ratio of the population of a state with $J=1$ and any *one* of its three states M_J to the population of the single state with $J=0$ is therefore

$$\frac{N_{J,M_J}}{N_0}=\mathrm{e}^{-2hc\tilde{B}\beta}$$

The relative populations of the *levels*, taking into account the threefold degeneracy of the upper state, is

$$\frac{N_J}{N_0}=3\mathrm{e}^{-2hc\tilde{B}\beta}$$

Insertion of $hc\tilde{B}\beta=hc\tilde{B}/kT=(10.591\,\mathrm{cm}^{-1})/(207.22\,\mathrm{cm}^{-1})=0.05111$ then gives

$$\frac{N_J}{N_0}=3\mathrm{e}^{-2\times0.05111}=2.708$$

We see that because the $J=1$ level is triply degenerate, it has a higher population than the level with $J=0$, despite being of higher energy. As the example illustrates, it is very important to take note of whether you are asked for the relative populations of individual states or of a (possibly degenerate) energy level.

Self-test 51.3 What is the ratio of the populations of the levels with $J=2$ and $J=1$ at the same temperature?

Answer: 1.359

51.2 The derivation of the Boltzmann distribution

We remarked earlier that ln $\mathcal{W}$ is easier to handle than $\mathcal{W}$. Therefore, to find the form of the Boltzmann distribution, we look for the condition for ln $\mathcal{W}$ being a maximum rather than dealing directly with $\mathcal{W}$. Because ln $\mathcal{W}$ depends on all the N_i, when a configuration changes and the N_i change to $N_i+\mathrm{d}N_i$, the function ln $\mathcal{W}$ changes to ln $\mathcal{W}$+d ln $\mathcal{W}$, where

$$\mathrm{d}\ln\mathcal{W}=\sum_i\left(\frac{\partial\ln\mathcal{W}}{\partial N_i}\right)\mathrm{d}N_i$$

(a) The role of constraints

All the last expression states is that a change in ln $\mathcal{W}$ is the sum of contributions arising from changes in each value of N_i. At a maximum, d ln $\mathcal{W}=0$. However, when the N_i change, they do so subject to the two constraints

$$\sum_i\varepsilon_i\mathrm{d}N_i=0 \qquad \sum_i\mathrm{d}N_i=0 \qquad \text{Constraints} \qquad (51.9)$$

The first constraint recognizes that the total energy must not change, and the second recognizes that the total number of molecules must not change. These two constraints prevent us from solving d ln $\mathcal{W}=0$ simply by setting all $(\partial\ln\mathcal{W}/\partial N_i)=0$ because the $\mathrm{d}N_i$ are not all independent.

The way to take constraints into account was devised by the French mathematician Lagrange, and is called the **method of undetermined multipliers** (*The chemist's toolkit* 51.1). All we need here is the rule that:

- a constraint should be multiplied by a constant and then added to the main variation equation.

The variables are then treated as though they were all independent, and the constants are evaluated at the end of the calculation.

The chemist's toolkit 51.1 The method of undetermined multipliers

Suppose we need to find the maximum (or minimum) value of some function f that depends on several variables $x_1, x_2, \ldots, x_n$. When the variables undergo a small change from x_i to $x_i+\delta x_i$ the function changes from f to $f+\delta f$, where

$$\delta f=\sum_{i=1}^{n}\left(\frac{\partial f}{\partial x_i}\right)\delta x_i$$

At a minimum or maximum, $\delta f=0$, so then

$$\sum_{i=1}^{n}\left(\frac{\partial f}{\partial x_i}\right)\delta x_i=0$$

If the x_i were all independent, all the δx_i would be arbitrary, and this equation could be solved by setting each $(\partial f/\partial x_i)=0$ individually. When the x_i are not all independent, the δx_i are not all independent, and the simple solution is no longer valid. We proceed as follows.

Let the constraint connecting the variables be an equation of the form $g=0$. The constraint $g=0$ is always valid, so g remains unchanged when the x_i are varied:

$$\delta g=\sum_{i=1}^{n}\left(\frac{\partial g}{\partial x_i}\right)\delta x_i=0$$

Because δg is zero, we can multiply it by a parameter, λ, and add it to the preceding equation:

$$\sum_{i=1}^{n}\left\{\left(\frac{\partial f}{\partial x_i}\right)+\lambda\left(\frac{\partial g}{\partial x_i}\right)\right\}\delta x_i=0$$

This equation can be solved for one of the δx, δx_n for instance, in terms of all the other δx_i. All those other δx_i ($i=1, 2, \ldots,$

$n-1$) are independent, because there is only one constraint on the system. But λ is arbitrary; therefore we can choose it so that

$$\left(\frac{\partial f}{\partial x_n}\right)+\lambda\left(\frac{\partial g}{\partial x_n}\right)=0 \qquad \text{(A)}$$

Then

$$\sum_{i=1}^{n-1}\left\{\left(\frac{\partial f}{\partial x_i}\right)+\lambda\left(\frac{\partial g}{\partial x_i}\right)\right\}\delta x_i=0$$

Now the $n-1$ variations δx_i *are* independent, so the solution of this equation is

$$\left(\frac{\partial f}{\partial x_i}\right)+\lambda\left(\frac{\partial g}{\partial x_i}\right)=0 \quad i=1,2,\ldots,n-1$$

However, eqn A has exactly the same form as this equation, so the maximum or minimum of f can be found by solving

$$\left(\frac{\partial f}{\partial x_i}\right)+\lambda\left(\frac{\partial g}{\partial x_i}\right)=0 \quad i=1,2,\ldots,n$$

If there is more than one constraint, $g_1=0$, $g_2=0$, …, and this final result generalizes to

$$\left(\frac{\partial f}{\partial x_i}\right)+\lambda_1\left(\frac{\partial g_1}{\partial x_i}\right)+\lambda_2\left(\frac{\partial g_2}{\partial x_i}\right)+\cdots=0, \quad i=1,2,\ldots,n$$

with a corresponding multiplier, λ_1, λ_2, … for each constraint.

We employ the technique as follows. The two constraints in eqn 51.9 are multiplied by the constants $-\beta$ and α, respectively (the minus sign in $-\beta$ has been included for future convenience), and then added to the expression for $\mathrm{d}\ln\mathcal{W}$:

$$\begin{aligned}\mathrm{d}\ln\mathcal{W}&=\sum_i\left(\frac{\partial\ln\mathcal{W}}{\partial N_i}\right)\mathrm{d}N_i+\alpha\sum_i\mathrm{d}N_i-\beta\sum_i\varepsilon_i\mathrm{d}N_i\\&=\sum_i\left\{\left(\frac{\partial\ln\mathcal{W}}{\partial N_i}\right)+\alpha-\beta\varepsilon_i\right\}\mathrm{d}N_i\end{aligned}$$

Example 51.2 Using the method of Lagrange multipliers

Suppose you have a sheet of metal of area A and want to build a box of the greatest volume possible from that sheet. What is the maximum volume when $A=1.0\,\mathrm{m}^2$?

Method Identify the volume in terms of the lengths of the sides (which are mutually perpendicular in a box) and identify the constraint in the form $g=0$. Introduce the Lagrange multiplier λ for this constraint and construct and solve the corresponding Lagrange variation equations.

Answer Let the sides of the box be a, b, and c; then its volume is $V=abc$. The total area of the surface of the box is $2(ab+bc+ca)$, so the constraint on the construction is $ab+bc+ca=A/2$. In the notation used in *The chemist's toolkit* 51.1, $g=ab+bc+ca-A/2=0$. On introducing the Lagrange multiplier as λ, the three equations we have to solve to find the maximum volume subject to the constraint are

$$\frac{\partial V}{\partial x}-\lambda\frac{\partial g}{\partial x}=0 \quad x=a,b,c$$

That is,

$$\begin{aligned}\frac{\partial V}{\partial a}-\lambda\frac{\partial g}{\partial a}&=bc-\lambda(b+c)=0\\\frac{\partial V}{\partial b}-\lambda\frac{\partial g}{\partial b}&=ac-\lambda(a+c)=0\\\frac{\partial V}{\partial c}-\lambda\frac{\partial g}{\partial c}&=ab-\lambda(a+b)=0\end{aligned}$$

Multiplication of the first by a and the second by b and then subtracting the second from the first gives

$$\lambda(ab+bc)-\lambda(ab+ac)=0, \quad \text{or} \quad bc-ac=0$$

or $a=b$. Likewise, the other solutions are $a=c$ and $b=c$. We conclude that the box of greatest volume is a cube with sides $a=b=c$ and volume $V=a^3$. From the constraint, $g=3a^2-A/2=0$, so $a=(A/6)^{1/2}$. In this instance, with $A=1.0\,\mathrm{m}^2$, $a=0.41\,\mathrm{m}$, so $V=0.069\,\mathrm{m}^3$.

Self-test 51.4 Suppose that you require the height of the box, a, to be fixed at the value $h=0.40\,\mathrm{m}$. What is the maximum volume of the box given the same sheet of metal?

Answer: $V=0.067\,\mathrm{m}^3$

(b) Solving for the most probable distribution

All the $\mathrm{d}N_i$ are now treated as independent. Hence the only way of satisfying $\mathrm{d}\ln\mathcal{W}=0$ is to require that, for each i,

$$\left(\frac{\partial\ln\mathcal{W}}{\partial N_i}\right)+\alpha-\beta\varepsilon_i=0 \qquad (51.10)$$

when the N_i have their most probable values.

Equation 51.3 for $\mathcal{W}$ is

$$\ln\mathcal{W}=N\ln N-\sum_i N_i\ln N_i$$

There is a small housekeeping step to take before differentiating ln $\mathcal{W}$ with respect to N_i: this equation is identical to

$$\ln \mathcal{W} = N\ln N - \sum_j N_j \ln N_j$$

because all we have done is to change the 'name' of the states from i to j. This step makes sure that we do not confuse the i in the differentiation variable (N_i) with the i in the summation. Now differentiation of this expression gives

$$\frac{\partial \ln \mathcal{W}}{\partial N_i} = \frac{\partial N\ln N}{\partial N_i} - \sum_j \frac{\partial N_j \ln N_j}{\partial N_i} \tag{51.11}$$

The derivative of the first term on the right is obtained as follows:

$$\begin{aligned}\frac{\partial N\ln N}{\partial N_i} &= \left(\frac{\partial N}{\partial N_i}\right)\ln N + N\left(\frac{\partial \ln N}{\partial N_i}\right)\\ &= \ln N + \frac{\partial N}{\partial N_i} = \ln N + 1\end{aligned} \tag{51.12}$$

The ln N in the first term on the right in the second line arises because $N = N_1 + N_2 + \ldots$ and so the derivative of N with respect to any of the N_i is 1: that is, $\partial N/\partial N_i = 1$. The second term on the right in the second line arises because $\partial(\ln N)/\partial N_i = (1/N)\partial N/\partial N_i$. The final 1 is then obtained in the same way as in the preceding remark, by using $\partial N/\partial N_i = 1$.

For the derivative of the second term we first note that

$$\frac{\partial \ln N_j}{\partial N_i} = \frac{1}{N_j}\left(\frac{\partial N_j}{\partial N_i}\right) \tag{51.13}$$

Moreover, if $i \neq j$, N_j is independent of N_i, so $\partial N_j/\partial N_i = 0$. However, if $i = j$,

$$\frac{\partial N_j}{\partial N_i} = \frac{\partial N_i}{\partial N_i} = 1 \tag{51.14}$$

Therefore,

$$\frac{\partial N_j}{\partial N_i} = \delta_{ij} \tag{51.15}$$

with δ_{ij} the Kronecker delta ($\delta_{ij} = 1$ if $i = j$, $\delta_{ij} = 0$ otherwise). Then

$$\begin{aligned}\sum_j \frac{\partial N_j \ln N_j}{\partial N_i} &= \sum_j \left\{\left(\frac{\partial N_j}{\partial N_i}\right)\ln N_j + N_j\left(\frac{\partial \ln N_j}{\partial N_i}\right)\right\}\\ &= \sum_j \left\{\left(\frac{\partial N_j}{\partial N_i}\right)\ln N_j + \left(\frac{\partial N_j}{\partial N_i}\right)\right\}\\ &= \sum_j \left(\frac{\partial N_j}{\partial N_i}\right)(\ln N_j + 1)\\ &= \sum_j \delta_{ij}(\ln N_j + 1) = \ln N_i + 1\end{aligned}$$

and therefore

$$\frac{\partial \ln \mathcal{W}}{\partial N_i} = \ln N + 1 - (\ln N_i + 1) = -\ln\frac{N_i}{N} \tag{51.16}$$

It follows from eqn 51.10 that

$$-\ln\frac{N_i}{N} + \alpha - \beta\varepsilon_i = 0$$

and therefore that

$$\frac{N_i}{N} = \mathrm{e}^{\alpha - \beta\varepsilon_i} \tag{51.17}$$

(c) The final step

At this stage we note that

$$N = \sum_i N_i = \sum_i N\mathrm{e}^{\alpha-\beta\varepsilon_i} = N\mathrm{e}^{\alpha}\sum_i \mathrm{e}^{-\beta\varepsilon_i}$$

Because the N cancels on each side of this equality, it follows that

$$\mathrm{e}^{\alpha} = \frac{1}{\sum_i \mathrm{e}^{-\beta\varepsilon_i}} \tag{51.18}$$

and

$$\frac{N_i}{N} = \mathrm{e}^{\alpha-\beta\varepsilon_i} = \mathrm{e}^{\alpha}\mathrm{e}^{-\beta\varepsilon_i} = \frac{\mathrm{e}^{-\beta\varepsilon_i}}{\sum_i \mathrm{e}^{-\beta\varepsilon_i}} \qquad \text{Boltzmann distribution} \tag{51.19}$$

which is eqn 51.6a.

Checklist of concepts

☐ **1.** **The instantaneous configuration** of a system of N molecules is the specification of the set of populations N_0, N_1, … of the energy levels ε_0, ε_1, … .

☐ **2.** The **Boltzmann distribution** gives the numbers of molecules in each state of a system at any temperature.

☐ **3.** The principle of **equal *a priori* probabilities** assumes that all possibilities for the distribution of energy are equally probable.

☐ **4.** The **relative populations** of energy levels, as opposed to states, must take into account the degeneracies of the energy levels.

Checklist of equations

Property	Equation	Comment	Equation number
Boltzmann distribution	$N_i/N = \mathrm{e}^{-\beta\varepsilon_i}/q$	$\beta = 1/kT$	51.6a
Partition function	$q = \sum_i \mathrm{e}^{-\beta\varepsilon_i}$	See Topic 52	51.6b
Boltzmann ratio	$N_i/N_j = (g_i/g_j)\mathrm{e}^{-\beta(\varepsilon_i-\varepsilon_j)}$	g_i, g_j are degeneracies	51.8

TOPIC 52

Molecular partition functions

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➤ Why do you need to know this material?

Statistical thermodynamics provides the link between molecular properties that have been calculated or derived from spectroscopy and thermodynamic properties, including equilibrium concepts. The connection is the partition function. Therefore, this material is an essential foundation for understanding physical and chemical properties of bulk matter in terms of the properties of the constituent molecules.

➤ What is the key idea?

The partition function is calculated by drawing on calculated or spectroscopically derived structural information about molecules.

➤ What do you need to know already?

You need to know that the Boltzmann distribution expresses the most probable distribution of molecules over the available energy levels (Topic 51). In that Topic we introduce the concept of partition function, which is developed further here.

The partition function $q=\Sigma_i e^{-\beta\varepsilon_i}$ is introduced in Topic 51 simply as a symbol to denote the sum over states that occurs in the denominator of the Boltzmann distribution (eqn 51.6a). But it is far more important than that might suggest. For instance, it contains all the information needed to calculate the bulk properties of a system of independent particles. In this respect q plays a role for bulk matter very similar to that played by the wavefunction in quantum mechanics for individual molecules: q is a kind of thermal wavefunction. This Topic shows how the partition function is calculated in a variety of important cases in preparation for seeing how thermodynamic information is extracted.

52.1 The significance of the partition function

The **molecular partition function** is

$$q=\sum_{\text{states } i} e^{-\beta\varepsilon_i}$$

Definition Molecular partition function (52.1a)

where $\beta=1/kT$. As emphasized in Topic 51, the sum is over *states*, not energy *levels*. If g_i states have the same energy ε_i (so the level is g_i-fold degenerate), we write

$$q=\sum_{\text{levels } i} g_i e^{-\beta\varepsilon_i}$$

Alternative definition Molecular partition function (52.1b) where the sum is now over energy levels (sets of states with the same energy), not individual states. Also as emphasized in Topic 51, we always take the lowest available state as the zero of energy and set $\varepsilon_0=0$.

Brief illustration 52.1 A partition function

Suppose a molecule is confined to the following non-degenerate energy levels: 0, ε, 2ε, … (Fig. 52.1; later in this Topic we shall see that this array of levels is used when considering molecular vibration). Then the molecular partition function is

$$q=1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}+\ldots=1+e^{-\beta\varepsilon}+\left(e^{-\beta\varepsilon}\right)^2+\cdots$$

The sum of the geometrical series $1+x+x^2+\cdots$ is $1/(1-x)$, so in this case

$$q=\frac{1}{1-e^{-\beta\varepsilon}}$$

This function is plotted in Fig. 52.2.

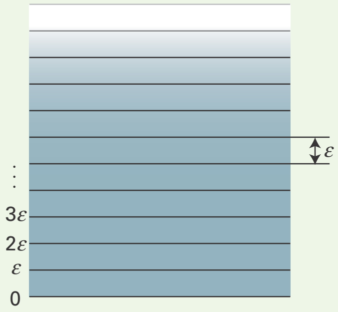


Figure 52.1 The equally spaced infinite array of energy levels used in the calculation of the partition function. A harmonic oscillator has the same spectrum of levels.

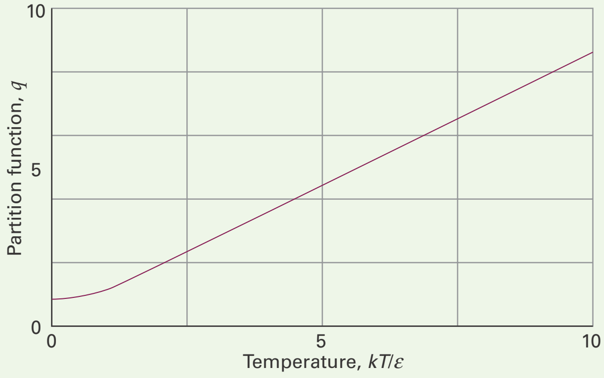


Figure 52.2 The partition function for the system shown in Fig. 52.1 (a harmonic oscillator) as a function of temperature.

Self-test 52.1 Suppose the molecule can exist in only two states, with energies 0 and ε. Derive and plot the expression for the partition function.

Answer: $q=1+e^{-\beta\varepsilon}$; see Fig 52.3.

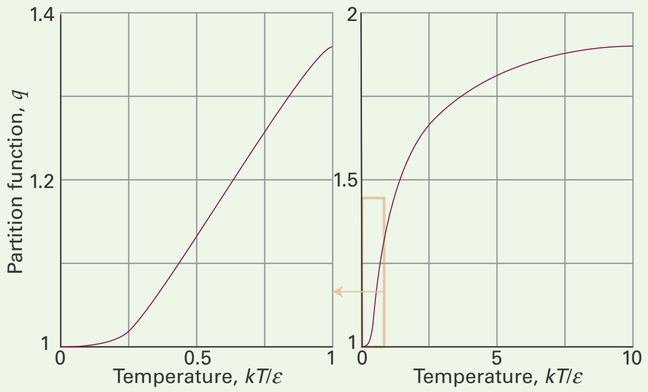


Figure 52.3 The partition function for a two-level system as a function of temperature. The two graphs differ in the scale of the temperature axis to show the approach to 1 as $T\to 0$ and the slow approach to 2 as $T\to\infty$.

We have derived the following important expression for the partition function for a uniform ladder of states of spacing ε:

$$q=\frac{1}{1-e^{-\beta\varepsilon}}$$

Uniform ladder Partition function (52.2a)

We can use this expression to interpret the physical significance of a partition function. To do so, we first note that the Boltzmann distribution for this arrangement of energy levels gives the fraction, $p_i=N_i/N$, of molecules in the state with energy ε_i as

$$p_i=\frac{e^{-\beta\varepsilon_i}}{q}=\left(1-e^{-\beta\varepsilon}\right)e^{-\beta\varepsilon_i}$$

Uniform ladder Population (52.2b)

Figure 52.4 shows how p_i varies with temperature. At very low temperatures (large β), where q is close to 1, only the lowest state is significantly populated. As the temperature is raised, the population breaks out of the lowest state, and the upper states become progressively more highly populated. At the same time, the partition function rises from 1 towards 2 and then higher, so we see that its value gives an indication of the range of states populated at any given temperature. The name 'partition function' reflects the sense in which q measures how the total number of molecules is distributed—partitioned—over the available states.

The corresponding expressions for a two-level system, derived in Self-test 52.1, are

$$q=1+e^{-\beta\varepsilon}$$

Two-level system Partition function (52.3a)

$$p_i=\frac{e^{-\beta\varepsilon_i}}{q}=\frac{e^{-\beta\varepsilon_i}}{1+e^{-\beta\varepsilon}}$$

Two-level system Population (52.3b)

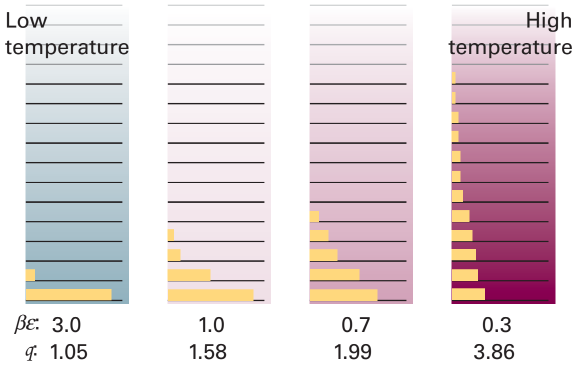


Figure 52.4 The populations of the energy levels of the system shown in Fig. 52.1 at different temperatures, and the corresponding values of the partition function as calculated from eqn 52.2a. Note that $\beta = 1/kT$.

In this case, because $\varepsilon_0 = 0$ and $\varepsilon_1 = \varepsilon$,

$$p_0 = \frac{1}{1+\mathrm{e}^{-\beta\varepsilon}} \qquad p_1 = \frac{\mathrm{e}^{-\beta\varepsilon}}{1+\mathrm{e}^{-\beta\varepsilon}} \tag{52.4}$$

These functions are plotted in Fig. 52.5. Notice how the populations are $p_0 = 1$ and $p_1 = 0$ and the partition function is $q = 1$ (one state occupied) at $T = 0$. However, the populations tend towards equality $(p_0 = \frac{1}{2}, p_1 = \frac{1}{2})$ and $q = 2$ (two states occupied) as $T \to \infty$. Incidentally, a common error is to suppose that when $T = \infty$ all the molecules in the system will be found in the upper energy state; however, we see from eqn 52.4 that as $T \to \infty$, the populations of states become equal. The same conclusion is true of multi-level systems too: as $T \to \infty$, all states become equally populated.

We can now generalize the conclusion that the partition function indicates the number of thermally accessible states.

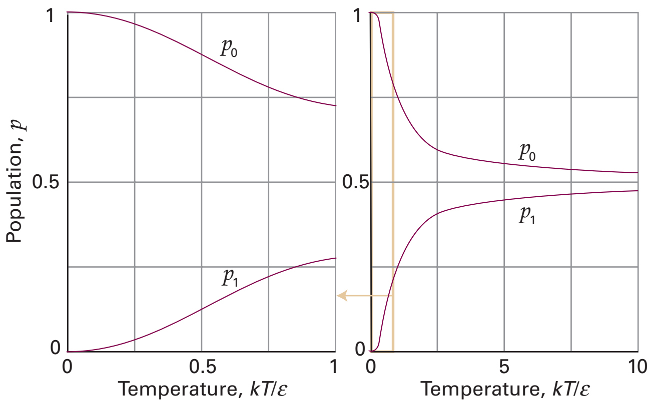


Figure 52.5 The fraction of populations of the two states of a two-level system as a function of temperature (eqn 52.4). Note that as the temperature approaches infinity, the populations of the two states become equal (and the fractions both approach 0.5).

When T is close to zero, the parameter $\beta = 1/kT$ is close to infinity. Then every term except one in the sum defining q is zero because each one has the form e^{-x} with $x \to \infty$. The exception is the term with $\varepsilon_0 \equiv 0$ (or the g_0 terms at zero energy if the ground state is g_0-fold degenerate), because then $\varepsilon_0/kT \equiv 0$ whatever the temperature, including zero. As there is only one surviving term when $T = 0$, and its value is g_0, it follows that

$$\lim_{T\to 0} q = g_0$$

That is, at $T = 0$, the partition function is equal to the degeneracy of the ground state (commonly, but not necessarily, 1).

Now consider the case when T is so high that for each term in the sum $\varepsilon_j/kT \approx 0$. Because $\mathrm{e}^{-x} = 1$ when $x = 0$, each term in the sum now contributes 1. It follows that the sum is equal to the number of molecular states, which in general is infinite:

$$\lim_{T\to\infty} q = \infty$$

In some idealized cases, the molecule may have only a finite number of states; then the upper limit of q is equal to the number of states, as we saw for the two-level system.

In summary:

> The molecular partition function gives an indication of the number of states that are thermally accessible to a molecule at the temperature of the system.

At $T = 0$, only the ground level is accessible and $q = g_0$. At very high temperatures, virtually all states are accessible, and q is correspondingly large.

52.2 Contributions to the partition function

The energy of a molecule is the sum of contributions from its different modes of motion:

$$\varepsilon_i = \varepsilon_i^{\mathrm{T}} + \varepsilon_i^{\mathrm{R}} + \varepsilon_i^{\mathrm{V}} + \varepsilon_i^{\mathrm{E}} \tag{52.5}$$

where T denotes translation, R rotation, V vibration, and E the electronic contribution. The separation of terms in eqn 52.5 is only approximate (except for translation) because the modes are not completely independent, but in most cases it is satisfactory. The separation of the electronic and vibrational motions is justified provided only the ground electronic state is occupied (for otherwise the vibrational characteristics depend on the electronic state) and, for the electronic ground state, that the Born–Oppenheimer approximation is valid (Topic 22). The separation of the vibrational and rotational modes is justified to the extent that the rotational constant (Topic 41) is independent of the vibrational state.

Given that the energy is a sum of independent contributions, the partition function factorizes into a product of contributions:

$$
\begin{aligned}
q&=\sum_i \mathrm{e}^{-\beta\varepsilon_i}=\sum_{i(\text{all states})}\mathrm{e}^{-\beta\varepsilon_i^{\mathrm{T}}-\beta\varepsilon_i^{\mathrm{R}}-\beta\varepsilon_i^{\mathrm{V}}-\beta\varepsilon_i^{\mathrm{E}}}\\
&=\sum_{i(\text{translational})}\ \sum_{i(\text{rotational})}\ \sum_{i(\text{vibrational})}\ \sum_{i(\text{electronic})}\mathrm{e}^{-\beta\varepsilon_i^{\mathrm{T}}-\beta\varepsilon_i^{\mathrm{R}}-\beta\varepsilon_i^{\mathrm{V}}-\beta\varepsilon_i^{\mathrm{E}}}\\
&=\left(\sum_{i(\text{translational})}\mathrm{e}^{-\beta\varepsilon_i^{\mathrm{T}}}\right)\left(\sum_{i(\text{rotational})}\mathrm{e}^{-\beta\varepsilon_i^{\mathrm{R}}}\right)\\
&\quad\times\left(\sum_{i(\text{vibrational})}\mathrm{e}^{-\beta\varepsilon_i^{\mathrm{V}}}\right)\left(\sum_{i(\text{electronic})}\mathrm{e}^{-\beta\varepsilon_i^{\mathrm{E}}}\right)
\end{aligned}
$$

That is,

$$q=q^{\mathrm{T}}q^{\mathrm{R}}q^{\mathrm{V}}q^{\mathrm{E}}\qquad\text{Factorization of the partition function}\qquad(52.6)$$

This factorization means that we can investigate each contribution separately. In general, exact analytical expressions for partition functions cannot be obtained. However, closed approximate expressions can often be found and prove to be very important for understanding chemical phenomena; they are derived in the following sections and collected at the end of the Topic.

(a) The translational contribution

The translational partition function for a particle of mass m free to move in a one-dimensional container of length X can be evaluated by making use of the fact that the separation of energy levels is very small and that large numbers of states are accessible at normal temperatures. As shown in the following *Justification*, in this case

$$q_X^{\mathrm{T}}=\left(\frac{2\pi m}{h^2\beta}\right)^{1/2}X\qquad\textit{One-dimensional}\qquad\text{Translational partition function}\qquad(52.7\text{a})$$

It will prove convenient to anticipate once again that $\beta=1/kT$ and to write this expression as $q_X^{\mathrm{T}}=X/\Lambda$, with

$$\Lambda=\frac{h}{(2\pi mkT)^{1/2}}\qquad\textit{Definition}\qquad\text{Thermal wavelength}\qquad(52.7\text{b})$$

The quantity Λ (uppercase lambda) has the dimensions of length and is called the **thermal wavelength** (sometimes the 'thermal de Broglie wavelength') of the molecule. The thermal wavelength decreases with increasing mass and temperature. This expression shows that the partition function for translational motion increases with the length of the box and the mass of the particle, for in each case the separation of the energy levels becomes smaller and more levels become thermally accessible. For a given mass and length of the box, the partition function also increases with increasing temperature (decreasing β), because more states become accessible.

Justification 52.1 The partition function for a particle in a one-dimensional box

The energy levels of a molecule of mass m in a container of length X are given by eqn 9.8b with $L=X$:

$$E_n=\frac{n^2h^2}{8mX^2}$$

The lowest level ($n=1$) has energy $h^2/8mX^2$, so the energies relative to that level are

$$\varepsilon_n=(n^2-1)\varepsilon\qquad\varepsilon=h^2/8mX^2$$

The sum to evaluate is therefore

$$q_X^{\mathrm{T}}=\sum_{n=1}^{\infty}\mathrm{e}^{-(n^2-1)\beta\varepsilon}$$

The translational energy levels are very close together in a container the size of a typical laboratory vessel, in the sense $h^2/8mkTX^2\ll 1$ (for instance, for $\mathrm{H_2}$ in a vessel of length 1 cm at 298 K, $h^2/8mkTX^2\approx 4\times 10^{-17}$); therefore, the sum can be approximated by an integral:

$$q_X^{\mathrm{T}}=\int_1^{\infty}\mathrm{e}^{-(n^2-1)\beta\varepsilon}\mathrm{d}n\approx\int_0^{\infty}\mathrm{e}^{-n^2\beta\varepsilon}\mathrm{d}n$$

The extension of the lower limit to $n=0$ and the replacement of n^2-1 by n^2 introduces negligible error but turns the integral into standard form (Integral G.1 of the *Resource section*). We make the substitution $x^2=n^2\beta\varepsilon$, implying $\mathrm{d}n=\mathrm{d}x/(\beta\varepsilon)^{1/2}$, and therefore that

$$q_X^{\mathrm{T}}=\left(\frac{1}{\beta\varepsilon}\right)^{1/2}\overbrace{\int_0^{\infty}\mathrm{e}^{-x^2}\mathrm{d}x}^{\pi^{1/2}/2}=\left(\frac{1}{\beta\varepsilon}\right)^{1/2}\frac{\pi^{1/2}}{2}=\left(\frac{2\pi m}{h^2\beta}\right)^{1/2}X$$

The total energy of a molecule free to move in three dimensions is the sum of its translational energies in all three directions:

$$\varepsilon_{n_1n_2n_3}=\varepsilon_{n_1}^{(X)}+\varepsilon_{n_2}^{(Y)}+\varepsilon_{n_3}^{(Z)}\qquad(52.8)$$

where n_1, n_2, and n_3 are the quantum numbers for motion in the x-, y-, and z-directions, respectively. Therefore, because $\mathrm{e}^{a+b+c}=\mathrm{e}^a\mathrm{e}^b\mathrm{e}^c$, the partition function factorizes as follows:

$$
\begin{aligned}
q^{\mathrm{T}}&=\sum_{n_1,n_2,n_3}\mathrm{e}^{-\beta\varepsilon_{n_1}^{(X)}-\beta\varepsilon_{n_2}^{(Y)}-\beta\varepsilon_{n_3}^{(Z)}}=\sum_{n_1,n_2,n_3}\mathrm{e}^{-\beta\varepsilon_{n_1}^{(X)}}\mathrm{e}^{-\beta\varepsilon_{n_2}^{(Y)}}\mathrm{e}^{-\beta\varepsilon_{n_3}^{(Z)}}\\
&=\left(\sum_{n_1}\mathrm{e}^{-\beta\varepsilon_{n_1}^{(X)}}\right)\left(\sum_{n_2}\mathrm{e}^{-\beta\varepsilon_{n_2}^{(Y)}}\right)\left(\sum_{n_3}\mathrm{e}^{-\beta\varepsilon_{n_3}^{(Z)}}\right)
\end{aligned}
$$

That is,

$$q^{\mathrm{T}}=q_X^{\mathrm{T}}q_Y^{\mathrm{T}}q_Z^{\mathrm{T}} \tag{52.9}$$

Equation 52.7a gives the partition function for translational motion in the x-direction. The only change for the other two directions is to replace the length X by the lengths Y or Z. Hence the partition function for motion in three dimensions is

$$q^{\mathrm{T}}=\left(\frac{2\pi m}{h^2\beta}\right)^{3/2}XYZ \tag{52.10a}$$

The product of lengths XYZ is the volume, V, of a rectangular container, so we can write

$$q^{\mathrm{T}}=\frac{V}{\Lambda^3} \tag{52.10b}$$

Three-dimensional Translational partition function

with Λ as defined in eqn 52.7b. As in the one-dimensional case, the partition function increases with the mass of the particle (as $m^{3/2}$) and the volume of the container (as V); for a given mass and volume, the partition function increases with temperature (as $T^{3/2}$). As in one dimension, $q^{\mathrm{T}}\to\infty$ as $T\to\infty$ because an infinite number of states becomes accessible as the temperature is raised. Even at room temperature, $q^{\mathrm{T}}\approx 2\times10^{28}$ for an O_2 molecule in a vessel of volume 100 cm³.

Brief illustration 52.2 The translational partition function

To calculate the translational partition function of an H_2 molecule confined to a 100 cm³ vessel at 25 °C we use $m=2.016m_{\mathrm{u}}$; then

$$\Lambda=\frac{6.626\times10^{-34}\,\mathrm{J\,s}}{\left\{\begin{matrix}2\pi\times(2.016\times1.6605\times10^{-27}\,\mathrm{kg})\\ \times(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})\end{matrix}\right\}^{1/2}}$$
$$=7.12\times10^{-11}\,\mathrm{m}$$

where we have used $1\,\mathrm{J}=1\,\mathrm{kg\,m^2\,s^{-2}}$. Therefore,

$$q^{\mathrm{T}}=\frac{1.00\times10^{-4}\,\mathrm{m}^3}{(7.12\times10^{-11}\,\mathrm{m})^3}=2.77\times10^{26}$$

About 10^{26} quantum states are thermally accessible, even at room temperature and for this light molecule. Many states are occupied if the thermal wavelength (which in this case is 71.2 pm) is small compared with the linear dimensions of the container.

Self-test 52.2 Calculate the translational partition function for a D_2 molecule under the same conditions.

Answer: $q^{\mathrm{T}}=7.8\times10^{26}$, $2^{3/2}$ times larger

The validity of the approximations that led to eqn 52.10 can be expressed in terms of the average separation, d, of the particles in the container. Because q is the total number of accessible states, the average number of states per molecule is q^{T}/N. For this quantity to be large, we require $V/N\Lambda^3\gg1$. However, V/N is the volume occupied by a single particle, and therefore the average separation of the particles is $d=(V/N)^{1/3}$. The condition for there being many states available per molecule is therefore $d^3/\Lambda^3\gg1$, and therefore $d\gg\Lambda$. That is, for eqn 52.10 to be valid, *the average separation of the particles must be much greater than their thermal wavelength*. For H_2 molecules at 1 bar and 298 K, the average separation is 3 nm, which is significantly larger than their thermal wavelength (71.2 pm).

The validity of eqn 52.10 can be expressed in a different way by noting that the approximations that led to it are valid if many states are occupied, which requires V/Λ^3 to be large. That will be so if Λ is small compared with the linear dimensions of the container. For H_2 at 25 °C, $\Lambda=71$ pm, which is far smaller than any conventional container is likely to be (but comparable to pores in zeolites or cavities in clathrates). For O_2, a heavier molecule, $\Lambda=18$ pm.

(b) The rotational contribution

The energy levels of a linear rotor are $\varepsilon_J=hc\tilde{B}J(J+1)$ with $J=0$, 1, 2, … (Topic 41). The state of lowest energy has zero energy, so no adjustment need be made to the energies given by this expression. Each level consists of $2J+1$ degenerate states. Therefore, the partition function of a non-symmetrical (AB) linear rotor is

$$q^{\mathrm{R}}=\sum_J\overbrace{(2J+1)}^{g_J}\mathrm{e}^{-\beta\overbrace{hc\tilde{B}J(J+1)}^{\varepsilon_J}} \tag{52.11}$$

The direct method of calculating q^{R} is to substitute the experimental values of the rotational energy levels into this expression and to sum the series numerically.

Example 52.1 Evaluating the rotational partition function explicitly

Evaluate the rotational partition function of $^1H^{35}Cl$ at 25 °C, given that $\tilde{B}=10.591\,\mathrm{cm^{-1}}$.

Method We need to evaluate eqn 52.11 term by term. We use $kT/hc=207.224\,\mathrm{cm^{-1}}$ at 298.15 K. The sum is readily evaluated by using mathematical software.

Answer To show how successive terms contribute, we draw up the following table by using $hc\tilde{B}/kT=0.05111$ (Fig. 52.6):

J	0	1	2	3	4	…	10
$(2J+1)e^{-0.05111J(J+1)}$	1	2.71	3.68	3.79	3.24	…	0.08

The sum required by eqn 52.11 (the sum of the numbers in the second row of the table) is 19.9, hence $q^R = 19.9$ at this temperature. Taking J up to 50 gives $q^R = 19.902$. Notice that about ten J-levels are significantly populated but the number of populated *states* is larger on account of the $(2J+1)$-fold degeneracy of each level.

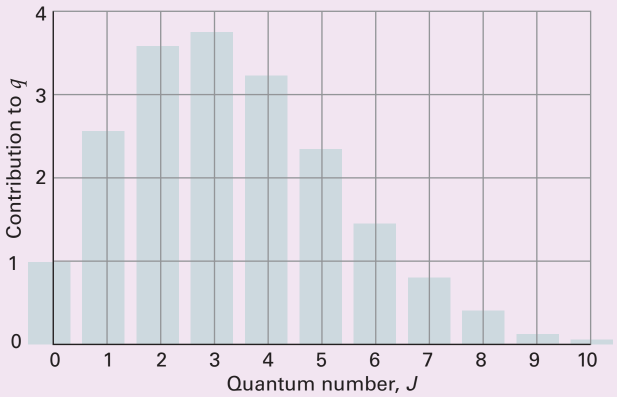


Figure 52.6 The contributions to the rotational partition function of an HCl molecule at 25 °C. The vertical axis is the value of $(2J+1)e^{-\beta hc\tilde{B}J(J+1)}$. Successive terms (which are proportional to the populations of the levels) pass through a maximum because the population of individual states decreases exponentially, but the degeneracy of the levels increases with J.

Self-test 52.3 Evaluate the rotational partition function for $^1H^{35}Cl$ at 0 °C.

Answer: 18.26

At room temperature, $kT/hc \approx 200\,\text{cm}^{-1}$. The rotational constants of many molecules are close to $1\,\text{cm}^{-1}$ (Table 43.1) and often smaller (though the very light H_2 molecule, for which $\tilde{B} = 60.9\,\text{cm}^{-1}$, is one exception). It follows that many rotational levels are populated at normal temperatures. When this is the case, we show in the following two *Justifications* that the partition function may be approximated by

$$q^R = \frac{kT}{hc\tilde{B}} \qquad \text{Linear rotor} \qquad (52.12a)$$

$$q^R = \left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2} \qquad \text{Nonlinear rotor} \qquad (52.12b)$$

where $\tilde{A}$, $\tilde{B}$, and $\tilde{C}$ are the rotational constants of the molecule expressed as wavenumbers. However, before using these expressions, read on (to eqns 52.13 and 52.14).

Justification 52.2 The rotational contribution for linear molecules

When many rotational states are occupied and kT is much larger than the separation between neighbouring states, the sum in the partition function can be approximated by an integral, much as we did for translational motion:

$$q^R = \int_0^\infty (2J+1)e^{-\beta hc\tilde{B}J(J+1)}\,dJ$$

This integral can be evaluated without much effort by making the substitution $x = \beta hc\tilde{B}J(J+1)$, so that $dx/dJ = \beta hc\tilde{B}(2J+1)$ and therefore $(2J+1)dJ = dx/\beta hc\tilde{B}$. Then

$$q^R = \frac{1}{\beta hc\tilde{B}}\overbrace{\int_0^\infty e^{-x}dx}^{1} = \frac{1}{\beta hc\tilde{B}}$$

which (because $\beta = 1/kT$) is eqn 52.12a.

Brief illustration 52.3 The rotational contribution

For $^1H^{35}Cl$ at 298.15 K we use $kT/hc = 207.224\,\text{cm}^{-1}$ and $\tilde{B} = 10.591\,\text{cm}^{-1}$. Then

$$q^R = \frac{kT}{hc\tilde{B}} = \frac{207.224\,\text{cm}^{-1}}{10.591\,\text{cm}^{-1}} = 19.59$$

The value is in good agreement with the exact value (19.02, Example 52.1) and with much less work.

Self-test 52.4 Evaluate the rotational contribution to the partition function for $^1H^{35}Cl$ at 0 °C.

Answer: 17.93; exact value 18.26, Self-test 52.3

Justification 52.3 The rotational contribution for nonlinear molecules

The energies of a symmetric rotor (Topic 41) are

$$E_{J,K,M_J} = hc\tilde{B}J(J+1) + hc(\tilde{A}-\tilde{B})K^2$$

with $J = 0, 1, 2, \ldots$; $K = J, J-1, \ldots, -J$; and $M_J = J, J-1, \ldots, -J$. Instead of considering these ranges, the same values can be covered by allowing K to range from $-\infty$ to ∞, with J confined to $|K|, |K|+1, \ldots, \infty$ for each value of K (Fig. 52.7). Because the energy is independent of M_J, and there are $2J+1$ values of M_J for each value of J, each value of J is $(2J+1)$-fold degenerate. It follows that the partition function

$$q = \sum_{J=0}^{\infty}\sum_{K=-J}^{J}\sum_{M_J=-J}^{J} e^{-\beta E_{J,K,M_J}}$$

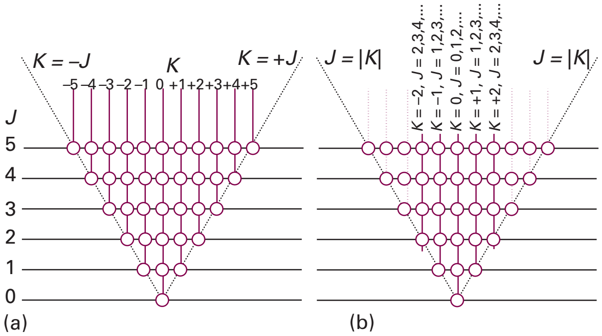


Figure 52.7 (a) The sum over $J=0, 1, 2, \ldots$ and $K=J, J-1, \ldots, -J$ (depicted by the circles) can be covered (b) by allowing K to range from $-\infty$ to ∞, with J confined to $|K|, |K|+1, \ldots, \infty$ for each value of K.

can be written equivalently as

$$q=\sum_{J=0}^{\infty}\sum_{K=-J}^{J}(2J+1)\mathrm{e}^{-\beta E_{J,K,M_J}}=\sum_{K=-\infty}^{\infty}\sum_{J=|K|}^{\infty}(2J+1)\mathrm{e}^{-\beta E_{J,K,M_J}}$$

$$=\sum_{K=-\infty}^{\infty}\mathrm{e}^{-hc\beta\left(\tilde{A}-\tilde{B}\right)K^2}\sum_{J=|K|}^{\infty}(2J+1)\mathrm{e}^{-hc\beta\tilde{B}J(J+1)}$$

As in *Justification* 52.2 we assume that the temperature is so high that numerous states are occupied and that the sums may be approximated by integrals. Then

$$q=\int_{-\infty}^{\infty}\mathrm{e}^{-hc\beta\left(\tilde{A}-\tilde{B}\right)K^2}\int_{|K|}^{\infty}(2J+1)\mathrm{e}^{-hc\beta\tilde{B}J(J+1)}\mathrm{d}J\mathrm{d}K$$

As before, the integral over J can be recognized as the integral of the derivative of a function, which is the function itself, so, as you should verify,

$$\int_{|K|}^{\infty}(2J+1)\mathrm{e}^{-hc\beta\tilde{B}J(J+1)}\mathrm{d}J=\frac{1}{hc\beta\tilde{B}}\mathrm{e}^{-hc\beta\tilde{B}K^2}$$

We have also supposed that $|K|\gg 1$ for most contributions and replaced $|K|$ $(|K|+1)$ by K^2. Now we can write

$$q=\frac{1}{hc\beta\tilde{B}}\int_{-\infty}^{\infty}\mathrm{e}^{-hc\beta\left(\tilde{A}-\tilde{B}\right)K^2}\mathrm{e}^{-hc\beta\tilde{B}K^2}\mathrm{d}K=\frac{1}{hc\beta\tilde{B}}\int_{-\infty}^{\infty}\mathrm{e}^{-hc\beta\tilde{A}K^2}\mathrm{d}K$$

$$=\frac{1}{hc\beta\tilde{B}}\left(\frac{\pi}{hc\beta\tilde{A}}\right)^{1/2}$$

For the final integration, we have used Integral G.1 of the *Resource section*. We conclude that

$$q=\frac{1}{(hc\beta)^{3/2}}\left(\frac{\pi}{\tilde{A}\tilde{B}^2}\right)^{1/2}=\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}^2}\right)^{1/2}$$

For an asymmetric rotor, one of the $\tilde{B}$ is replaced by $\tilde{C}$, to give eqn 52.12b.

A useful way of expressing the temperature above which the rotational approximation is valid is to introduce the **characteristic rotational temperature**, $\theta^{\mathrm{R}}=hc\tilde{B}/k$. Then 'high temperature' means $T\gg\theta^{\mathrm{R}}$ and under these conditions the rotational partition function of a linear molecule is simply T/θ^{R}. Some typical values of θ^{R} are shown in Table 52.1. The value for H_2 is abnormally high and we must be careful with the approximation for this molecule.

The general conclusion at this stage is that molecules with large moments of inertia (and hence small rotational constants and low characteristic rotational temperatures) have large rotational partition functions. The large value of q^{R} reflects the closeness in energy (compared with kT) of the rotational levels in large, heavy molecules, and the large number of rotational states that are accessible at normal temperatures.

We must take care, however, not to include too many rotational states in the sum. For a homonuclear diatomic molecule or a symmetrical linear molecule (such as CO_2 or $HC{\equiv}CH$), a rotation through 180° results in an indistinguishable state of the molecule. Hence, the number of thermally accessible states is only half the number that can be occupied by a heteronuclear diatomic molecule, where rotation through 180° does result in a distinguishable state. Therefore, for a symmetrical linear molecule,

$$q^{\mathrm{R}}=\frac{kT}{2hc\tilde{B}}=\frac{T}{2\theta^{\mathrm{R}}}\qquad(52.13\mathrm{a})$$

Symmetrical linear rotor Rotational partition function

The equations for symmetrical and non-symmetrical molecules can be combined into a single expression by introducing the **symmetry number**, σ, which is the number of indistinguishable orientations of the molecule. Then

$$q^{\mathrm{R}}=\frac{T}{\sigma\theta^{\mathrm{R}}}\qquad(52.13\mathrm{b})$$

Linear rotor Rotational partition function

For a heteronuclear diatomic molecule, $\sigma=1$; for a homonuclear diatomic molecule or a symmetrical linear molecule, $\sigma=2$.

The same care must be exercised for other types of symmetrical molecule, and for a nonlinear molecule we write

$$q^{\mathrm{R}}=\frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2}\qquad(52.14)$$

Nonlinear rotor Rotational partition function

Table 52.1* Rotational and vibrational temperatures

Molecule	Mode	θ^{V}/K	θ^{R}/K
H_2		6330	88
HCl		4300	15
I_2		39	0.053
CO_2	ν_1	1997	0.561
	ν_2	3380	
	ν_3	960	

* More value are given in the *Resource section*; use $hc/k=1.439$ K cm.

Justification 52.4 The origin of the symmetry number

The quantum mechanical origin of the symmetry number is the Pauli principle, which forbids the occupation of certain states. We saw in Topic 42, for example, that H_2 may occupy rotational states with even J only if its nuclear spins are paired (*para*-hydrogen), and odd J states only if its nuclear spins are parallel (*ortho*-hydrogen). There are three states of *ortho*-H_2 to each value of J (because there are three parallel spin states of the two nuclei).

To set up the rotational partition function we note that 'ordinary' molecular hydrogen is a mixture of one part *para*-H_2 (with only its even-J rotational states occupied) and three parts *ortho*-H_2 (with only its odd-J rotational states occupied). Therefore, the average partition function per molecule is

$$q^{\mathrm{R}}=\frac{1}{4}\sum_{\text{even }J}(2J+1)\mathrm{e}^{-\beta hc\tilde{B}J(J+1)}+\frac{3}{4}\sum_{\text{odd }J}(2J+1)\mathrm{e}^{-\beta hc\tilde{B}J(J+1)}$$

The odd-J states are more heavily weighted than the even-J states (Fig. 52.8). From the illustration we see that we would obtain approximately the same answer for the partition function (the sum of all the populations) if each J term contributed half its normal value to the sum. That is, the last equation can be approximated as

$$q^{\mathrm{R}}=\frac{1}{2}\sum_{J}(2J+1)\mathrm{e}^{-\beta hc\tilde{B}J(J+1)}$$

and this approximation is very good when many terms contribute (at high temperatures, $T \gg 88\,\mathrm{K}$).

The same type of argument may be used for linear symmetrical molecules in which identical bosons are interchanged by rotation (such as CO_2). As pointed out in Topic 42, if the nuclear spin of the bosons is 0, then only even-J states are admissible. Because only half the rotational states are occupied, the rotational partition function is only half the value of the sum obtained by allowing all values of J to contribute (Fig. 52.9).

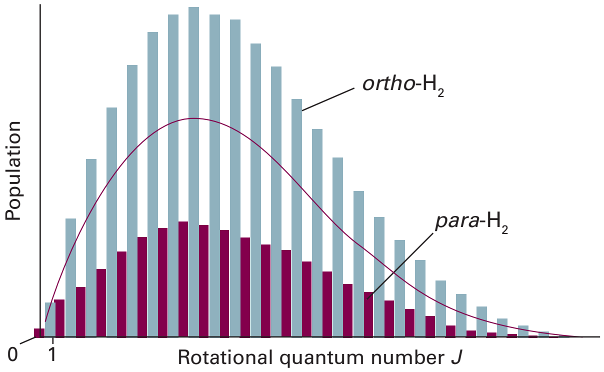


Figure 52.8 The values of the individual terms $(2J+1)\mathrm{e}^{-\beta hc\tilde{B}J(J+1)}$ contributing to the mean partition function of a 3:1 mixture of *ortho*- and *para*-H_2. The partition function is the sum of all these terms. At high temperatures, the sum is approximately equal to the sum of the terms over all values of J, each with a weight of $\frac{1}{2}$. This is the sum of the contributions indicated by the curve.

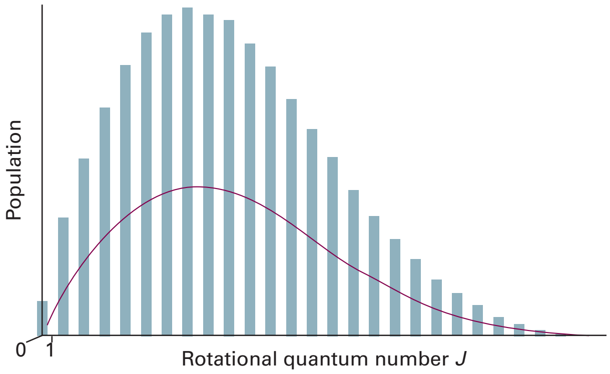


Figure 52.9 The relative populations of the rotational energy levels of CO_2. Only states with even J values are occupied. The full line shows the smoothed, averaged population of levels.

Some typical values of the symmetry numbers are given in Table 52.2. For the way that group theory is used to identify the value of the symmetry number, see Problem 52.9.

Table 52.2* Symmetry numbers

Molecule	σ
H_2O	2
NH_3	3
CH_4	12
C_6H_6	12

* More values are given in the *Resource section*.

Brief illustration 52.4 The symmetry number

The value $\sigma(H_2O)=2$ reflects the fact that a 180° rotation about the bisector of the HOH angle interchanges two indistinguishable atoms. In NH_3, there are three indistinguishable orientations around the axis, as shown in **1**. For CH_4, any of three 120° rotations about any of its four C—H bonds leaves the molecule in an indistinguishable state (**2**), so the symmetry number is $3\times4=12$. For benzene, any of six orientations around the axis perpendicular to the plane of the molecule leaves it apparently unchanged (Fig. 52.10), as does a rotation of 180° around any of six axes in the plane of the molecule (three of which pass along each C—H bond with

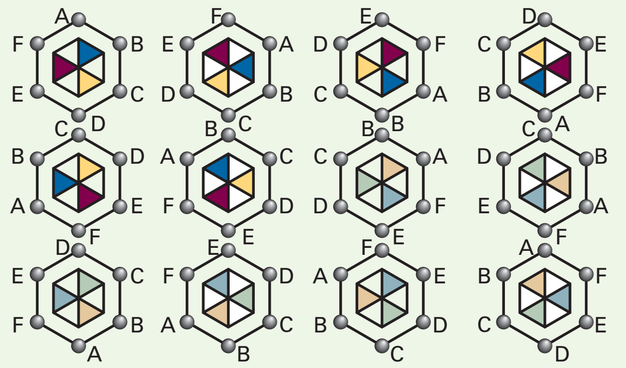
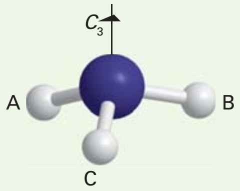


Figure 52.10 The 12 equivalent orientations of a benzene molecule that can be reached by pure rotations, and give rise to a symmetry number of 12. The six pale colours are the underside of the hexagon after that face has been rotated into view.

the remaining three passing through each C—C bond in the plane of the molecule).



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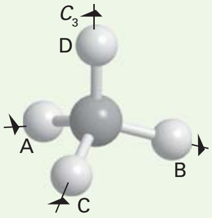

2

Self-test 52.5 What is the symmetry number for a naphthalene molecule?

Answer: 3

(c) The vibrational contribution

The vibrational partition function of a molecule is calculated by substituting the measured vibrational energy levels into the exponentials appearing in the definition of $q^{\rm V}$, and summing them numerically. However, provided it is permissible to assume that the vibrations are harmonic, there is a much simpler way. In that case, the vibrational energy levels form a uniform ladder of separation $hc\tilde{\nu}$ (Topic 43), which is exactly the problem treated in *Brief illustration* 52.1 and summarized in eqn 52.2a. Therefore we can use that result with $\varepsilon = hc\tilde{\nu}$ and conclude immediately that

$$q^{\rm V} = \frac{1}{1-e^{-\beta hc\tilde{\nu}}} \qquad \textit{Harmonic approximation} \qquad \text{Vibrational partition function} \qquad (52.15)$$

This function is plotted in Fig. 52.11 (which is essentially the same as Fig. 52.1). Similarly, the population of each state is given by eqn 52.2b.

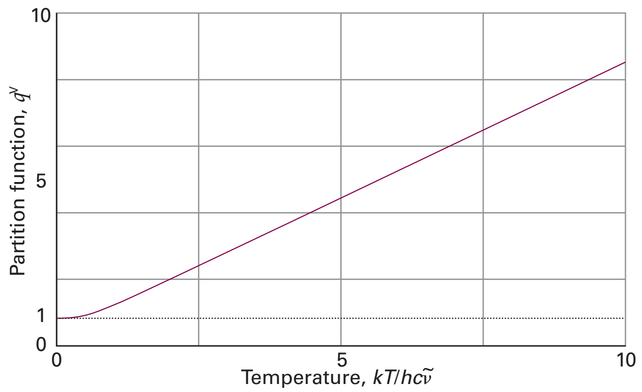

Figure 52.11 The vibrational partition function of a molecule in the harmonic approximation. Note that the partition function is linearly proportional to the temperature when the temperature is high ($T \gg \theta^{\rm V}$, with $\theta^{\rm V} = hc\tilde{\nu}/k$).

Brief illustration 52.5 The vibrational partition function

To calculate the partition function of I_2 molecules at 298.15 K we note from Table 43.1 that their vibrational wavenumber is $214.6\,\text{cm}^{-1}$. Then, because, at 298.15 K, $kT/hc = 207.224\,\text{cm}^{-1}$, we have

$$\beta\varepsilon = \frac{hc\tilde{\nu}}{kT} = \frac{214.6\,\text{cm}^{-1}}{207.244\,\text{cm}^{-1}} = 1.036$$

Then it follows from eqn 52.15 that

$$q^{\rm V} = \frac{1}{1-e^{-1.036}} = 1.55$$

We can infer that only the ground and first excited states are significantly populated.

Self-test 52.6 Evaluate the populations of the first three vibrational states.

Answer: $p_0 = 0.645$, $p_1 = 0.229$, $p_2 = 0.081$

In a polyatomic molecule each normal mode (Topic 44) has its own partition function (provided the anharmonicities are so small that the modes are independent). The overall vibrational partition function is the product of the individual partition functions, and we can write $q^{\rm V} = q^{\rm V}(1)q^{\rm V}(2)\ldots$, where $q^{\rm V}(K)$ is the partition function for the Kth normal mode and is calculated by direct summation of the observed spectroscopic levels.

Example 52.2 Calculating a vibrational partition function

The wavenumbers of the three normal modes of H_2O are $3656.7\,\text{cm}^{-1}$, $1594.8\,\text{cm}^{-1}$, and $3755.8\,\text{cm}^{-1}$. Evaluate the vibrational partition function at 1500 K.

Method Use eqn 52.15 for each mode, and then form the product of the three contributions. At 1500 K, $kT/hc = 1042.6\,\text{cm}^{-1}$.

Answer We draw up the following table displaying the contributions of each mode:

Mode:	1	2	3
$\tilde{\nu}/\text{cm}^{-1}$	3656.7	1594.8	3755.8
$hc\tilde{\nu}/kT$	3.507	1.530	3.602
q^V	1.031	1.276	1.028

The overall vibrational partition function is therefore

$$q^V = 1.031 \times 1.276 \times 1.028 = 1.352$$

The three normal modes of H_2O are at such high wavenumbers that even at 1500 K most of the molecules are in their vibrational ground state. However, there may be so many normal modes in a large molecule that their excitation may be significant even though each mode is not appreciably excited. For example, a nonlinear molecule containing 10 atoms has $3N-6=24$ normal modes (Topic 44). If we assume a value of about 1.1 for the vibrational partition function of one normal mode, the overall vibrational partition function is about $q^V \approx (1.1)^{24} = 9.8$, which indicates significant vibrational excitation relative to a smaller molecule, such as H_2O.

Self-test 52.7 Repeat the calculation for CO_2, where the vibrational wavenumbers are $1388\,\text{cm}^{-1}$, $667.4\,\text{cm}^{-1}$, and $2349\,\text{cm}^{-1}$, the second being the doubly degenerate bending mode.

Answer: 6.79

In many molecules the vibrational wavenumbers are so great that $\beta hc\tilde{\nu} > 1$. For example, the lowest vibrational wavenumber of CH_4 is $1306\,\text{cm}^{-1}$, so $\beta hc\tilde{\nu} = 6.3$ at room temperature. Most C—H stretches normally lie in the range 2850 to $2960\,\text{cm}^{-1}$, so for them $\beta hc\tilde{\nu} \approx 14$. In these cases, $e^{-\beta hc\tilde{\nu}}$ in the denominator of q^V is very close to zero (for example, $e^{-6.3} = 0.002$), and the vibrational partition function for a single mode is very close to 1 ($q^V = 1.002$ when $\beta hc\tilde{\nu} = 6.3$), implying that only the zero-point level is significantly occupied.

Now consider the case of bonds with such low vibrational frequencies that $\beta hc\tilde{\nu} \ll 1$. When this condition is satisfied, the partition function may be approximated by expanding the exponential ($e^x = 1 + x + \ldots$):

$$q^V = \frac{1}{1-e^{-\beta hc\tilde{\nu}}} = \frac{1}{1-(1-\beta hc\tilde{\nu}+\cdots)}$$

That is, for weak bonds at high temperatures,

$$q^V \approx \frac{kT}{hc\tilde{\nu}} \qquad \textit{High-temperature approximation} \qquad \text{Vibrational partition function} \qquad (52.16)$$

The temperatures for which eqn 52.16 is valid can be expressed in terms of the **characteristic vibrational temperature**, $\theta^V = hc\tilde{\nu}/k$ (Table 52.1). The value for H_2 is abnormally high because the atoms are so light and the vibrational frequency is correspondingly high. In terms of the vibrational temperature, 'high temperature' means $T \gg \theta^V$, and when this condition is satisfied, $q^V = T/\theta^V$ (the analogue of the rotational expression).

(d) The electronic contribution

Electronic energy separations from the ground state are usually very large, so for most cases $q^E = 1$ because only the ground state is occupied. An important exception arises in the case of atoms and molecules having electronically degenerate ground states, in which case $q^E = g^E$, where g^E is the degeneracy of the electronic ground state. Alkali metal atoms, for example, have doubly degenerate ground states (corresponding to the two orientations of their electron spin), so $q^E = 2$.

Brief illustration 52.6 The electronic partition function

Some atoms and molecules have low-lying electronically excited states. An example is NO, which has a configuration of the form $\ldots\pi^1$ (Topic 25). The energy of the two degenerate states in which the orbital and spin momenta are parallel (giving the ${}^2\Pi_{3/2}$ term, Fig. 52.12) is slightly greater than that of the two degenerate states in which they are antiparallel (giving the ${}^2\Pi_{1/2}$ term). The separation, which arises from spin–orbit coupling, is only $121\,\text{cm}^{-1}$. If we denote the energies of the two levels as $E_{1/2} = 0$ and $E_{3/2} = \varepsilon$, the partition function is

$$q^E = \sum_{\text{levels } i} g_i e^{-\beta\varepsilon_i} = 2 + 2e^{-\beta\varepsilon}$$

This function is plotted in Fig. 52.13. At $T = 0$, $q^E = 2$, because only the doubly degenerate ground state is accessible. At high temperatures, q^E approaches 4 because all four states are accessible. At 25 °C, $q^E = 3.1$.

Self-test 52.8 A certain atom has a fourfold degenerate ground state and a sixfold degenerate excited state at $400\,\text{cm}^{-1}$ above the ground state. Calculate its electronic partition function at 25 °C.

Answer: 4.87

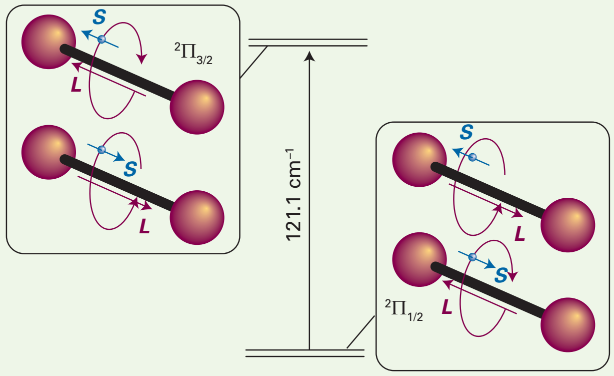

Figure 52.12 The doubly degenerate ground electronic level of NO (with the spin and orbital angular momentum around the axis in opposite directions) and the doubly degenerate first excited level (with the spin and orbital momenta parallel). The upper level is thermally accessible at room temperature.

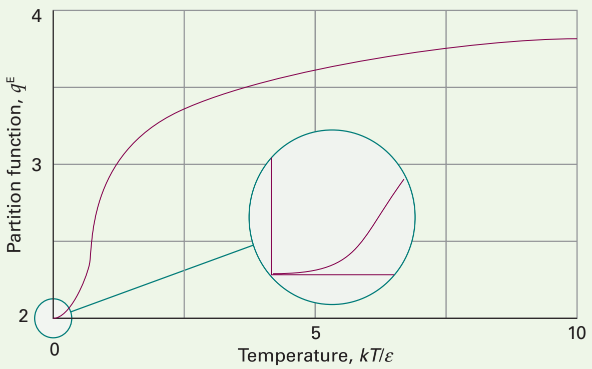

Figure 52.13 The variation with temperature of the electronic partition function of an NO molecule. Note that the curve resembles that for a two-level system (Fig. 52.3), but rises from 2 (the degeneracy of the lower level) and approaches 4 (the total number of states) at high temperatures.

Checklist of concepts

☐ 1. The **molecular partition function** is an indication of the number of thermally accessible states at the temperature of interest.

☐ 2. If the energy of a molecule is given by the sum of contributions, then the molecular partition function is a product of contributions from the different modes.

☐ 3. The **symmetry number** takes into account the number of indistinguishable orientations of a symmetrical molecule.

☐ 4. The **vibrational partition function** of a molecule may be approximated by that of a harmonic oscillator.

☐ 5. Because electronic energy separations from the ground state are usually very big, in most cases the **electronic partition function** is equal to the degeneracy of the electronic ground state.

Checklist of equations

Property	Equation	Comment	Equation number
Molecular partition function	$q = \sum_{\text{states } i} \mathrm{e}^{-\beta\varepsilon_i}$	Definition, independent molecules	52.1a
	$q = \sum_{\text{levels } i} g_i \mathrm{e}^{-\beta\varepsilon_i}$	Definition, independent molecules	52.1b
Uniform ladder	$q = 1/(1 - \mathrm{e}^{-\beta\varepsilon})$		52.2a
Two-level system	$q = 1 + \mathrm{e}^{-\beta\varepsilon}$		52.3a
Thermal wavelength	$\Lambda = h/(2\pi mkT)^{1/2}$		52.7b
Translation	$q^{\mathrm{T}} = V/\Lambda^3$		52.10b
Rotation	$q^{\mathrm{R}} = kT/\sigma hc\tilde{B}$	$T \gg \theta^{\mathrm{R}}$, linear rotor, $\theta^{\mathrm{R}} = hc\tilde{B}/k$	52.13
	$q^{\mathrm{R}} = (1/\sigma)\left(kT/hc\right)^{3/2}\left(\pi/\tilde{A}\tilde{B}\tilde{C}\right)^{1/2}$	$T \gg \theta^{\mathrm{R}}$, nonlinear rotor	52.14
Vibration	$q^{\mathrm{V}} = 1/(1 - \mathrm{e}^{-\beta hc\tilde{\nu}})$	Harmonic approximation	52.15

TOPIC 53

Molecular energies

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➤ Why do you need to know this material?

The partition function contains thermodynamic information, but it needs to be extracted. Here we show how to extract one particular property: the average energy of molecules, which plays a central role in thermodynamics.

➤ What is the key idea?

The average energy of a molecule in a collection of independent molecules can be calculated from the molecular partition function.

➤ What do you need to know already?

You need know how to calculate the molecular partition function from calculated or spectroscopic data (Topic 52) and its significance as a measure of the number of accessible states. The Topic also draws on expressions for the rotational and vibrational energies of molecules (Topics 41 and 43).

This Topic sets up the basic equations that show how to use the molecular partition function to calculate the mean energy of a collection of independent molecules. In Topic 58 we see how those mean energies are used to calculate the thermodynamic property of 'internal energy', and in Topic 60 we extend the discussion to the calculation of the other central thermodynamic property, the 'entropy'. The equations for collections of interacting molecules are very similar (Topic 54), but much more difficult to implement.

53.1 The basic equations

We begin by considering a collection of N molecules that do not interact with one another. Any member of the collection can exist in a state i of energy ε_i measured from the lowest energy state of the molecule. The mean energy of a molecule, $\langle\varepsilon\rangle$, relative to its energy in its ground state, is the total energy of the collection, E, divided by the total number of molecules:

$$\langle\varepsilon\rangle=\frac{E}{N}=\frac{1}{N}\sum_i N_i\varepsilon_i \tag{53.1}$$

In Topic 51 it is shown that the overwhelmingly most probable population of a state in a collection at a temperature T is given by the Boltzmann distribution (eqn 51.6, $N_i/N=(1/q)\mathrm{e}^{-\beta\varepsilon_i}$), so we can write

$$\langle\varepsilon\rangle=\frac{1}{q}\sum_i \varepsilon_i\mathrm{e}^{-\beta\varepsilon_i} \tag{53.2}$$

with $\beta=1/kT$. To manipulate this expression into a form involving only q we note that

$$\varepsilon_i\mathrm{e}^{-\beta\varepsilon_i}=-\frac{\mathrm{d}}{\mathrm{d}\beta}\mathrm{e}^{-\beta\varepsilon_i}$$

It follows that[1]

$$\langle\varepsilon\rangle=-\frac{1}{q}\sum_i\frac{\mathrm{d}}{\mathrm{d}\beta}\mathrm{e}^{-\beta\varepsilon_i}=-\frac{1}{q}\frac{\mathrm{d}}{\mathrm{d}\beta}\sum_i\mathrm{e}^{-\beta\varepsilon_i}=-\frac{1}{q}\frac{\mathrm{d}q}{\mathrm{d}\beta} \tag{53.3}$$

---

[1] To reinforce the analogy between statistical thermodynamics and quantum mechanics, note the resemblance of eqn 53.3 written as $\langle\varepsilon\rangle q=-\mathrm{d}q/\mathrm{d}\beta$ to the time-dependent Schrödinger equation written as $\hat{H}\Psi=-\mathrm{d}\Psi/\mathrm{d}(\mathrm{i}t/\hbar)$.

There are several points that need to be made in relation to eqn 53.3. Because $\varepsilon_0=0$ (remember that we measure all energies from the lowest available level), $\langle\varepsilon\rangle$ should be interpreted as the value of the mean energy relative to its ground-state (zero-point) energy. If the lowest energy of the molecule is in fact ε_{gs} rather than 0, then the true mean energy is $\varepsilon_{\text{gs}}+\langle\varepsilon\rangle$. For instance, for a harmonic oscillator, we would set ε_{gs} equal to the zero-point energy, $\frac{1}{2}hc\tilde{\nu}$. Secondly, because the partition function may depend on variables other than the temperature (for example, the volume), the derivative with respect to β in eqn 53.3 is actually a *partial* derivative with these other variables held constant. The complete expression relating the molecular partition function to the mean energy of a molecule is therefore

$$\langle\varepsilon\rangle=\varepsilon_{\text{gs}}-\frac{1}{q}\left(\frac{\partial q}{\partial\beta}\right)_V \qquad \text{Mean molecular energy} \qquad (53.4\text{a})$$

An equivalent form is obtained by noting that $\mathrm{d}x/x=\mathrm{d}\ln x$:

$$\langle\varepsilon\rangle=\varepsilon_{\text{gs}}-\left(\frac{\partial\ln q}{\partial\beta}\right)_V \qquad \text{Mean molecular energy} \qquad (53.4\text{b})$$

These two equations confirm that we need know only the partition function (as a function of temperature) to calculate the mean energy.

Brief illustration 53.1 Mean energy of a two-level system

If a molecule has only two available energy levels, one at 0 and the other at an energy ε, its partition function is

$$q=1+\mathrm{e}^{-\beta\varepsilon}$$

Therefore, the mean energy of a collection of these molecules at a temperature T is

$$\langle\varepsilon\rangle=-\frac{1}{1+\mathrm{e}^{-\beta\varepsilon}}\frac{\mathrm{d}(1+\mathrm{e}^{-\beta\varepsilon})}{\mathrm{d}\beta}=\frac{\varepsilon\mathrm{e}^{-\beta\varepsilon}}{1+\mathrm{e}^{-\beta\varepsilon}}=\frac{\varepsilon}{\mathrm{e}^{\beta\varepsilon}+1}$$

This function is plotted in Fig. 53.1. Notice how the mean energy is zero at $T=0$, when only the lower state (at the zero of energy) is occupied, and rises to $\frac{1}{2}\varepsilon$ as $T\to\infty$, when the two levels become equally populated.

Self-test 53.1 Deduce an expression for the mean energy when each molecule can exist in states with energies 0, ε, and 2ε.

Answer: $\langle\varepsilon\rangle=\varepsilon(1+2x)x/(1+x+x^2)$, $x=\mathrm{e}^{-\beta\varepsilon}$

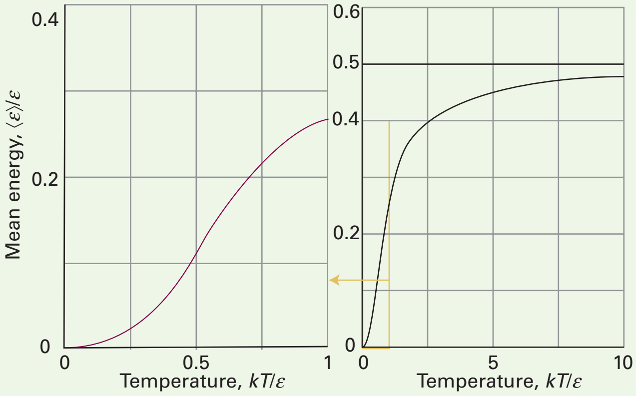

Figure 53.1 The mean energy of a two-level system (expressed as a multiple of ε) as a function of temperature, on two temperature scales. The graph on the left shows the slow rise away from zero energy at low temperatures; the slope of the graph at $T=0$ is 0. The graph on the right shows the slow rise to 0.5 as $T\to\infty$ as both states become equally populated.

53.2 The translational contribution

For a one-dimensional container of length X, for which $q^{\mathrm{T}}=X/\Lambda$ with $\Lambda=h(\beta/2\pi m)^{1/2}$ (Topic 52), we note that Λ is a constant multiplied by $\beta^{1/2}$, and obtain

$$\begin{aligned}\langle\varepsilon^{\mathrm{T}}\rangle&=-\frac{1}{q^{\mathrm{T}}}\left(\frac{\partial q^{\mathrm{T}}}{\partial\beta}\right)_V=-\frac{\Lambda}{X}\left(\frac{\partial}{\partial\beta}\frac{X}{\Lambda}\right)_V\\&=-\frac{\text{constant}\times\beta^{1/2}}{X}\times X\times\frac{\mathrm{d}}{\mathrm{d}\beta}\left(\frac{1}{\text{constant}\times\beta^{1/2}}\right)\\&=-\beta^{1/2}\overbrace{\frac{\mathrm{d}}{\mathrm{d}\beta}\frac{1}{\beta^{1/2}}}^{-\frac{1}{2}\beta^{-3/2}}=\frac{1}{2\beta}\end{aligned}$$

That is,

$$\langle\varepsilon^{\mathrm{T}}\rangle=\tfrac{1}{2}kT \qquad \textit{One dimension} \qquad \text{Mean translational energy} \qquad (53.5\text{a})$$

For a molecule free to move in three dimensions, the analogous calculation leads to

$$\langle\varepsilon^{\mathrm{T}}\rangle=\tfrac{3}{2}kT \qquad \textit{Three dimensions} \qquad \text{Mean translational energy} \qquad (53.5\text{b})$$

The **equipartition theorem** of classical mechanics is consistent with this result and provides a useful shortcut. First, we need to know that a 'quadratic contribution' to the energy means a contribution that can be expressed as the square of a variable, such as the position or the velocity. For example, the kinetic energy of an atom of mass m as it moves through three-dimensional space is

$$E_\mathrm{k}=\tfrac{1}{2}mv_x^2+\tfrac{1}{2}mv_y^2+\tfrac{1}{2}mv_z^2$$

and there are three quadratic contributions to its energy. In its simplest form, and as developed in the following *Justification*, the equipartition theorem then states that:

> For a collection of particles at thermal equilibrium at a temperature T, the average value of each quadratic contribution to the energy is the same and equal to $\tfrac{1}{2}kT$.

where k is Boltzmann's constant. (For the molar energy, multiply by Avogadro's constant and use $N_\mathrm{A}k=R$.) The equipartition theorem is a conclusion from classical mechanics and is applicable only when the effects of quantization can be ignored. In practice, it can be used for molecular translation and rotation for all but the lightest of molecules, but not for vibration.

A note on good practice You will commonly see the equipartition theorem expressed in terms of the 'degrees of freedom' rather than quadratic contributions. That can be misleading and is best avoided, for a single vibrational degree of freedom has two quadratic contributions (the kinetic energy and the potential energy).

Brief illustration 53.2 The equipartition theorem

According to the equipartition theorem, the average energy of each term in the expression above for E_k is $\tfrac{1}{2}kT$. Therefore, the mean energy of the atoms is $\tfrac{3}{2}kT$ and their molar energy is $\tfrac{3}{2}RT$. At 25 °C, $\tfrac{3}{2}RT=3.7\,\mathrm{kJ\,mol^{-1}}$, so translational motion contributes about 4 kJ mol^{-1} to the molar internal energy of a gaseous sample of atoms or molecules (the remaining contribution arises from the internal structure of the atoms and molecules).

Self-test 53.2 Estimate the mean molar rotational energy of a linear molecule.

Answer: RT; see *Brief illustration* 53.3

Justification 53.1 The equipartition theorem

We consider a one-dimensional system; the approach is easily generalized to more dimensions. In general, the energy depends on the position of a particle, x, and the linear momentum, p, both of which can range from $-\infty$ to $+\infty$. Both quantities are continuously variable (this is a classical system), so any sums can be replaced by integrals. The average value of any term that depends on x^2 is therefore

$$\langle x^2\rangle=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}x^2\,\frac{\mathrm{e}^{-\beta\varepsilon(x,p)}}{q}\,\mathrm{d}x\mathrm{d}p$$

The term in blue is the Boltzmann factor and the partition function is

$$q=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\mathrm{e}^{-\beta\varepsilon(x,p)}\mathrm{d}x\mathrm{d}p$$

If the energy has the form $\varepsilon(x,p)=ap^2+bx^2$ (for instance, a free particle has $a=1/2m$ and $b=0$), then

$$\langle x^2\rangle=\frac{\int_{-\infty}^{\infty}x^2\mathrm{e}^{-b\beta x^2}\mathrm{d}x\int_{-\infty}^{\infty}\mathrm{e}^{-a\beta p^2}\mathrm{d}p}{\int_{-\infty}^{\infty}\mathrm{e}^{-b\beta x^2}\mathrm{d}x\int_{-\infty}^{\infty}\mathrm{e}^{-a\beta p^2}\mathrm{d}p}=\frac{\overbrace{\int_{-\infty}^{\infty}x^2\mathrm{e}^{-b\beta x^2}\mathrm{d}x}^{\frac{1}{2}(\pi/b^3\beta^3)^{1/2}}}{\underbrace{\int_{-\infty}^{\infty}\mathrm{e}^{-b\beta x^2}\mathrm{d}x}_{(\pi/b\beta)^{1/2}}}=\tfrac{1}{2}\left(\frac{1}{b\beta}\right)$$

where we have used Integrals G.1 and G.3 from the *Resource section*. It follows that the average value of a contribution to the energy of the form bx^2 is $1/2\beta=\tfrac{1}{2}kT$ A similar argument applies for the average value of p^2 and its analogues (for instance, angular momentum).

53.3 The rotational contribution

The mean rotational energy of a linear molecule is obtained from the rotational partition function (eqn 52.11):

$$q^\mathrm{R}=\sum_J(2J+1)\mathrm{e}^{-\beta hc\tilde{B}J(J+1)}$$

When the temperature is low (in the sense $T<\theta^\mathrm{R}$), the series must be summed term by term, which for a heteronuclear diatomic molecule or other non-symmetrical linear molecule gives

$$q^\mathrm{R}=1+3\mathrm{e}^{-2\beta hc\tilde{B}}+5\mathrm{e}^{-6\beta hc\tilde{B}}+\cdots$$

Hence, because

$$\frac{\mathrm{d}q^\mathrm{R}}{\mathrm{d}\beta}=-hc\tilde{B}(6\mathrm{e}^{-2\beta hc\tilde{B}}+30\mathrm{e}^{-6\beta hc\tilde{B}}+\cdots)$$

(q^{R} is independent of V, so the partial derivative has been replaced by a complete derivative), we find

$$\begin{aligned}\langle\varepsilon^{\mathrm{R}}\rangle &= -\frac{1}{q^{\mathrm{R}}}\frac{\mathrm{d}q^{\mathrm{R}}}{\mathrm{d}\beta}\\ &= \frac{hc\tilde{B}(6\mathrm{e}^{-2\beta hc\tilde{B}}+30\mathrm{e}^{-6\beta hc\tilde{B}}+\cdots)}{1+3\mathrm{e}^{-2\beta hc\tilde{B}}+5\mathrm{e}^{-6\beta hc\tilde{B}}+\cdots}\end{aligned}$$

Unsymmetrical linear molecule Mean rotational energy (53.6a)

This ungainly function is plotted in Fig. 53.2. At high temperatures ($T \gg \theta^{\mathrm{R}}$), q^{R} is given by eqn 52.13 in the form

$$q^{\mathrm{R}} = \frac{1}{\sigma\beta hc\tilde{B}}$$

where $\sigma=1$ for a heteronuclear diatomic molecule. It then follows that

$$\langle\varepsilon^{\mathrm{R}}\rangle = -\frac{1}{q^{\mathrm{R}}}\frac{\mathrm{d}q^{\mathrm{R}}}{\mathrm{d}\beta} = -\sigma\beta hc\tilde{B}\frac{\mathrm{d}}{\mathrm{d}\beta}\frac{1}{\sigma\beta hc\tilde{B}} = -\beta\overbrace{\frac{\mathrm{d}}{\mathrm{d}\beta}\frac{1}{\beta}}^{-1/\beta^2}$$

and therefore that

$$\langle\varepsilon^{\mathrm{R}}\rangle = \frac{1}{\beta} = kT$$

Linear molecule, high temperature ($T \gg \theta^{\mathrm{R}}$) Mean rotational energy (53.6b)

The high-temperature result, which is valid when many rotational states are occupied, is also in agreement with the equipartition theorem, because the classical expression for the energy of a linear rotor is $E_{\mathrm{k}} = \frac{1}{2}I_{\perp}\omega_a^2 + \frac{1}{2}I_{\perp}\omega_b^2$ and therefore has two quadratic contributions. (There is no rotation around the line of atoms.) It follows from the equipartition theorem that the mean rotational energy is $2\times\frac{1}{2}kT = kT$.

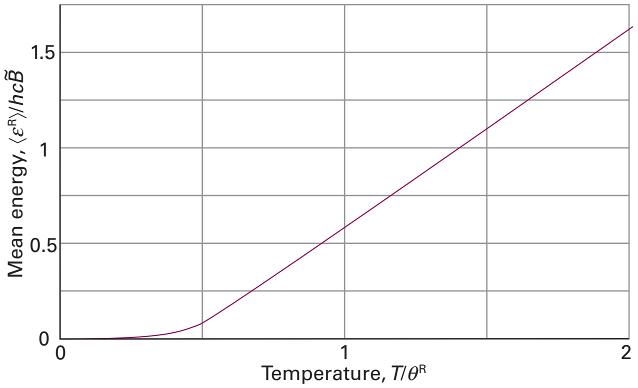

Figure 53.2 The mean rotational energy of a non-symmetrical linear rotor as a function of temperature. At high temperatures ($T \gg \theta^{\mathrm{R}}$), the energy is linearly proportional to the temperature, in accord with the equipartition theorem.

Brief illustration 53.3 Mean rotational energy

To estimate the mean energy of a nonlinear molecule we recognize that its rotational kinetic energy (the only contribution to its rotational energy) is $E_{\mathrm{k}} = \frac{1}{2}I_a\omega_a^2 + \frac{1}{2}I_b\omega_b^2 + \frac{1}{2}I_c\omega_c^2$. As there are three quadratic contributions, its mean rotational energy is $\frac{3}{2}kT$. The molar contribution is $\frac{3}{2}RT$. At 25 °C, this contribution is 3.7 kJ mol^{-1}, the same as the translational contribution, for a total of 7.4 kJ mol^{-1}. A monatomic gas has no rotational contribution.

Self-test 53.3 How much energy does it take to raise the temperature of 1.0 mol H_2O(g) from 100 °C to 200 °C? Consider only translational and rotational contributions to the mean energy.

Answer: 2.5 kJ

53.4 The vibrational contribution

The vibrational partition function in the harmonic approximation is given in eqn 52.15:

$$q^{\mathrm{V}} = \frac{1}{1-\mathrm{e}^{-\beta hc\tilde{\nu}}}$$

Because q^{V} is independent of the volume, it follows that

$$\frac{\mathrm{d}q^{\mathrm{V}}}{\mathrm{d}\beta} = \frac{\mathrm{d}}{\mathrm{d}\beta}\frac{1}{1-\mathrm{e}^{-\beta hc\tilde{\nu}}} = -\frac{hc\tilde{\nu}\mathrm{e}^{-\beta hc\tilde{\nu}}}{(1-\mathrm{e}^{-\beta hc\tilde{\nu}})^2} \qquad (53.7)$$

and hence from

$$\begin{aligned}\langle\varepsilon^{\mathrm{V}}\rangle &= -\frac{1}{q^{\mathrm{V}}}\frac{\mathrm{d}q^{\mathrm{V}}}{\mathrm{d}\beta} = (1-\mathrm{e}^{-\beta hc\tilde{\nu}})\frac{hc\tilde{\nu}\mathrm{e}^{-\beta hc\tilde{\nu}}}{(1-\mathrm{e}^{-\beta hc\tilde{\nu}})^2}\\ &= \frac{hc\tilde{\nu}\mathrm{e}^{-\beta hc\tilde{\nu}}}{1-\mathrm{e}^{-\beta hc\tilde{\nu}}}\end{aligned}$$

that

$$\langle\varepsilon^{\mathrm{V}}\rangle = \frac{hc\tilde{\nu}}{\mathrm{e}^{\beta hc\tilde{\nu}}-1}$$

Harmonic approximation Mean vibrational energy (53.8)

The zero-point energy, $\frac{1}{2}hc\tilde{\nu}$, can be added to the right-hand side if the mean energy is to be measured from 0 rather than the lowest attainable level (the zero-point level). The variation of the mean energy with temperature is illustrated in Fig. 53.3.

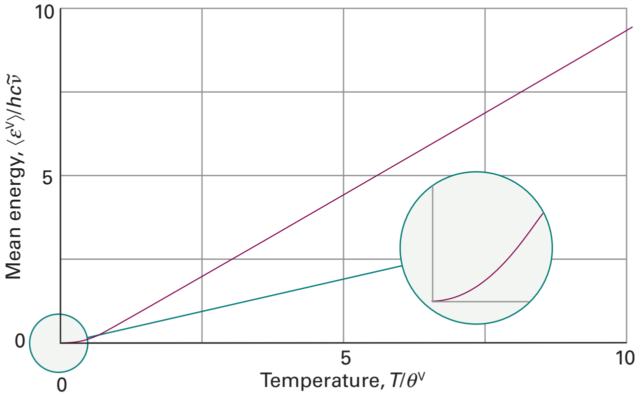

Figure 53.3 The mean vibrational energy of a molecule in the harmonic approximation as a function of temperature. At high temperatures ($T \gg \theta^V$), the energy is linearly proportional to the temperature, in accord with the equipartition theorem.

At high temperatures, when $T \gg \theta^V$, or $\beta hc\tilde{\nu} \ll 1$ (from Topic 52, $\theta^V = hc\tilde{\nu}/k$), the exponential functions can be expanded ($e^x = 1 + x + \cdots$) and all but the leading terms discarded. This approximation leads to

$$\langle \varepsilon^V \rangle = \frac{hc\tilde{\nu}}{(1+\beta hc\tilde{\nu}+\cdots)-1} \approx \frac{1}{\beta} = kT \qquad (53.9)$$

High-temperature approximation ($T \gg \theta^V$) Mean vibrational energy

This result is in agreement with the value predicted by the classical equipartition theorem, because the energy of a one-dimensional oscillator is $E = \frac{1}{2}mv_x^2 + \frac{1}{2}k_f x^2$ and the mean energy of each quadratic term is is $\frac{1}{2}kT$. Bear in mind, however, that the condition $T \gg \theta^V$ is rarely satisfied.

Brief illustration 53.4 The mean vibrational energy

To calculate the mean vibrational energy of I_2 molecules at 298.15 K we note from Table 43.1 that their vibrational wavenumber is 214.6 cm^{-1}. Then, because, at 298.15 K, $kT/hc = 207.224\,\text{cm}^{-1}$, from eqn 53.8 with

$$\beta\varepsilon = \frac{hc\tilde{\nu}}{kT} = \frac{214.6\,\text{cm}^{-1}}{207.244\,\text{cm}^{-1}} = 1.036$$

it follows that

$$\langle \varepsilon^V \rangle / hc = \frac{214.6\,\text{cm}^{-1}}{e^{1.036}-1} = 118.0\,\text{cm}^{-1}$$

The addition of the zero-point energy (corresponding to $\frac{1}{2} \times 214.6\,\text{cm}^{-1}$) increases this value to 225.3 cm^{-1}. The equipartition result is 207.224 cm^{-1} the discrepancy reflecting the fact that in this case it is not true that $T \gg \theta^V$ and (as deduced in *Brief illustration* 52.5) only the ground and first excited states are significantly populated.

Self-test 53.4 What must the temperature be before the energy estimated from the equipartition theorem is within 2 per cent of the energy given by eqn 53.8?

Answer: 625 K; use a spreadsheet

When there are several normal modes that can be treated as harmonic, the overall vibrational partition function is the product of each individual partition function, and the total mean vibrational energy is the sum of the mean energies of each mode.

53.5 The electronic contribution

We shall consider two types of electronic contribution: one arising from the electronically excited states of a molecule and one from the spin contribution.

In most cases of interest, the electronic states of atoms and molecules are so widely separated that only the electronic ground state is occupied. As we are adopting the convention that all energies are measured from the ground state of each mode, we can write

$$\langle \varepsilon^E \rangle = 0 \qquad (53.10)$$

Mean electronic energy

In certain cases, there are thermally accessible states at the temperature of interest. In that case the partition function and hence the mean electronic energy are best calculated by direct summation over the available states. Care must be taken to take any degeneracies into account, as we illustrate in Example 53.1.

Example 53.1 Calculating the electronic contribution to the energy

A certain atom has a doubly degenerate electronic ground state and a fourfold degenerate excited state at 600 cm^{-1} above the ground state. What is its mean electronic energy at 25 °C expressed as a wavenumber?

Method Write down the expression for the partition function at a general temperature T (in terms of β) and then derive the mean energy by differentiating with respect to β. Finally, substitute the data. Use $\varepsilon = hc\tilde{\nu}$, $\langle \varepsilon^E \rangle = hc\langle \tilde{\nu}^E \rangle$, and $kT/hc = 207.226\,\text{cm}^{-1}$ at 25 °C.

Answer The partition function is

$$q^E = 2 + 4e^{-\beta\varepsilon}$$

The mean energy is therefore

$$\langle \varepsilon^{\mathrm{E}} \rangle = -\frac{1}{q^{\mathrm{E}}}\frac{\mathrm{d}q^{\mathrm{E}}}{\mathrm{d}\beta} = -\frac{1}{2+4\mathrm{e}^{-\beta\varepsilon}}\overbrace{\frac{\mathrm{d}}{\mathrm{d}\beta}(2+4\mathrm{e}^{-\beta\varepsilon})}^{-4\varepsilon\mathrm{e}^{-\beta\varepsilon}}$$

$$= \frac{4\varepsilon\mathrm{e}^{-\beta\varepsilon}}{2+4\mathrm{e}^{-\beta\varepsilon}} = \frac{\varepsilon}{\frac{1}{2}\mathrm{e}^{\beta\varepsilon}+1}$$

and expressed as a wavenumber

$$\langle \tilde{\nu}^{\mathrm{E}} \rangle = \frac{\tilde{\nu}}{\frac{1}{2}\mathrm{e}^{hc\tilde{\nu}/kT}+1}$$

From the data,

$$\langle \tilde{\nu}^{\mathrm{E}} \rangle = \frac{600\,\mathrm{cm}^{-1}}{\frac{1}{2}\mathrm{e}^{600/207.226}+1} = 59.7\,\mathrm{cm}^{-1}$$

Self-test 53.5 Repeat the problem for an atom that has a threefold degenerate ground state and a sevenfold degenerate excited state 400 cm^{-1} above.

Answer: 101 cm^{-1}

An electron spin in a magnetic field $\mathcal{B}$ has two possible energy states that depend on its orientation as expressed by the magnetic quantum number m_s and which are given by

$$E_{m_s} = 2\mu_{\mathrm{B}}\mathcal{B}m_s \qquad \text{Electron spin energies} \qquad (53.11)$$

where μ_{B} is the Bohr magneton (see inside the front cover). These energies are discussed in more detail in Topic 50, where we see that the integer 2 needs to be replaced by a number very close to 2. The lower state has $m_s = -\frac{1}{2}$, so the two energy levels available to the electron lie (according to our convention) at $\varepsilon_{-1/2} = 0$ and at $\varepsilon_{+1/2} = 2\mu_{\mathrm{B}}\mathcal{B}$. The spin partition function is therefore

$$q^{\mathrm{S}} = \sum_{m_s} \mathrm{e}^{-\beta\varepsilon_{m_s}} = 1+\mathrm{e}^{-2\beta\mu_{\mathrm{B}}\mathcal{B}} \qquad \text{Spin partition function} \qquad (53.12)$$

The mean energy of the spin is therefore

$$\langle \varepsilon^{\mathrm{S}} \rangle = -\frac{1}{q^{\mathrm{S}}}\frac{\mathrm{d}q^{\mathrm{S}}}{\mathrm{d}\beta} = -\frac{1}{1+\mathrm{e}^{-2\beta\mu_{\mathrm{B}}\mathcal{B}}}\overbrace{\frac{\mathrm{d}}{\mathrm{d}\beta}(1+\mathrm{e}^{-2\beta\mu_{\mathrm{B}}\mathcal{B}})}^{-2\mu_{\mathrm{B}}\mathcal{B}\mathrm{e}^{-2\beta\mu_{\mathrm{B}}B}}$$

$$= \frac{2\mu_{\mathrm{B}}\mathcal{B}\mathrm{e}^{-2\beta\mu_{\mathrm{B}}\mathcal{B}}}{1+\mathrm{e}^{-2\mu_{\mathrm{B}}\mathcal{B}}}$$

That is,

$$\langle \varepsilon^{\mathrm{S}} \rangle = \frac{2\mu_{\mathrm{B}}\mathcal{B}}{\mathrm{e}^{2\beta\mu_{\mathrm{B}}\mathcal{B}}+1} \qquad \text{Mean spin energy} \qquad (53.13)$$

This function is essentially the same as that plotted in Fig. 53.1.

Brief illustration 53.5 The spin contribution to the energy

Suppose a collection of radicals is exposed to a magnetic field of 2.5 T (T denotes tesla). With $\mu_{\mathrm{B}} = 9.274 \times 10^{-24}\,\mathrm{J\,T^{-1}}$ and a temperature of 25 °C,

$$2\mu_{\mathrm{B}}\mathcal{B} = 2\times(9.274\times10^{-24}\,\mathrm{J\,T^{-1}})\times2.5\,\mathrm{T} = 4.6\ldots\times10^{-23}\,\mathrm{J}$$

$$2\beta\mu_{\mathrm{B}}\mathcal{B} = \frac{2\times(9.274\times10^{-24}\,\mathrm{J\,T^{-1}})\quad(2.5\,\mathrm{T})}{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})} = 0.011\ldots$$

The mean energy is therefore

$$\langle \varepsilon^{\mathrm{S}} \rangle = \frac{4.6\ldots\times10^{-23}\,\mathrm{J}}{\mathrm{e}^{0.011\ldots}+1} = 2.3\times10^{-23}\,\mathrm{J}$$

This energy is equivalent to 14 J mol^{-1} (note joules, not kilojoules).

Self-test 53.6 Repeat the calculation for a species with $S=1$ in the same magnetic field.

Answer: 0.0046 zJ, 28 J mol^{-1}

Checklist of concepts

☐ 1. The **mean molecular energy** can be calculated from the molecular partition function (see the following list of equations).

☐ 2. The (classical) **equipartition theorem** states that, for a collection of particles at thermal equilibrium at a temperature T, the average value of each quadratic contribution to the energy is the same and equal to $\frac{1}{2}kT$.

Checklist of equations

Property	Equation	Comment	Equation number
Mean energy	$\langle\varepsilon\rangle=\varepsilon_{\text{gs}}-(1/q)(\partial q/\partial\beta)_V$		53.4a
	$\langle\varepsilon\rangle=\varepsilon_{\text{gs}}-(\partial\ln q/\partial\beta)_V$	Alternative version	53.4b
Translation	$\langle\varepsilon^{\text{T}}\rangle=\frac{d}{2}kT$	In *d* dimensions	53.5
Rotation	$\langle\varepsilon^{\text{R}}\rangle=kT$	Linear molecule, $T\gg\theta^{\text{R}}$	53.6b
	$\langle\varepsilon^{\text{R}}\rangle=\frac{3}{2}kT$	Nonlinear molecule, $T\gg\theta^{\text{R}}$; see *Brief illustration* 53.3	
Vibration	$\langle\varepsilon^{\text{V}}\rangle=hc\tilde{\nu}/(\text{e}^{\beta hc\tilde{\nu}}-1)$	Harmonic approximation	53.8
	$\langle\varepsilon^{\text{V}}\rangle=kT$	$T\gg\theta^{\text{V}}$	53.9

TOPIC 54

The canonical ensemble

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➤ Why do you need to know this material?

Whereas the derivation of the molecular partition function (Topic 52) deals with independent molecules, in practice, molecules do interact. So, this material is essential for constructing models of real gases, liquids, and solids and of any system in which intermolecular interactions cannot be neglected.

➤ What is the key idea?

A system composed of interacting molecules is described in terms of a canonical partition function, from which its thermodynamic properties may be deduced.

➤ What do you need to know already?

This material draws on the calculations in Topic 52: the calculations here are analogous to those, and are not repeated in detail. This Topic also draws on the calculation of energies from partition functions (Topic 53); here too the calculations are analogous to those presented in that Topic.

Topic 52 deals with a system composed of independent molecules. Here we consider the formalism appropriate to systems in which the molecules interact with one another, as in real gases and liquids. The crucial concept we need when treating systems of interacting particles is the 'ensemble'. Like so many scientific terms, the term has basically its normal meaning of 'collection', but it has been sharpened and refined into a precise significance.

The expressions presented in this Topic are the analogues of those derived in Topics 52 and 53, and details of the calculations are found there. The implementation of the equations, however, is much more difficult, and except in certain cases is best left to specialized texts. This Topic is included principally for the sake of completeness and as the endpoint of our journey laying the foundations of statistical thermodynamics.

54.1 The concept of ensemble

To set up an ensemble, we take a closed system of specified volume, composition, and temperature and think of it as replicated $\tilde{N}$ times (Fig. 54.1). All the identical closed systems are regarded as being in thermal contact with one another, so they can exchange energy. The total energy of all the systems is $\tilde{E}$ and, because they are in thermal equilibrium with one another, they all have the same temperature, T. The volume of each member of the ensemble is the same, so the energy levels available to the molecules are the same in each system, and each member contains the same number of molecules, so there is a fixed number of molecules to distribute within each system. This imaginary collection of replications of the actual system with a common temperature is called the **canonical ensemble**. The word 'canonical' means 'according to a rule'.

There are two other important ensembles. In the **microcanonical ensemble** the condition of constant temperature is replaced by the requirement that all the systems should have exactly the same energy: each system is individually isolated. In the **grand canonical ensemble** the volume and temperature of each system is the same, but they are open, which means that matter can be imagined as able to pass between the systems; the

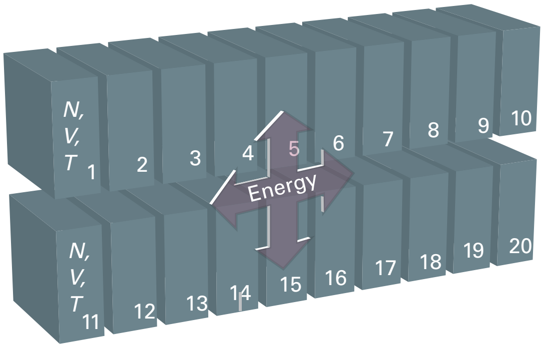

Figure 54.1 A representation of the canonical ensemble, in this case for $\tilde{N}=20$. The individual replications of the actual system all have the same composition and volume. They are all in mutual thermal contact, and so all have the same temperature. Energy may be transferred between them as heat, and so they do not all have the same energy. The total $\tilde{E}$ of all 20 replications is a constant because the ensemble is isolated overall.

composition of each one may fluctuate, but now the property known as the chemical potential, μ (which is described in Topic 69), is the same in each system:

Microcanonical ensemble: N, V, E common
Canonical ensemble: N, V, T common
Grand canonical ensemble: μ, V, T common

The microcanonical ensemble is the basis of the discussion in Topic 51 (but not so called there); we shall not consider the grand canonical ensemble explicitly.

The important point about an ensemble is that it is a collection of *imaginary* replications of the system, so we are free to let the number of members be as large as we like; when appropriate, we can let $\tilde{N}$ become infinite. The number of members of the ensemble in a state with energy E_i is denoted $\tilde{N}_i$, and we can speak of the configuration of the ensemble (by analogy with the configuration of the system used in Topic 51) and its weight, $\tilde{W}$. Note that $\tilde{N}$ is unrelated to N, the number of molecules in the actual system; $\tilde{N}$ is the number of *imaginary* replications of that system.

(a) Dominating configurations

Just as in Topic 51, some of the configurations of the canonical ensemble will be very much more probable than others. For instance, it is very unlikely that the whole of the total energy, $\tilde{E}$, will accumulate in one system. By analogy with the discussion in Topic 51, we can anticipate that there will be a dominating configuration, and that we can evaluate the thermodynamic properties by taking the average over the ensemble using that single, most probable, configuration. In the **thermodynamic limit** of $\tilde{N}\to\infty$, this dominating configuration is overwhelmingly the most probable, and it dominates the properties of the system virtually completely.

The quantitative discussion follows the argument in Topic 51 with the modification that N and N_i are replaced by $\tilde{N}$ and $\tilde{N}_i$. The weight $\tilde{\mathcal{W}}$ of a configuration $\{\tilde{N}_0,\tilde{N}_1,\ldots\}$ is

$$\tilde{\mathcal{W}}=\frac{\tilde{N}!}{\tilde{N}_1!\tilde{N}_2!\cdots} \qquad \text{Weight} \qquad (54.1)$$

The configuration of greatest weight, subject to the constraints that the total energy of the ensemble is constant at $\tilde{E}$ and that the total number of members is fixed at $\tilde{N}$, is given by the **canonical distribution**:

$$\frac{\tilde{N}_i}{\tilde{N}}=\frac{e^{-\beta E_i}}{Q} \qquad \text{Canonical distribution} \qquad (54.2a)$$

where

$$Q=\sum_i e^{-\beta E_i} \qquad \text{Canonical partition function} \qquad (54.2b)$$

in which the sum is over all members of the ensemble, each one having an energy E_i. The quantity Q, which is a function of the temperature, is called the **canonical partition function**. Like the molecular partition function, the canonical partition function contains all the thermodynamic information about a system, but in this case allowing for the possibility of interactions between the constituent molecules.

Brief illustration 54.1 The canonical distribution

Suppose that we are considering a sample of a monatomic real gas that contains 1.00 mol atoms. Then at 298 K its total energy is close to $\frac{3}{2}nRT=\frac{3}{2}(1.00\,\text{mol})\times 8.3145\,\text{J K}^{-1}\text{mol}^{-1})\times(298\,\text{K})=3.72\,\text{kJ}$. Suppose that for an instant the molecules are present at separations where the total energy is 3.72 kJ and an instant later are present at separations where the total energy is lower than 3.72 kJ by 0.000 000 01 per cent (that is, by 3.72×10^{-7} J). To predict the ratio of numbers of members of the ensemble with these two energies we use eqn 54.2 in the form

$$\frac{\tilde{N}(\text{lower})}{\tilde{N}(\text{higher})}=e^{-(-3.70\times10^{-7}\,\text{J})/(1.381\times10^{-23}\,\text{J K}^{-1})\times(298\,\text{K})}$$
$$=e^{3.33\times10^{7}}$$

At first sight, the number of members that have the lower energy vastly outweighs the number with the higher energy. Why that is not necessarily the case is explained below.

Self-test 54.1 Repeat the calculation for members of the same ensemble with energies that differ by 1.0×10^{-20} per cent.

Answer: $\tilde{N}(\text{lower})/\tilde{N}(\text{higher})=e^{90}\approx1\times10^{39}$

(b) Fluctuations from the most probable distribution

The canonical distribution in eqn 54.2 is only apparently an exponentially decreasing function of the energy of the system. We must appreciate that the equation gives the probability of occurrence of members in a single state i of the entire system of energy E_i. There may in fact be numerous states with almost identical energies. For example, in a gas the identities of the molecules moving slowly or quickly can change without necessarily affecting the total energy. The **density of states**, the number of states in an energy range divided by the width of the range (Fig. 54.2), is a very sharply increasing function of energy. It follows that the probability of a member of an ensemble having a specified energy (as distinct from being in a specified state) is given by eqn 54.2, a sharply decreasing function, multiplied by a sharply increasing function (Fig. 54.3). Therefore, the overall distribution is a sharply peaked function. We conclude that most members of the ensemble have an energy very close to the mean value.

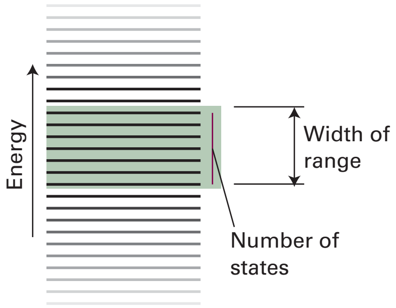

Figure 54.2 The energy density of states is the number of states in an energy range divided by the width of the range.

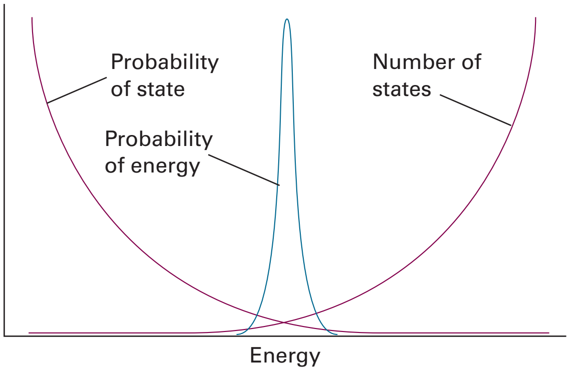

Figure 54.3 To construct the form of the distribution of members of the canonical ensemble in terms of their energies, we multiply the probability that any one is in a state of given energy, eqn 54.2, by the number of states corresponding to that energy (a steeply rising function). The product is a sharply peaked function at the mean energy, which shows that almost all the members of the ensemble have that energy.

Brief illustration 54.2 The role of the density of states

A function that increases rapidly is x^N, with N a large value. A function that decreases rapidly is e^{-Nx}, once again with N a large value. The product of these two functions, normalized so that their maxima coincide,

$$f(x) = e^N x^N e^{-Nx}$$

is plotted for three values of N in Fig. 54.4. We see that the width of the product does indeed decrease as N increases.

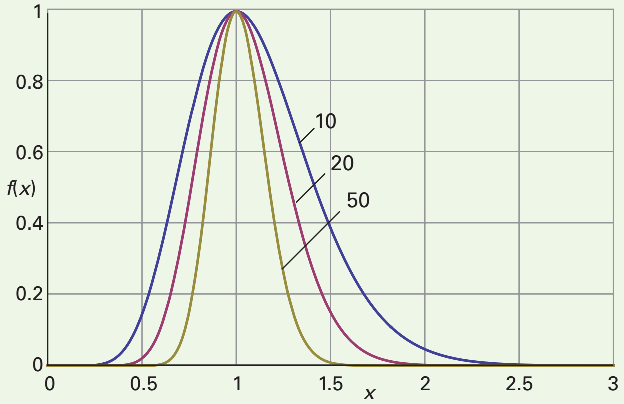

Figure 54.4 The product of the two functions discussed in *Brief illustration* 54.2, for three different values of N.

Self-test 54.2 Show that the product of the functions x^{2N} and e^{-Nx}, suitably normalized, behaves similarly.

Answer: Plot $f(x) = (1/2)^{2N} e^{2N} x^{2N} e^{-Nx}$ for $0 \le x \le 4$

54.2 The mean energy of a system

Just as the molecular partition function can be used to calculate the mean value of a molecular property, so the canonical partition function can be used to calculate the mean energy of an entire system composed of molecules (that might or might not be interacting with one another). Thus, Q is more general than q because it does not assume that the molecules are independent. We can therefore use Q to discuss the properties of condensed phases and real gases where molecular interactions are important.

If the total energy of the ensemble is $\tilde{E}$, and there are $\tilde{N}$ members, the average energy of a member is $\langle E \rangle = \tilde{E}/\tilde{N}$. Because the fraction, $\tilde{p}_i$, of members of the ensemble in a state i with energy E_i is given by the analogue of eqn 51.6 ($N_i/N = e^{-\beta\varepsilon_i}/\sum_i e^{-\beta\varepsilon_i}$ written as $p_i = e^{-\beta\varepsilon_i}/q$) as

$$\tilde{p}_i = \frac{e^{-\beta E_i}}{Q} \tag{54.3}$$

it follows that

$$\langle E\rangle=\sum_i p_i E_i=\frac{1}{Q}\sum_i E_i \mathrm{e}^{-\beta E_i} \qquad (54.4)$$

By the same argument that led to eqn 53.4,

$$\langle E\rangle=-\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_V=-\left(\frac{\partial \ln Q}{\partial \beta}\right)_V \qquad (54.5)$$

Mean energy of a system

As in the case of the mean molecular energy, we must add to this expression the ground-state energy of the entire system if that is not zero.

Brief illustration 54.3 The expression for the energy

If the canonical partition function is a product of the molecular partition function of each molecule (which we see below is the case when the N molecules of the system are independent), then we can write $Q=q^N$, and infer that the energy of the system is

$$\langle E\rangle=-\frac{1}{q^N}\left(\frac{\partial q^N}{\partial \beta}\right)_V=-\frac{Nq^{N-1}}{q^N}\left(\frac{\partial q}{\partial \beta}\right)_V=-\frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V=N\langle \varepsilon\rangle$$

That is, the mean energy of the system is N times the mean energy of a single molecule.

Self-test 54.3 Confirm that the same expression is obtained if $Q=q^N/N!$, which is another case described below.

54.3 Independent molecules revisited

We shall now see how to recover the molecular partition function from the more general canonical partition function when the molecules are independent. When the molecules are independent and distinguishable (in the sense to be described), the relation between Q and q is

$$Q=q^N \qquad (54.6)$$

Justification 54.1 The relation between Q and q

The total energy of a collection of N independent molecules is the sum of the energies of the molecules. Therefore, we can write the total energy of a state i of the system as

$$E_i=\varepsilon_i(1)+\varepsilon_i(2)+\cdots+\varepsilon_i(N)$$

In this expression, $\varepsilon_i(1)$ is the energy of molecule 1 when the system is in the state i, $\varepsilon_i(2)$ the energy of molecule 2 when the system is in the same state i, and so on. The canonical partition function is then

$$Q=\sum_i \mathrm{e}^{-\beta\varepsilon_i(1)-\beta\varepsilon_i(2)-\cdots-\beta\varepsilon_i(N)}$$

The sum over the states of the system can be reproduced by letting each molecule enter all its own individual states (although we meet an important proviso shortly). Therefore, instead of summing over the states i of the system, we can sum over all the individual states j of molecule 1, all the states j of molecule 2, and so on. This rewriting of the original expression leads to

$$Q=\left(\sum_j \mathrm{e}^{-\beta\varepsilon_j}\right)\left(\sum_j \mathrm{e}^{-\beta\varepsilon_j}\right)\cdots\left(\sum_j \mathrm{e}^{-\beta\varepsilon_j}\right)=q^N$$

If all the molecules are identical and free to move through space, we cannot distinguish them and the relation $Q=q^N$ is not valid. Suppose that molecule 1 is in some state a, molecule 2 is in b, and molecule 3 is in c, then one member of the ensemble has an energy $E=\varepsilon_a+\varepsilon_b+\varepsilon_c$. This member, however, is indistinguishable from one formed by putting molecule 1 in state b, molecule 2 in state c, and molecule 3 in state a, or some other permutation. There are six such permutations in all, and $N!$ in general. In the case of indistinguishable molecules, it follows that we have counted too many states in going from the sum over system states to the sum over molecular states, so writing $Q=q^N$ overestimates the value of Q. The detailed argument is quite involved, but at all except very low temperatures it turns out that the correction factor is $1/N!$. Therefore:

$$\text{For distinguishable independent molecules}: Q=q^N \qquad (54.7\text{a})$$

$$\text{For indistinguishable independent molecules}: Q=q^N/N! \qquad (54.7\text{b})$$

At low temperatures, where only a few states are thermally accessible, account must be taken of the role of the Pauli principle in governing the occupation of states. This is the role of **Bose–Einstein statistics** (for bosons) and **Fermi–Dirac statistics** (for fermions), both of which are beyond the scope of this discussion.

Brief illustration 54.4 Indistinguishability

For molecules to be indistinguishable, they must be of the same kind: an Ar atom is never indistinguishable from a Ne atom. Their identity, however, is not the only criterion. Each identical molecule in a crystal lattice, for instance, can be 'named' with a set of coordinates. Identical molecules in a lattice can therefore be treated as distinguishable because their sites are distinguishable, and we use eqn 54.7b. On the other hand, identical molecules in a gas are free to move to different locations, and there is no way of keeping track of the identity of a given molecule; we therefore use eqn 54.7b.

Self-test 54.4 Are identical molecules in a liquid indistinguishable?

Answer: Yes

54.4 The variation of energy with volume

When there are interactions between molecules, the energy of a collection depends on the average distance between them, and therefore on the volume that a fixed number occupy. This dependence on volume is particularly important for the discussion of real gases (Topic 36), but we have enough information to establish the dependence here.

We need to evaluate $(\partial\langle E\rangle/\partial V)_T$, the variation in energy of a system with volume at constant pressure. (In Topic 36, this quantity is identified with the 'internal pressure' of a gas and denoted π_T.) To proceed, we substitute eqn 54.5 and obtain

$$\left(\frac{\partial E}{\partial V}\right)_T = -\left(\frac{\partial}{\partial V}\left(\frac{\partial \ln Q}{\partial \beta}\right)_V\right)_T \qquad (54.8)$$

We need to consider the translational contribution to Q since translational energy levels depend on volume, but to develop eqn 54.8 we also need to find a way to build an intermolecular potential energy into the expression for Q.

The total kinetic energy of a gas is the sum of the kinetic energies of the individual molecules. Therefore, even in a real gas the canonical partition function factorizes into a part arising from the kinetic energy, which for the perfect gas is $Q = V^N/\Lambda^{3N}N!$, where Λ is the thermal wavelength, eqn 52.7b, and a factor called the **configuration integral**, $\mathcal{Z}$, which depends on the intermolecular potentials (don't confuse this $\mathcal{Z}$ with the compression factor in Topic 36). We therefore write

$$Q = \frac{\mathcal{Z}}{\Lambda^{3N}} \qquad (54.9)$$

with $\mathcal{Z}$ replacing $V^N/N!$, and expect $\mathcal{Z}$ to equal $V^N/N!$ for a perfect gas (see *Brief illustration* 54.5). It then follows that

$$\left(\frac{\partial E}{\partial V}\right)_T = -\left(\frac{\partial}{\partial V}\left(\frac{\partial \ln(\mathcal{Z}/\Lambda^{3N})}{\partial \beta}\right)_V\right)_T$$

$$= -\left(\frac{\partial}{\partial V}\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_V\right)_T - \left(\frac{\partial}{\partial \beta}\overbrace{\left(\frac{\partial \ln(1/\Lambda^{3N})}{\partial V}\right)_T}^{0}\right)_V \qquad (54.10)$$

$$= -\left(\frac{\partial}{\partial V}\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_V\right)_T = -\left(\frac{\partial}{\partial V}\frac{1}{\mathcal{Z}}\left(\frac{\partial \mathcal{Z}}{\partial \beta}\right)_V\right)_T$$

In the second line, we have used the relation $(\partial^2 f/\partial x\partial y) = (\partial^2 f/\partial y\partial x)$ and then noted that Λ is independent of volume, so its derivative with respect to volume is zero.

For a real gas of atoms (for which the intermolecular interactions are isotropic), $\mathcal{Z}$ is related to the total potential energy E_P of interaction of all the particles, which depends on all their relative locations, by

$$\mathcal{Z} = \frac{1}{N!}\int \mathrm{e}^{-\beta E_\mathrm{P}}\,\mathrm{d}\tau_1\mathrm{d}\tau_2\cdots\mathrm{d}\tau_N \qquad \text{Configuration integral} \qquad (54.11)$$

where $\mathrm{d}\tau_i$ is the volume element for atom i. The physical origin of this term is that the probability of occurrence of each arrangement of molecules possible in the sample is given by a Boltzmann distribution in which the exponent is given by the potential energy corresponding to that arrangement.

Brief illustration 54.5 A configuration integral

Equation 54.11 is very difficult to manipulate in practice, even for quite simple intermolecular potentials, except for a perfect gas for which $E_\mathrm{P} = 0$. In that case, the exponential function becomes 1 and

$$\mathcal{Z} = \frac{1}{N!}\int \mathrm{d}\tau_1\mathrm{d}\tau_2\cdots\mathrm{d}\tau_N = \frac{1}{N!}\left(\int \mathrm{d}\tau\right)^N = \frac{V^N}{N!}$$

just as it should be for a perfect gas.

Self-test 54.5 Go on to show that, for a perfect gas, $\left(\partial\langle E\rangle/\partial V\right)_T = 0$.

Answer: $\mathcal{Z}$ in this case is independent of temperature

If the potential has the form of a central hard sphere surrounded by a shallow attractive well (Fig. 54.5), then detailed calculation, which is too involved to reproduce here, leads to

$$\left(\frac{\partial\langle E\rangle}{\partial V}\right)_T = \frac{an^2}{V^2} \qquad \text{Attractive potential} \qquad (54.12)$$

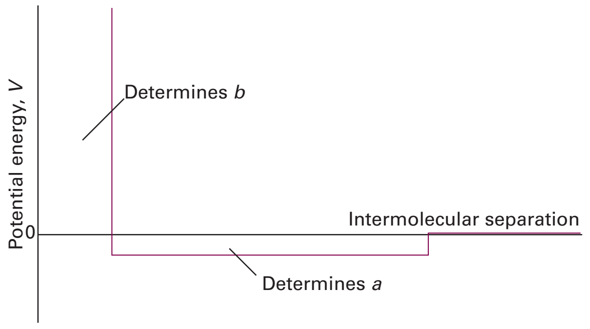

Figure 54.5 The van der Waals equation of state (Topic 36) can be derived on the basis that the intermolecular potential energy has a hard core of range b surrounded by a long-range, shallow attractive well with an area proportional to a.

where n is the amount of molecules present in the volume V and a is a constant that is proportional to the area under the attractive part of the potential. In Topic 36 we see that exactly the same expression is implied by the van der Waals equation of state. At this point we can conclude that if there are attractive interactions between molecules in a gas, then its energy increases as it expands isothermally (because $(\partial\langle E\rangle/\partial V)_T > 0$, and the slope of $\langle E\rangle$ with respect to V is positive). The energy rises because, at greater average separations, the molecules spend less time in regions where they interact favourably.

Checklist of concepts

☐ 1. The **canonical ensemble** is an imaginary collection of replications of the actual system with a common temperature.

☐ 2. The **canonical distribution** gives the number of members of the ensemble with a specified total energy.

☐ 3. The **mean energy** of the members of the ensemble can be calculated from the canonical partition function.

Checklist of equations

Property	Equation	Comment	Equation number
Canonical distribution	$\tilde{N}_i/\tilde{N} = e^{-\beta E_i}/Q$		54.2a
Canonical partition function	$Q = \sum_i e^{-\beta E_i}$	Definition	54.2b
Mean energy	$\langle E\rangle = -(1/Q)(\partial Q/\partial\beta)_V = -(\partial \ln Q/\partial\beta)_V$		54.5
Configuration integral	$Q = Z/\Lambda^{3N}$		54.9
	$Z = (1/N!)\int e^{-\beta E_p} d\tau_1 d\tau_2 \cdots d\tau_N$	Isotropic interaction	54.11
Variation of mean energy with volume	$(\partial\langle E\rangle/\partial V)_T = an^2/V^2$	van der Waals gas; 0 for a perfect gas	54.12

Focus 11 on Statistical thermodynamics

Assume that all gases are perfect and that data refer to 298 K unless otherwise stated.

Topic 51 The Boltzmann distribution

Discussion questions

51.1 Discuss the relationship between 'population', 'configuration', and 'weight'. What is the significance of the most probable configuration?

51.2 What is the significance and importance of the principle of equal *a priori* probabilities?

51.3 What is temperature?

51.4 Summarize the role of the Boltzmann distribution in chemistry.

Exercises

51.1(a) Calculate the weight of the configuration in which 16 objects are distributed in the arrangement 0, 1, 2, 3, 8, 0, 0, 0, 0, 2.
51.1(b) Calculate the weight of the configuration in which 21 objects are distributed in the arrangement 6, 0, 5, 0, 4, 0, 3, 0, 2, 0, 0, 1.

51.2(a) Evaluate 8! by using (a) the exact formula; (b) Stirling's approximation, eqn 51.2b; (c) the more accurate version of Stirling's approximation, eqn 51.2a.
51.2(b) Evaluate 10! by using (a) the exact formula; (b) Stirling's approximation, eqn 51.2b; (c) the more accurate version of Stirling's approximation, eqn 51.2a.

51.3(a) What are the relative populations of the states of a two-level system when the temperature is infinite?
51.3(b) What are the relative populations of the states of a two-level system as the temperature approaches zero?

51.4(a) What is the temperature of a two-level system of energy separation equivalent to 400 cm^{-1} when the population of the upper state is one-third that of the lower state?

51.4(b) What is the temperature of a two-level system of energy separation equivalent to 300 cm^{-1} when the population of the upper state is one-half that of the lower state?

51.5(a) Calculate the relative populations of a linear rotor in the levels with $J=0$ and $J=5$, given that $\tilde{B}=2.71\,\text{cm}^{-1}$ and a temperature of 298 K.
51.5(b) Calculate the relative populations of a spherical rotor in the levels with $J=0$ and $J=5$, given that $\tilde{B}=2.71\,\text{cm}^{-1}$ and a temperature of 298 K.

51.6(a) A certain molecule has a non-degenerate excited state lying at 540 cm^{-1} above the non-degenerate ground state. At what temperature will 10 per cent of the molecules be in the upper state?
51.6(b) A certain molecule has a doubly degenerate excited state lying at 360 cm^{-1} above the non-degenerate ground state. At what temperature will 15 per cent of the molecules be in the upper state?

Problems

51.1 A sample consisting of five molecules has a total energy 5ε. Each molecule is able to occupy states of energy $j\varepsilon$, with $j=0, 1, 2, \ldots$. (a) Calculate the weight of the configuration in which the molecules are distributed evenly over the available states. (b) Draw up a table with columns headed by the energy of the states and write beneath them all configurations that are consistent with the total energy. Calculate the weights of each configuration and identify the most probable configurations.

51.2 A sample of nine molecules is numerically tractable but on the verge of being thermodynamically significant. Draw up a table of configurations for $N=9$, total energy 9ε, in a system with energy levels $j\varepsilon$ (as in Problem 51.1). Before evaluating the weights of the configurations, guess (by looking for the most 'exponential' distribution of populations) which of the configurations will turn out to be the most probable. Go on to calculate the weights and identify the most probable configuration.

51.3 Use mathematical software to evaluate $\mathcal{W}$ for $N=20$ for a series of distributions over a uniform ladder of energy levels, ensuring that the total energy is constant. Identify the configuration of greatest weight and compare it to the distribution predicted by the Boltzmann expression. Explore what happens as the value of the total energy is changed.

51.4 A certain atom has a doubly degenerate ground level pair and an upper level of four degenerate states at 450 cm^{-1} above the ground level. In an atomic-beam study of the atoms it was observed that 30 per cent of the atoms were in the upper level, and the translational temperature of the beam was 300 K. Are the electronic states of the atoms in thermal equilibrium with the translational states?

51.5 Explore the consequences of using the full version of Stirling's approximation (eqn 51.2a), $x!\approx(2\pi)^{1/2}x^{x+1/2}\mathrm{e}^{-x}$, in the development of the expression for the configuration of greatest weight. Does the more accurate approximation have a significant effect on the form of the Boltzmann distribution?

51.6 The most probable configuration is characterised by a parameter we know as the 'temperature'. The temperatures of the system specified in Problems 51.1 and 51.2 must be such as to give a mean value of ε for the energy of each molecule and a total energy $N\varepsilon$ for the system. (a) Show that the temperature can be obtained by plotting p_j against j, where p_j is the (most probable) fraction of molecules in the state with energy $j\varepsilon$. Apply the procedure to the system in Problem 51.2. What is the temperature of the system when ε corresponds to 50 cm^{-1}? (b) Choose configurations other than the most probable, and show that the same procedure gives a worse straight line, indicating that a temperature is not well defined for them.

51.7‡ The variation of the atmospheric pressure p with altitude h is predicted by the *barometric formula* to be $p=p_0e^{-h/H}$, where p_0 is the pressure at sea level and $H=RT/Mg$ with M the average molar mass of air and T the average temperature. Obtain the barometric formula from the Boltzmann distribution. Recall that the potential energy of a particle at height h above the surface of the Earth is mgh. Convert the barometric formula from pressure to number density, $\mathcal{N}$. Compare the relative number densities, $\mathcal{N}(h)/\mathcal{N}(0)$, for O_2 and H_2O at $h=8.0$ km, a typical cruising altitude for commercial aircraft.

51.8‡ Planets lose their atmospheres over time unless they are replenished. A complete analysis of the overall process is very complicated and depends upon the radius of the planet, temperature, atmospheric composition, and other factors. Prove that the atmosphere of planets cannot be in an equilibrium state by demonstrating that the Boltzmann distribution leads to a uniform finite number density as $r\to\infty$. *Hint*: Recall that in a gravitational field the potential energy is $V(r)=-GMm/r$, where G is the gravitational constant, M is the mass of the planet, and m is the mass of the particle.

51.9 Consider a protein P with four distinct sites, with each site capable of binding one ligand L. Show that the possible varieties ('configurations') of the species PL_i (with PL_0 denoting P) are given by the binomial coefficients (for binomial coefficients, see *Mathematical background* 7).

Topic 52 Partition functions

Discussion questions

52.1 Describe the physical significance of the partition function.

52.2 Describe how the mean energy of a system composed of two levels varies with temperature.

52.3 What is the difference between a 'state' and an 'energy level'? Why is it important to make this distinction?

52.4 Why and when is it necessary to include a symmetry number in the calculation of a partition function?

Exercises

52.1(a) Calculate (a) the thermal wavelength, (b) the translational partition function at (i) 300 K and (ii) 3000 K of a molecule of molar mass 150 g mol^{-1} in a container of volume 1.00 cm^3.
52.1(b) Calculate (a) the thermal wavelength, (b) the translational partition function of a Ne atom in a cubic box of side 1.00 cm at (i) 300 K and (ii) 3000 K.

52.2(a) Calculate the ratio of the translational partition functions of H_2 and He at the same temperature and volume.
52.2(b) Calculate the ratio of the translational partition functions of Ar and Ne at the same temperature and volume.

52.3(a) The bond length of O_2 is 120.75 pm. Use the high-temperature approximation to calculate the rotational partition function of the molecule at 300 K.
52.3(b) The bond length of N_2 is 109.75 pm. Use the high-temperature approximation to calculate the rotational partition function of the molecule at 300 K.

52.4(a) The NOF molecule is an asymmetric rotor with rotational constants 3.1752 cm^{-1}, 0.3951 cm^{-1}, and 0.3505 cm^{-1}. Calculate the rotational partition function of the molecule at (a) 25 °C, (b) 100 °C.
52.4(b) The H_2O molecule is an asymmetric rotor with rotational constants 27.877 cm^{-1}, 14.512 cm^{-1}, and 9.285 cm^{-1}. Calculate the rotational partition function of the molecule at (a) 25 °C, (b) 100 °C.

52.5(a) The rotational constant of CO is 1.931 cm^{-1}. Evaluate the rotational partition function explicitly (without approximation) and plot its value as a function of temperature. At what temperature is the value within 5 per cent of the value calculated from the approximate formula?
52.5(b) The rotational constant of HI is 6.511 cm^{-1}. Evaluate the rotational partition function explicitly (without approximation) and plot its value as a function of temperature. At what temperature is the value within 5 per cent of the value calculated from the approximate formula?

52.6(a) The rotational constant of CH_4 is 5.241 cm^{-1}. Evaluate the rotational partition function explicitly (without approximation but ignoring the role of nuclear statistics) and plot its value as a function of temperature. At what temperature is the value within 5 per cent of the value calculated from the approximate formula?
52.6(b) The rotational constant of CCl_4 is 0.0572 cm^{-1}. Evaluate the rotational partition function explicitly (without approximation but ignoring the role of nuclear statistics) and plot its value as a function of temperature. At what temperature is the value within 5 per cent of the value calculated from the approximate formula?

52.7(a) The rotational constants of CH_3Cl are $\tilde{A}=5.097\ \text{cm}^{-1}$ and $\tilde{B}=0.443\ \text{cm}^{-1}$. Evaluate the rotational partition function explicitly (without approximation but ignoring the role of nuclear statistics) and plot its value as a function of temperature. At what temperature is the value within 5 per cent of the value calculated from the approximate formula?
52.7(b) The rotational constants of NH_3 are $\tilde{A}=6.196\ \text{cm}^{-1}$ and $\tilde{B}=9.444\ \text{cm}^{-1}$. Evaluate the rotational partition function explicitly (without approximation but ignoring the role of nuclear statistics) and plot its value as a function of temperature. At what temperature is the value within 5 per cent of the value calculated from the approximate formula?

52.8(a) Give the symmetry number for each of the following molecules: (a) CO, (b) O_2, (c) H_2S, (d) SiH_4, and (e) $CHCl_3$.
52.8(b) Give the symmetry number for each of the following molecules: (a) CO_2, (b) O_3, (c) SO_3, (d) SF_6, and (e) Al_2Cl_6.

52.9(a) Estimate the rotational partition function of ethene at 25 °C given that $\tilde{A}=4.828\ \text{cm}^{-1}$, $\tilde{B}=1.0012\ \text{cm}^{-1}$, and $\tilde{C}=0.8282\ \text{cm}^{-1}$. Take the symmetry number into account.
52.9(b) Evaluate the rotational partition function of pyridine, C_5H_5N, at 25 °C given that $\tilde{A}=0.2014\ \text{cm}^{-1}$, $\tilde{B}=0.1936\ \text{cm}^{-1}$, $\tilde{C}=0.0987\ \text{cm}^{-1}$. Take the symmetry number into account.

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‡ These problems were supplied by Charles Trapp and Carmen Giunta.

52.10(a) The vibrational wavenumber of Br_2 is 323.2 cm^{-1}. Evaluate the vibrational partition function explicitly (without approximation) and plot its value as a function of temperature. At what temperature is the value within 5 per cent of the value calculated from the approximate formula?
52.10(b) The vibrational wavenumber of I_2 is 214.5 cm^{-1}. Evaluate the vibrational partition function explicitly (without approximation) and plot its value as a function of temperature. At what temperature is the value within 5 per cent of the value calculated from the approximate formula?

52.11(a) Calculate the vibrational partition function of CS_2 at 500 K given the wavenumbers 658 cm^{-1} (symmetric stretch), 397 cm^{-1} (bend; two modes), 1535 cm^{-1} (asymmetric stretch).
52.11(b) Calculate the vibrational partition function of HCN at 900 K given the wavenumbers 3311 cm^{-1} (symmetric stretch), 712 cm^{-1} (bend; two modes), 2097 cm^{-1} (asymmetric stretch).

52.12(a) Calculate the vibrational partition function of CCl_4 at 500 K given the wavenumbers 459 cm^{-1} (symmetric stretch, A), 217 cm^{-1} (deformation, E), 776 cm^{-1} (deformation, T), 314 cm^{-1} (deformation, T).
52.12(b) Calculate the vibrational partition function of CI_4 at 500 K given the wavenumbers 178 cm^{-1} (symmetric stretch, A), 90 cm^{-1} (deformation, E), 555 cm^{-1} (deformation, T), 125 cm^{-1} (deformation, T).

52.13(a) A certain atom has a fourfold degenerate ground level, a non-degenerate electronically excited level at 2500 cm^{-1}, and a twofold degenerate level at 3500 cm^{-1}. Calculate the partition function of these electronic states at 1900 K. What is the relative population of each level at 1900 K?
52.13(b) A certain atom has a triply degenerate ground level, a non-degenerate electronically excited level at 850 cm^{-1}, and a fivefold degenerate level at 1100 cm^{-1}. Calculate the partition function of these electronic states at 2000 K. What is the relative population of each level at 2000 K?

Problems

52.1 This problem is best done using mathematical software. Equation 52.15 is the partition function for a harmonic oscillator. Consider a Morse oscillator (Topic 43) in which the energy levels are given by eqn 43.15 in the form

$$E_\upsilon = \left(\upsilon + \frac{1}{2}\right)hc\tilde{\nu} - \left(\upsilon + \frac{1}{2}\right)^2 hcx_e\tilde{\nu}$$

Evaluate the partition function for this oscillator, remembering to measure energies from the lowest level and to note that there is only a finite number of bound-state levels. Plot the partition function against temperature for a variety of values of x_e, and—on the same graph—compare your results with that for a harmonic oscillator.

52.2 Explore the conditions under which the 'integral' approximation for the translational partition function is not valid by considering the translational partition function of an H atom in a one-dimensional box of side comparable to that of a typical nanoparticle, 100 nm. Estimate the temperature at which, according to the integral approximation, $q = 10$ and evaluate the exact partition function at that temperature.

52.3 (a) Calculate the electronic partition function of a tellurium atom at (i) 298 K, (ii) 5000 K by direct summation using the following data:

Term	Degeneracy	Wavenumber/cm^{-1}
Ground	5	0
1	1	4707
2	3	4751
3	5	10 559

(b) What proportion of the Te atoms are in the ground term and in the term labelled 2 at the two temperatures?

52.4 The four lowest electronic levels of a Ti atom are: $^3F_2$, $^3F_3$, $^3F_4$, and $^5F_1$, at 0, 170, 387, and 6557 cm^{-1}, respectively. There are many other electronic states at higher energies. The boiling point of titanium is 3287 °C. What are the relative populations of these levels at the boiling point? *Hint*: The degeneracies of the levels are $2J + 1$.

52.5‡ J. Sugar and A. Musgrove (*J. Phys. Chem. Ref. Data* **22**, 1213 (1993)) have published tables of energy levels for germanium atoms and cations from Ge$^+$ to Ge^{+31}. The lowest-lying energy levels in neutral Ge are as follows:

	$^3P_0$	$^3P_1$	$^3P_2$	$^1D_2$	$^1S_0$
(E/hc)/cm^{-1}	0	557.1	1410.0	7125.3	16 367.3

Calculate the electronic partition function at 298 K and 1000 K by direct summation. *Hint*: The degeneracy of a level J is $2J + 1$.

52.6 The pure rotational microwave spectrum of HCl has absorption lines at the following wavenumbers (in cm^{-1}): 21.19, 42.37, 63.56, 84.75, 105.93, 127.12, 148.31, 169.49, 190.68, 211.87, 233.06, 254.24, 275.43, 296.62, 317.80, 338.99, 360.18, 381.36, 402.55, 423.74, 444.92, 466.11, 487.30, 508.48. Calculate the rotational partition function at 25 °C by direct summation.

52.7 Calculate, by explicit summation, the vibrational partition function and the vibrational contribution to the energy of I_2 molecules at (a) 100 K, (b) 298 K given that its vibrational energy levels lie at the following wavenumbers above the zero-point energy level: 0, 213.30, 425.39, 636.27, 845.93 cm^{-1}. What proportion of I_2 molecules are in the ground and first two excited levels at the two temperatures?

52.8‡ Consider the electronic partition function of a perfect atomic hydrogen gas at a density of 1.99×10^{-4} kg m^{-3} and 5780 K. These are the mean conditions within the Sun's photosphere, the surface layer of the Sun that is about 190 km thick. (a) Show that this partition function, which involves a sum over an infinite number of quantum states that are solutions to the Schrödinger equation for an isolated atomic hydrogen atom, is infinite. (b) Develop a theoretical argument for truncating the sum and estimate the maximum number of quantum states that contribute to the sum. (c) Calculate the equilibrium probability that an atomic hydrogen electron is in each quantum state. Are there any general implications concerning electronic states that will be observed for other atoms and molecules? Is it wise to apply these calculations in the study of the Sun's photosphere?

52.9 A formal way of arriving at the value of the symmetry number is to note that σ is the order (the number of elements) of the *rotational subgroup* of the molecule, the point group of the molecule with all but the identity and the rotations removed. The rotational subgroup of H_2O is $\{E,C_2\}$, so $\sigma = 2$. The rotational subgroup of NH_3 is $\{E,2C_3\}$, so $\sigma = 3$. This recipe makes it easy to find the symmetry numbers for more complicated molecules. The rotational subgroup of CH_4 is obtained from the T character table as $\{E,8C_3,3C_2\}$, so $\sigma = 12$. For benzene, the rotational subgroup of D_{6h} is $\{E,2C_6,2C_3,C_2,3C_2',3C_2''\}$, so $\sigma = 12$. (a) Estimate the rotational partition function of ethene at 25 °C given that $\tilde{A} = 4.828$ cm^{-1}, $\tilde{B} = 1.0012$ cm^{-1}, and $\tilde{C} = 0.8282$ cm^{-1}. (b) Evaluate the rotational partition function of pyridine, C_5H_5N, at room temperature ($\tilde{A} = 0.2014$ cm^{-1}, $\tilde{B} = 0.1936$ cm^{-1}, $\tilde{C} = 0.0987$ cm^{-1}).

Topic 53 Molecular energies

Discussion questions

53.1 Discuss the conditions under which energies predicted from the equipartition theorem coincide with energies computed by using partition functions.

53.2 Describe the behaviour of the mean energy of a two-level system in the limit of (i) very low and (ii) very high temperature.

Exercises

53.1(a) Compute the mean energy at 298 K of a two-level system of energy separation equivalent to 500 cm^{-1}.
53.1(b) Compute the mean energy at 400 K of a two-level system of energy separation equivalent to 600 cm^{-1}.

53.2(a) Evaluate, by explicit summation, the mean rotational energy of CO and plot its value as a function of temperature. At what temperature is the equipartition value within 5 per cent of the accurate value? $\tilde{B}(\mathrm{CO})=1.931\,\mathrm{cm}^{-1}$.
53.2(b) Evaluate, by explicit summation, the mean rotational energy of HI and plot its value as a function of temperature. At what temperature is the equipartition value within 5 per cent of the accurate value? $\tilde{B}(\mathrm{HI})=6.511\,\mathrm{cm}^{-1}$.

53.3(a) Evaluate, by explicit summation, the mean rotational energy of CH_4 and plot its value as a function of temperature. At what temperature is the equipartition value within 5 per cent of the accurate value? $\tilde{B}(\mathrm{CH_4})=5.241\,\mathrm{cm}^{-1}$.
53.3(b) Evaluate, by explicit summation, the mean rotational energy of CCl_4 and plot its value as a function of temperature. At what temperature is the equipartition value within 5 per cent of the accurate value? $\tilde{B}(\mathrm{CCl_4})=0.0572\,\mathrm{cm}^{-1}$.

53.4(a) Evaluate, by explicit summation, the mean rotational energy of CH_3Cl and plot its value as a function of temperature. At what temperature is the equipartition value within 5 per cent of the accurate value? $\tilde{A}=5.097\,\mathrm{cm}^{-1}$ and $\tilde{B}=0.443\,\mathrm{cm}^{-1}$.
53.4(b) Evaluate, by explicit summation, the mean rotational energy of NH_3 and plot its value as a function of temperature. At what temperature is the equipartition value within 5 per cent of the accurate value? $\tilde{A}=6.196\,\mathrm{cm}^{-1}$ and $\tilde{B}=9.444\,\mathrm{cm}^{-1}$.

53.5(a) Evaluate, by explicit summation, the mean vibrational energy of Br_2 and plot its value as a function of temperature. At what temperature is the equipartition value within 5 per cent of the accurate value? Use $\tilde{\nu}=323.2\,\mathrm{cm}^{-1}$.
53.5(b) Evaluate, by explicit summation, the mean vibrational energy of I_2 and plot its value as a function of temperature. At what temperature is the equipartition value within 5 per cent of the accurate value? Use $\tilde{\nu}=214.5\,\mathrm{cm}^{-1}$.

53.6(a) Evaluate, by explicit summation, the mean vibrational energy of CS_2 and plot its value as a function of temperature. At what temperature is the equipartition value within 5 per cent of the accurate value? Use the wavenumbers 658 cm^{-1} (symmetric stretch), 397 cm^{-1} (bend; two modes), 1535 cm^{-1} (asymmetric stretch).
53.6(b) Evaluate, by explicit summation, the mean vibrational energy of HCN and plot its value as a function of temperature. At what temperature is the equipartition value within 5 per cent of the accurate value? Use the wavenumbers 3311 cm^{-1} (symmetric stretch), 712 cm^{-1} (bend; two modes), 2097 cm^{-1} (asymmetric stretch).

53.7(a) Evaluate, by explicit summation, the mean vibrational energy of CCl_4 and plot its value as a function of temperature. At what temperature is the equipartition value within 5 per cent of the accurate value? Use the wavenumbers 459 cm^{-1} (symmetric stretch, A), 217 cm^{-1} (deformation, E), 776 cm^{-1} (deformation, T), 314 cm^{-1} (deformation, T). A modes are non-degenerate, E modes are doubly degenerate, and T modes are triply degenerate.
53.7(b) Evaluate, by explicit summation, the mean vibrational energy of CI_4 and plot its value as a function of temperature. At what temperature is the equipartition value within 5 per cent of the accurate value? Use the wavenumbers 178 cm^{-1} (symmetric stretch, A), 90 cm^{-1} (deformation, E), 555 cm^{-1} (deformation, T), 125 cm^{-1} (deformation, T). A modes are non-degenerate, E modes are doubly degenerate, and T modes are triply degenerate.

53.8(a) Calculate the mean contribution to the electronic energy at 1900 K for a sample composed of the atoms specified in Exercise 52.13(a).
53.8(b) Calculate the mean contribution to the electronic energy at 2000 K for a sample composed of the atoms specified in Exercise 52.13(b).

Problems

53.1 An electron trapped in an infinitely deep spherical well of radius R, such as may be encountered in the investigation of nanoparticles, has energies given by the expression $E_{nl}=\hbar^2X_{nl}^2/2m_eR^2$, with X_{nl} the value obtained by searching for the zeroes of the spherical Bessel functions. The first six values (with a degeneracy of the corresponding energy level equal to $2l+1$) are as follows:

Evaluate the partition function and mean energy of an electron as a function of temperature. Choose the temperature range and radius to be so low that only these six energy levels need be considered. *Hint*: Remember to measure energies from the lowest level.

n	1	1	1	2	1	2
l	0	1	2	0	3	1
X_{nl}	3.142	4.493	5.763	6.283	6.988	7.725

53.2 The NO molecule has a doubly degenerate excited electronic level 121.1 cm^{-1} above the doubly degenerate electronic ground term. Calculate and plot the electronic partition function of NO from $T=0$ to 1000 K. Evaluate (a) the term populations and (b) the mean electronic energy at 300 K.

53.3 Consider a system with energy levels $\varepsilon_j=j\varepsilon$ and N molecules. (a) Show that if the mean energy per molecule is $a\varepsilon$, then the temperature is given by

$$\beta=\frac{1}{\varepsilon}\ln\left(1+\frac{1}{a}\right)$$

Evaluate the temperature for a system in which the mean energy is ε, taking ε equivalent to $50\,\text{cm}^{-1}$. (b) Calculate the molecular partition function q for the system when its mean energy is $a\varepsilon$.

53.4 Deduce an expression for the root mean square energy, $\langle\varepsilon^2\rangle^{1/2}$, in terms of the partition function and hence an expression for the root mean square deviation from the mean, $\Delta\varepsilon = (\langle\varepsilon^2\rangle - \langle\varepsilon\rangle^2)^{1/2}$. Evaluate the resulting expression for a harmonic oscillator.

Topic 54 The canonical ensemble

Discussion questions

54.1 Why is the concept of a canonical ensemble required?

54.2 Explain what is meant by an ensemble and why it is useful in statistical thermodynamics.

54.3 Under what circumstances may identical particles be regarded as distinguishable?

54.4 What is meant by the 'thermodynamic limit'?

Exercises

54.1(a) Identify the systems for which it is essential to include a factor of $1/N!$ on going from Q to q: (a) a sample of helium gas, (b) a sample of carbon monoxide gas, (c) a solid sample of carbon monoxide, (d) water vapour.

54.1(b) Identify the systems for which it is essential to include a factor of $1/N!$ on going from Q to q: (a) a sample of carbon dioxide gas, (b) a sample of graphite, (c) a sample of diamond, (d) ice.

Problem

54.1‡ For a perfect gas, the canonical partition function, Q, is related to the molecular partition function q by $Q = q^N/N!$. In Topic 66 it is established that $p = kT(\partial \ln Q/\partial V)_T$. Use the expression for q to derive the perfect gas law $pV = nRT$.

Integrated activities

F11.1 An electron spin can adopt either of two orientations in a magnetic field, and its energies are $\pm\mu_B\mathcal{B}$, where μ_B is the Bohr magneton. Deduce an expression for the partition function and mean energy of the electron and sketch the variation of the functions with $\mathcal{B}$. Calculate the relative populations of the spin states at (a) 4.0 K, (b) 298 K when $\mathcal{B} = 1.0$ T.

F11.2 A nitrogen nuclear spin can adopt any of three orientations in a magnetic field, and its energies are $0, \pm\gamma_N\mathcal{B}$, where γ_N is the magnetogyric ratio of the nucleus. Deduce an expression for the partition function and mean energy of the nucleus and sketch the variation of the functions with $\mathcal{B}$. Calculate the relative populations of the spin states at (a) 1.0 K, (b) 298 K when $\mathcal{B} = 20.0$ T.

F11.3 Use mathematical software, a spreadsheet, or the *Living graphs* (labelled$^{\text{LG}}$) on the website of this book for the following:
(a)$^{\text{LG}}$ Plot the partition function of a harmonic oscillator against temperature for several values of the energy separation ε. How does q vary with temperature when T is high, in the sense that $kT \gg \varepsilon$ (or $\beta\varepsilon \ll 1$)?
(b)$^{\text{LG}}$ Consider a three-level system with levels 0, ε, and 2ε. Plot the partition function against kT/ε.
(c)$^{\text{LG}}$ To visualize the content of Fig. 52.4 in a different way, plot the functions p_0, p_1, p_2, and p_3 against kT/ε.
(d)$^{\text{LG}}$ Consider a three-level system with levels 0, ε, and 2ε. Plot the functions p_0, p_1, and p_2 against kT/ε.
(e)$^{\text{LG}}$ Plot the temperature dependence of the vibrational contribution to the molecular partition function for several values of the vibrational wavenumber. Estimate from your plots the temperature above which the harmonic oscillator is in the 'high-temperature' limit.
(f)$^{\text{LG}}$ Plot the temperature dependence of the electronic partition function for several values of the energy separation ε between two doubly degenerate levels. From your plots, estimate the temperature at which the population of the excited level begins to increase sharply.
(g)$^{\text{LG}}$ Draw graphs similar to those in Fig. 53.1 for a three-level system with levels 0, ε, and 2ε.
(h)$^{\text{LG}}$ Plot the temperature dependence of the mean rotational energy for several values of the rotational constant (for reasonable values of the rotational constant, see the *Resource section*). From your plots, estimate the temperature at which the mean rotational energy begins to increase sharply.
(i)$^{\text{LG}}$ Plot the temperature dependence of the mean vibrational energy for several values of the vibrational wavenumber (for reasonable values of the vibrational wavenumber, see the *Resource section*). From your plots, estimate the temperature at which the mean vibrational energy begins to increase sharply.

Mathematical background 7 Probability theory

Probability theory deals with quantities and events that are distributed randomly and shows how to calculate average values of various kinds. We shall consider variables that take discrete values (as in a one-dimensional random walk with a fixed step length) and continuous values (as in the diffusion of a particle through a fluid).

MB7.1 Discrete distributions

We denote a variable x and the discrete values that it may take x_i, $i=1, 2, \ldots, N$. If the probability that x_i occurs is p_i, then the **mean value** (or *expectation value*) of x is

$$\langle x\rangle=\sum_{i=1}^{N}x_i p_i$$

Mean value (MB7.1a)

The mean values of higher powers of x may be computed similarly:

$$\langle x^n\rangle=\sum_{i=1}^{N}x_i^n p_i$$

Mean nth power (MB7.1b)

Although the mean is a useful measure, it is important to know the width in the scatter of outcomes around the mean. There are two related measures: one is the **variance,** $V(x)$, and the other is the **standard deviation,** $\sigma(x)$, the square root of the variance:

$$V(x)=\langle x^2\rangle-\langle x\rangle^2$$

Variance (MB7.2a)

$$\sigma(x)=V(x)^{1/2}=\left\{\langle x^2\rangle-\langle x\rangle^2\right\}^{1/2}$$

Standard deviation (MB7.2b)

In certain cases, the probabilities can be expressed in a simple way, depending on the nature of the events being considered.

(a) The binomial distribution

In a **Bernoulli trial,** the outcome of an observation is one of a mutually exclusive pair (such as 'heads' or 'tails' in a coin toss) and successive trials are independent (so that getting 'heads' on one toss does not influence the following toss). Suppose the probability of outcome 1 is p and that of the alternative outcome 2 is q, with $p+q=1$. For a fair coin, $p=q=\frac{1}{2}$. Then one series of $N=12$ trials might be

thhtththttht Probability of occurrence $=p^5q^7$,

and in general p^nq^{N-n}

However, if the order in which 'heads' come up is unimportant, there are 12!/5!7! ways of achieving 5 'heads' in 12 tosses, and in general $N!/n!(N-n)!$ ways of achieving n 'heads' in N trials. The probability of getting exactly n 'heads' is therefore the product of p^nq^{N-n} and the number of ways of distributing n 'heads' over N trials:

$$P(n)=\binom{N}{n}p^nq^{N-n} \quad \text{where} \quad \binom{N}{n}=\frac{N!}{n!(N-n)!}$$

Binomial distribution (MB7.3)

The symbol $\binom{N}{n}$ is the **binomial coefficient,** as it occurs in the **binomial expansion**:

$$(x+y)^N=\sum_{n=0}^{N}\binom{N}{n}x^ny^{N-n}$$

Binomial expansion (MB7.4)

The expression $P(n)$ is accordingly called the **binomial distribution** (Fig. MB7.1).

Manipulations of the binomial distribution are often facilitated by the following summation procedure:

1. Introduce a dummy variable a.
2. Express the sum as a derivative with respect to a, using $na^n=a\mathrm{d}a^n/\mathrm{d}a$ to eliminate the factor n; if a power of n occurs, apply $\mathrm{d}/\mathrm{d}a$ the appropriate number of times.
3. Evaluate the resulting sum: note the binomial expansion (eqn MB7.4).
4. Evaluate the derivative.
5. Finally, set $a=1$.

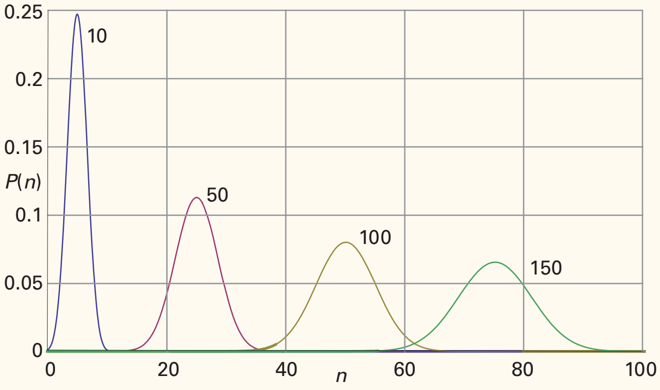


Figure MB7.1 The binomial distribution for different values of N and $p=q=½$.

Brief illustration MB7.1 The binomial distribution

We can use the binomial distribution to determine the mean number of times that 'heads' will be obtained in a series of N trials (this is the average value of n, denoted $\langle n\rangle$):

$$\langle n\rangle=\sum_{n=0}^{N} nP(n)=\sum_{n=0}^{N} n\binom{N}{n}p^n q^{N-n}=\sum_{n=0}^{N} n\binom{N}{n}p^n(1-p)^{N-n}$$

Application of the summation procedure to this expression gives:

$$\begin{aligned}\langle n\rangle &\overset{\text{Step1}}{=} \sum_{n=0}^{N} n\binom{N}{n}a^n p^n(1-p)^{N-n} \overset{\text{Step2}}{=} a\frac{\mathrm{d}}{\mathrm{d}a}\sum_{n=0}^{N}\binom{N}{n}a^n p^n(1-p)^{N-n}\\ &\overset{\text{Step3}}{=} a\frac{\mathrm{d}}{\mathrm{d}a}(ap+[1-p])^N \overset{\text{Step4}}{=} Nap(ap+[1-p])^{N-1}\\ &\overset{\text{Step5}}{=} Np\end{aligned}$$

For example, the mean number of times 'heads' is obtained for a fair coin $(p=\tfrac{1}{2})$ in 10 trials is 5.

Note that although the width of the distribution increases (as $N^{1/2}$), its value relative to the mean decreases (as $N^{1/2}/N=1/N^{1/2}$). For tosses of a fair coin, when $p=\tfrac{1}{2}$, $\langle n\rangle=\tfrac{1}{2}N$ (half the tosses turn up 'heads') and $\sigma(n)=\tfrac{1}{2}N^{1/2}$.

(b) The Poisson distribution

In another important type of trial, an event either takes place or does not, such as an excited molecule dissociating into fragments or (more mundanely) a bus arriving. At first sight it appears that we cannot assign a meaning to the number of times an event does not occur (how many times did the bus not arrive in an interval?). However, we can still assign a probability that an event occurs by imagining an interval of time Δt that is divided into N regions, each of duration $\Delta t/N$ (or, similarly, regions of space $\Delta x/N$) that are so small that the probability that two or more events occurs in it is negligible and we have a 'heads' for the event occurring in that brief interval or tiny region and a 'tails' if it does not.

If the events occur at random, the probability of an event occurring within this tiny interval is proportional to the length of the interval, and we can write $p=\Delta t/N\tau$, where $1/\tau$ is a constant of proportionality (we give it a physical meaning later). It then follows that in a set of Bernouilli trials (where 'heads' now corresponds to 'did occur' and 'tails' to 'did not occur') the total probability that n events occur in the interval $\Delta t=N(\Delta t/N)$ is just the probability of getting n 'heads' in a total interval that spans N of the tiny intervals:

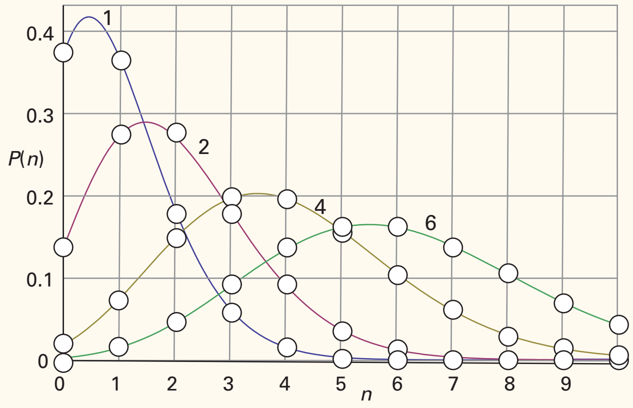


Figure MB7.2 The Poisson distribution for different values of $\Delta t/\tau$.

$$P(n)=\binom{N}{n}p^n(1-p)^{N-n}=\binom{N}{n}\left(\frac{\Delta t}{N\tau}\right)^n\left(1-\frac{\Delta t}{N\tau}\right)^{N-n}$$

If then we suppose that N is very large and make use of the relation

$$\lim_{x\to 0}(1+x)^{1/x}=\mathrm{e} \tag{MB7.3}$$

then in a slightly involved but straightforward calculation (which we do not reproduce here) we arrive at the **Poisson distribution**:

$$P(n)=\frac{(\Delta t/\tau)^n}{n!}\mathrm{e}^{-\Delta t/\tau} \tag{MB7.4}$$

Poisson distribution

for the probability that n events will occur in the interval Δt (Fig. MB7.2). As shown in the following *Brief illustration*, the mean number of events in the interval Δt is just $\Delta t/\tau$, so τ can be interpreted as the average time between events.

Brief illustration MB6.2 The Poisson distribution

To calculate the average number of events that occur in an interval Δt (and in the limit $N\to\infty$), we need to evaluate

$$\begin{aligned}\langle n\rangle &=\sum_{n=1}^{N} nP(n)=\sum_{n=1}^{N} n\frac{(\Delta t/\tau)^n}{n!}\mathrm{e}^{-\Delta t/\tau}=\mathrm{e}^{-\Delta t/\tau}\sum_{n=1}^{N}\frac{(\Delta t/\tau)^n}{(n-1)!}\\ &=(\Delta t/\tau)\mathrm{e}^{-\Delta t/\tau}\sum_{n=1}^{N}\frac{(\Delta t/\tau)^{n-1}}{(n-1)!}=(\Delta t/\tau)\mathrm{e}^{-\Delta t/\tau}\sum_{n=0}^{N}\frac{(\Delta t/\tau)^n}{n!}\\ &=(\Delta t/\tau)\mathrm{e}^{-\Delta t/\tau}\mathrm{e}^{\Delta t/\tau}=\Delta t/\tau\end{aligned}$$

where we have used the Taylor series expansion (eqn MB1.7b) of e^x.

(c) The Gaussian distribution

Suppose that a variable can take positive and negative integer values centred on zero and that to reach a certain value n the system jumps to the left or right by taking steps of length λ at random for a total of N steps. The number of ways of taking N_R steps to the right and N_L to the left (with $N=N_R+N_L$) in any one such trial of N steps is

$$\mathcal{W}=\frac{N!}{N_L!N_R!} \tag{MB7.7}$$

Then, because there are 2^N possible choices of direction in the course of N steps, the probability of being n steps from the origin, with $n=N_R-N_L$ in a trial of N steps, is

$$P(n)=\frac{\mathcal{W}}{2^N}=\frac{N!}{2^N N_L!N_R!}=\frac{N!}{2^N\left(\dfrac{N+n}{2}\right)!\left(\dfrac{N-n}{2}\right)!} \tag{MB7.8}$$

A point of some subtlety and which we draw on later is that if N is even, then n must be even (you cannot end up an odd number of steps from the origin if you take an even number of steps; think about $N=4$); similarly, if N is odd, then n must be odd too (you cannot end up an even number of steps from the origin if you take an odd number of steps; think about $N=5$). Because it then follows that $N+n$ and $N-n$ are both even numbers, the factorials we have to evaluate in $P(n)$ are of whole numbers.

To develop this expression in the case of large numbers of steps, we take logarithms and use **Stirling's approximation**:

$$\ln x!\approx\ln(2\pi)^{1/2}+\left(x+\frac{1}{2}\right)\ln x-x \tag{MB7.9}$$

Stirling's approximation

This approximation leads, after a fair amount of algebra, to the **Gaussian distribution**

$$P(n)=\frac{2}{(2N\pi)^{1/2}}\mathrm{e}^{-n^2/2N} \tag{MB7.5}$$

Gaussian distribution

with, remember, n even if N is even and n odd if N is odd. This bell-shaped curve is illustrated in Fig. MB7.3 for N even and N odd. The Gaussian distribution is commonly used to discuss a continuous function, as we demonstrate in the following section.

MB7.2 Continuous distributions

A **continuous distribution** is a distribution in which the variable can take on a continuum of values. One of the most important examples can be developed from the Gaussian distribution of the preceding section, as follows.

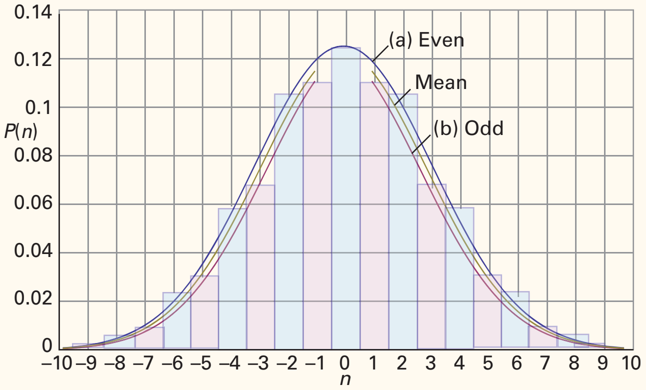


Figure MB7.3 The Gaussian distribution for N even (40) and N odd (41), and their mean. The bell-shaped mean curve is the average of the two distributions, and corresponds to the Gaussian distribution function for a continuous variable.

When N is very large and the x_i values are so closely spaced that x can be regarded as varying continuously, it is useful to express the probability that an outcome will lie between x and $x+\mathrm{d}x$ as $\rho(x)\mathrm{d}x$, where the function $\rho(x)$ is the **probability density**. The mean value of x continuously varying between $-\infty$ and ∞ is then given by

$$\langle x\rangle=\int_{-\infty}^{\infty}x\rho(x)\mathrm{d}x \tag{MB7.11}$$

with analogous expressions for the variance and standard deviation.

To derive the Gaussian version of the probability density we use the random-walk model in Section MB7.1 and write $x=n\lambda$, allowing λ to be very small and n to be very large and effectively continuous. If dx spreads over a sufficiently wide range of points, then instead of dealing with a distribution like that in Fig. MB7.3a or like that in Fig. MB7.3b, we can deal with the average of the two, as shown by the curves superimposed on the distribution. That is, for a continuous distribution we use

$$P(n)=\frac{1}{(2N\pi)^{1/2}}\mathrm{e}^{-n^2/2N} \tag{MB7.12}$$

The total probability of being in the range $\mathrm{d}x=\lambda\mathrm{d}n$ at $x=n\lambda$ is therefore

$$\rho(x)\mathrm{d}x=\frac{1}{(2N\pi)^{1/2}}\mathrm{e}^{-n^2/2N}\mathrm{d}n=\frac{1}{(2N\pi)^{1/2}}\mathrm{e}^{-x^2/2N\lambda^2}\frac{\mathrm{d}x}{\lambda} \tag{MB7.13}$$

It follows that

$$\rho(x)=\frac{1}{\left(2N\pi\lambda^2\right)^{1/2}}\mathrm{e}^{-x^2/2N\lambda^2} \tag{MB7.14}$$

This expression is commonly expressed as the **Gaussian distribution function** (or *normal distribution function*):

$$\rho(x)=\left(\frac{1}{2\pi\sigma^2}\right)^{1/2}\mathrm{e}^{-x^2/2\sigma^2} \qquad \text{(MB7.15)}$$

Gaussian distribution function

where $\sigma=N^{1/2}\lambda$ turns out to be the standard deviation of the distribution (see below).

Brief illustration MB7.3 Gaussian distribution function

If the bell-shaped curve of the Gaussian distribution function is centred on $\langle x\rangle$, the distribution becomes

$$\rho(x)=\left(\frac{1}{2\pi\sigma^2}\right)^{1/2}\mathrm{e}^{-(x-\langle x\rangle)^2/2\sigma^2}$$

To evaluate the mean square value of x we write

$$\langle x^2\rangle=\int_{-\infty}^{\infty}x^2\rho(x)\mathrm{d}x=\left(\frac{1}{2\pi\sigma^2}\right)^{1/2}\int_{-\infty}^{\infty}x^2\mathrm{e}^{-(x-\langle x\rangle)^2/2\sigma^2}\mathrm{d}x$$

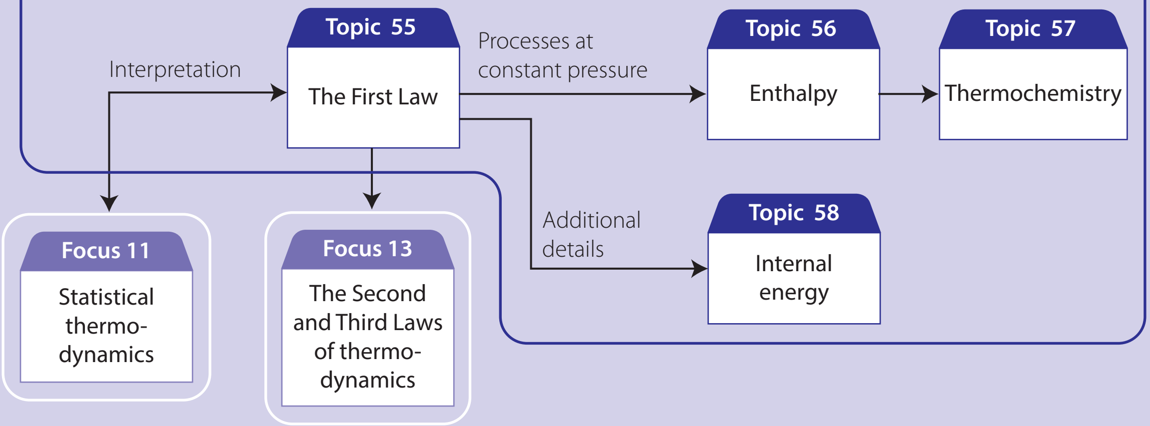
Now make the substitution $z=(x-\langle x\rangle)/(2\sigma^2)^{1/2}$, so $\mathrm{d}x=(2\sigma^2)^{1/2}\mathrm{d}z$ and $x^2=2\sigma^2z^2+2(2\sigma^2)^{1/2}z\langle x\rangle+\langle x\rangle^2$, and obtain

$$\langle x^2\rangle=\left(\frac{1}{2\pi\sigma^2}\right)^{1/2}(2\sigma^2)^{1/2}\times$$

$$\left\{\int_{-\infty}^{\infty}2\sigma^2z^2\mathrm{e}^{-z^2}\mathrm{d}z+2(2\sigma^2)^{1/2}\langle x\rangle\overbrace{\int_{-\infty}^{\infty}z\mathrm{e}^{-z^2}\mathrm{d}z}^{0}+\langle x\rangle^2\int_{-\infty}^{\infty}\mathrm{e}^{-z^2}\mathrm{d}z\right\}$$

$$=\frac{1}{\pi^{1/2}}\{\pi^{1/2}\sigma^2+\langle x\rangle^2\pi^{1/2}\}=\sigma^2+\langle x\rangle^2$$

FOCUS 12 ON The First Law of thermodynamics



The First Law of thermodynamics was introduced on the basis of a large number of experiments that led to the conclusion that the total energy of an isolated system is conserved. It goes beyond the law of the conservation of energy of dynamics, where the energy of a body can be changed when *work* is done on or by it, by introducing the concept of heat as a mode of transfer of energy. The First Law focuses on the concept of internal energy (**Topic 55**), which is essentially the total energy of a system. The discussion of internal energy and the recognition that it is a 'state function' is based on calculations of the energy that is transferred as work and as heat. Calculations of the former make use of the expression in physics for the work that is done when a body is moved against an opposing force. Transfers of energy as heat can typically be calculated from the change in temperature that occurs provided we know the property called the 'heat capacity' of the system. The internal energy can be calculated (in certain cases) and related to molecular properties by using the techniques of *Statistical thermodynamics*.

When a change, such as a reaction, takes place the system might expand (or contract). In other words, the system can do work by pushing back the surroundings (or have work done on it by being compressed by the surroundings). To avoid having to calculate this effect, the property known as the 'enthalpy' is introduced (**Topic 56**). This property takes the work of expansion into account automatically.

The enthalpy is the basis of 'thermochemistry' (**Topic 57**), the study of the heat output or requirement that accompanies a chemical reaction, which is of considerable importance for assessing fuels but also plays a role in determining the spontaneity of a reaction as explained in *The Second and Third Laws of thermodynamics*. Thermochemical calculations make use of measurements by 'calorimetry', the monitoring of energy transfers as heat, and tabulations of experimental and computed data to assess the enthalpy changes accompanying all kinds of reactions.

When we adopt the view that the internal energy of a system of constant composition depends on the volume and temperature, powerful relations can be derived that summarize how it changes when these parameters are changed (**Topic 58**). That takes us into a discussion of the molecular interpretation of heat capacity and of the pressure and temperature changes that accompany adiabatic processes.

What is the impact of this material?

The efficiency of fuels is central to the economies of nations, and thermochemistry is used to assess their suitability. Foods are fuels, and thermochemical analysis of food is a first step in the application of thermodynamics to bioenergetics (Impacts 12.1 and 12.2).

To read more about the impact of this material, scan the QR code or go to http://bcs.whfreeman.com/webpub/chemistry/qmc2e/impact/qchem_impact12.html.

TOPIC 55

The First Law

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➤ Why do you need to know this material?

The First Law of thermodynamics is the foundation of the discussion of the role of energy in chemistry. Wherever we are interested in the generation or use of energy in physical transformations or chemical reactions, lying in the background are the concepts introduced by the First Law.

➤ What is the key idea?

Energy may be transferred as either heat or work, and the total amount in an isolated system remains constant.

➤ What do you need to know already?

This Topic makes use of the discussion of the properties of gases (Topic 36), particularly the perfect gas law. The molecular interpretations draw on the Boltzmann distribution (Topic 51) and the discussion of partition functions (Topic 52).

Energy can be used to bring about a variety of processes, such as heating the surroundings or causing an electric current to flow through a circuit. In other words, the energy stored by a collection of molecules may be transformed into a variety of forms. **Thermodynamics** is the study of these transformations of energy. The historical development of thermodynamics was in terms of observations on the properties of bulk samples. It can still be explained in that way, but we shall see that our understanding of its concepts is greatly enriched by drawing on molecular concepts, and in particular the Boltzmann distribution (Topic 51).

For the purposes of thermodynamics, the universe is divided into two parts, the system and its surroundings. The **system** is the part of the world in which we have a special interest. It may be a reaction vessel, an engine, an electrochemical cell, a biological cell, and so on. The **surroundings** comprise the region outside the system and are where we make our measurements. The type of system depends on the characteristics of the boundary that divides it from the surroundings (Fig. 55.1). If matter can be transferred through the boundary between the system and its surroundings the system is classified as **open**. If matter cannot pass through the boundary the system is classified as **closed**. Both open and closed systems can exchange energy with their surroundings. For example, a closed system can expand and thereby raise a weight in the surroundings; it may also transfer energy to them if they are at a lower temperature. An

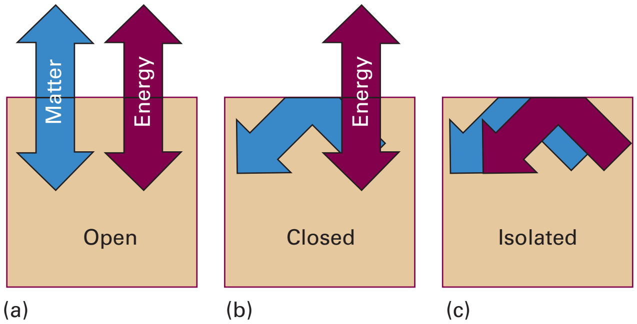

Figure 55.1 (a) An open system can exchange matter and energy with its surroundings. (b) A closed system can exchange energy with its surroundings, but it cannot exchange matter. (c) An isolated system can exchange neither energy nor matter with its surroundings.

isolated system can exchange neither energy nor matter with its surroundings.

55.1 Work, heat, and energy

A fundamental concept in thermodynamics is work: **work** is done when motion takes place against an opposing force. Doing work is equivalent to raising a weight somewhere in the surroundings. An example of doing work is the expansion of a gas that pushes out a piston and raises a weight. A chemical reaction that drives an electric current through a resistance also does work, because the same current could be driven through a motor and used to raise a weight.

In molecular terms, *work is the transfer of energy that makes use of organized motion* (Fig. 55.2). When a weight is raised or lowered, its atoms move in an organized way (up or down). The atoms in a spring move in an orderly way when it is wound; the electrons in an electric current move in an orderly direction when it flows. When a system does work it causes atoms or electrons in its surroundings to move in an organized way. Likewise, when work is done *on* a system, molecules in the surroundings are used to transfer energy to it in an organized way, as the atoms in a weight are lowered or a current of electrons is passed.

The **energy** of a system is its capacity to do work. When work is done on an otherwise isolated system (for instance, by compressing a gas or winding a spring), the capacity of the system to do work is increased; in other words, the energy of the system is increased. When the system does work (i.e. when the piston moves out or the spring unwinds), the energy of the system is reduced and it can do less work than before.

Experiments have shown that the energy of a system may be changed by means other than work itself. When the energy of a system changes as a result of a temperature difference between the system and its surroundings we say that energy has been transferred as **heat**. When a heater is immersed in a beaker of water (the system), the capacity of the system to do work increases because hot water can be used to do more work than the same amount of cold water.

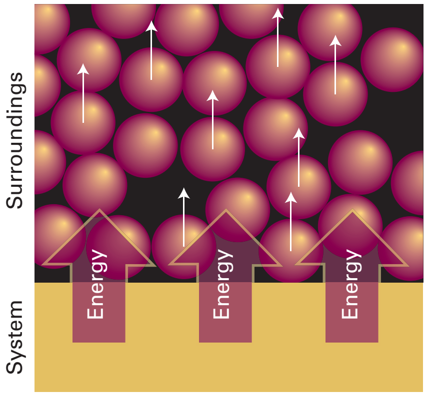

Figure 55.2 When a system does work, it stimulates orderly motion in the surroundings. For instance, the atoms shown here may be part of a weight that is being raised. The ordered motion of the atoms in a falling weight does work on the system.

An **exothermic process** is one that releases energy as heat. All combustion reactions are exothermic. An **endothermic process** is one in which energy is acquired as heat. An example of an endothermic process is the vaporization of water. To avoid a lot of awkward language, we say that in an exothermic process 'heat is released' and in an endothermic process 'heat is absorbed'. However, it must never be forgotten that heat is a process (the transfer of energy as a result of a temperature difference), not a thing. When an endothermic process takes place in a **diathermic** (thermally conducting) container, heat flows into the system from the surroundings. When an exothermic process takes place in a diathermic container, heat flows into the surroundings. When an endothermic process takes place in an **adiabatic** (thermally insulating) container, it results in a lowering of temperature of the system; an exothermic process results in a rise of temperature. These features are summarized in Fig. 55.3.

Brief illustration 55.1 Combustions in adiabatic and diathermic containers

All combustions are exothermic, provided the reaction is not confined to a thermally insulated vessel. Although the temperature rises in the course of the combustion, if we wait long enough, the system returns to the temperature of its surroundings, so we can speak of a combustion 'at 25 °C', for instance. If the combustion takes place in an adiabatic container, the energy released as heat remains inside the container and results in a permanent rise in temperature.

Self-test 55.1 How may the expansion of a gas at constant temperature be achieved?

Answer: Immerse the system in a water bath

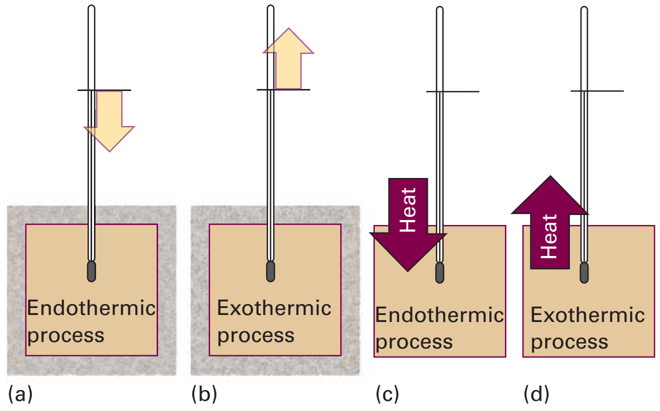

Figure 55.3 (a) When an endothermic process occurs in an adiabatic system, the temperature falls; (b) if the process is exothermic, then the temperature rises. (c) When an endothermic process occurs in a diathermic container, energy enters as heat from the surroundings, and the system remains at the same temperature. (d) If the process is exothermic, then energy leaves as heat, and the process is isothermal.

In molecular terms, heating is the transfer of energy that makes use of *random molecular motion*. The random motion of molecules is called **thermal motion**. The thermal motion of the molecules in the hot surroundings stimulates the molecules in the cooler system to move more vigorously and, as a result, the energy of the system is increased. When a system heats its surroundings, molecules of the system stimulate the thermal motion of the molecules in the surroundings (Fig. 55.4).

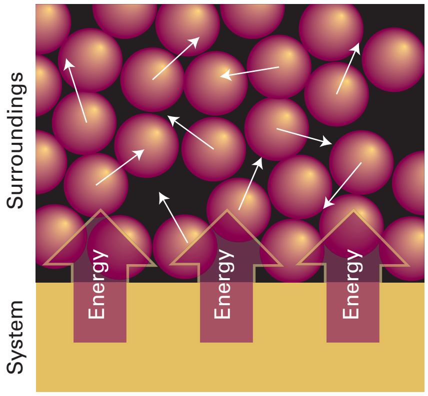

Figure 55.4 When energy is transferred to the surroundings as heat, the transfer stimulates random motion of the atoms in the surroundings. Transfer of energy from the surroundings to the system makes use of random motion (thermal motion) in the surroundings.

55.2 Internal energy

In thermodynamics, the total energy of a system is called its **internal energy**, U. The internal energy is the total kinetic and potential energy of the molecules in the system. It is 'internal' in the sense that it does not include the kinetic energy arising from the motion of the system as a whole, such as its kinetic energy as it accompanies the Earth on its orbit round the Sun.

For a system composed of N independent molecules, the internal energy at a temperature T is

$$U(T)=U(0)+N\langle\varepsilon\rangle \qquad \textit{Independent molecules} \qquad \text{Internal energy} \tag{55.1a}$$

where $U(0)$ is the internal energy at $T=0$ and $\langle\varepsilon\rangle$ is the mean molecular energy (as calculated from the molecular partition function in Topic 53) at the temperature T. For the more general case of a system composed of interacting molecules, we write

$$U(T)=U(0)+\langle E\rangle \qquad \textit{General case} \qquad \text{Internal energy} \tag{55.1b}$$

where $\langle E\rangle$ is the mean energy of the system (as calculated from the canonical partition function, Topic 54) at the temperature T. More formally, and as explained in Topic 54, $\langle E\rangle$ is the mean value of the energy of the members of a canonical ensemble in the thermodynamic limit of $\tilde{N}\to\infty$.

Brief illustration 55.2 The internal energy of a gas

The molar internal energy is obtained by setting $N=nN_A$, where N_A is Avogadro's constant, and dividing the total internal energy by the amount of molecules, n, in the sample:

$$U_m(T)=U_m(0)+N_A\langle\varepsilon\rangle$$

In Topic 53 it is shown that the mean energy of a molecule due to its translational motion is $\frac{3}{2}kT$; therefore, considering only the translational contribution to internal energy,

$$U_m(T)=U_m(0)+\tfrac{3}{2}N_AkT=U_m(0)+\tfrac{3}{2}RT$$

At 25 °C, $RT=2.48\ \text{kJ mol}^{-1}$, so the translational motion contributes $3.72\ \text{kJ mol}^{-1}$ to the molar internal energy of gases.

Self-test 55.2 Calculate the molar internal energy of carbon dioxide at 25 °C, taking into account its translational and rotational degrees of freedom.

Answer: $U_m(T)=U_m(0)+\frac{5}{2}RT$

We denote by ΔU the change in internal energy when a system changes from an initial state i with internal energy U_i to a final state f of internal energy U_f:

$$\Delta U=U_f-U_i \qquad \textit{Definition} \qquad \text{Change in internal energy} \tag{55.2}$$

The internal energy of a closed system may be changed either by work being done on (or by) the system or by heating (or cooling) it. Whereas we may know how the energy transfer has occurred (because we can see if a weight has been raised or lowered in the surroundings, indicating transfer of energy by doing work, or if ice has melted in the surroundings, indicating transfer of energy as heat), the system is blind to the mode employed. *Heat and work are equivalent ways of changing a system's internal energy*. A system is like a bank: it accepts deposits in either currency, but stores its reserves as internal energy. If we write w for the work done on a system, q for the energy transferred as heat to a system, and ΔU for the resulting change in internal energy, then

$$\Delta U = q + w \qquad \text{Contributions of work and heat} \qquad (55.3)$$

(Be careful to distinguish q, the symbol for energy transferred as heat, from $\mathcal{q}$, the symbol for the partition function. Later you will also need to distinguish p, for pressure, from $\mathcal{p}$, for population. We use script symbols for statistical properties.) This equation employs the 'acquisitive convention', in which $w > 0$ or $q > 0$ if energy is transferred to the system as work or heat and $w < 0$ or $q < 0$ if energy is lost from the system as work or heat. In other words, we view the flow of energy as work or heat from the system's perspective.

It is an experimental fact that we cannot use a system to do work, leave it isolated for a while, and then return to it to find its internal energy restored to its original value and ready to provide the same amount of work again. Despite the great amount of effort that has been spent trying to build a 'perpetual motion machine', a device that would be an exception to this rule by producing work without using fuel, no one has ever succeeded in building one. In other words, eqn 55.3 is a complete statement of how changes in internal energy may be achieved in a closed system: the only way to increase the internal energy of a closed system is to transfer energy into it as heat or as work. If the system is isolated, then even that ability is eliminated, and the internal energy cannot change at all. This conclusion is known as the **First Law of thermodynamics**, which states:

> The internal energy of an isolated system is constant.

Equation 55.3 is the mathematical statement of this law, for it implies the equivalence of heat and work as modes of transfer of energy and the fact that the internal energy is constant in an isolated system (for which $q = 0$ and $w = 0$). The First Law is closely related to the conservation of energy (*Foundations*, Topic 2) but goes beyond it: the concept of heat does not apply to the single particles treated in classical mechanics.

Brief illustration 55.3 Contributions to ΔU

If an electric motor produced 15 kJ of energy each second as mechanical work and lost 2 kJ as heat to the surroundings, then the change in the internal energy of the motor each second is

$$\Delta U = -2\ \text{kJ} - 15\ \text{kJ} = -17\ \text{kJ}$$

Suppose that when a spring was wound, 100 J of work was done on it but 15 J escaped to the surroundings as heat. The change in internal energy of the spring is

$$\Delta U = +100\ \text{kJ} - 15\ \text{kJ} = +85\ \text{kJ}$$

Self-test 55.3 What is the change in internal energy when an engine raises a mass of 100 kg through 20.0 m on the surface of the Earth (use mgh) and loses 10.0 kJ of energy as heat?

Answer: −29.6 kJ

According to the First Law, if an isolated system has a certain internal energy at one instant and is inspected again later, then it will be found to have exactly the same internal energy. Therefore, if a second system consisting of exactly the same amount of substance in exactly the same state as the first (and therefore indistinguishable from the first system) is inspected, it too would have the same internal energy as the first system. We summarize this conclusion by saying that the internal energy is a **state function**, a property that depends only on the current state of the system and is independent of how that state was prepared. The pressure, volume, temperature, and density of a system are also state functions.

The way can now be opened to powerful methods of calculation by switching attention to infinitesimal changes of state (such as an infinitesimal change in temperature) and infinitesimal changes in the internal energy $\mathrm{d}U$. Then, if the work done on a system is $\mathrm{d}w$ and the energy supplied to it as heat is $\mathrm{d}q$, in place of eqn 55.3 we write

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w \qquad (55.4)$$

To use this expression we must be able to relate $\mathrm{d}q$ and $\mathrm{d}w$ to events taking place in the surroundings.

55.3 Expansion work

We begin by discussing the important case of **expansion work**, the work arising from a change in volume. This type of work includes the work done by a gas as it expands and drives back the atmosphere. Many chemical reactions result in the generation or consumption of gases (for instance, the thermal decomposition of calcium carbonate or the combustion of octane), and the thermodynamic characteristics of a reaction depend on the work it can do. The term ‘expansion work’ also includes work associated with negative changes of volume, that is, compression.

(a) The general expression for work

The calculation of expansion work starts from the definition used in physics (*Foundations*, Topic 2), which states that the work required to move an object a distance dz against an opposing force of magnitude F is

$$\mathrm{d}w = -F\mathrm{d}z \qquad \textit{Definition} \quad \text{Work} \tag{55.5}$$

The negative sign tells us that when the system moves an object against an opposing force, the internal energy of the system doing the work will decrease. Now consider the arrangement shown in Fig. 55.5 in which one wall of a system is a massless, frictionless, rigid, perfectly fitting piston of area A. If the external pressure is p_{ex}, the magnitude of the force acting on the outer face of the piston is $F = p_{\mathrm{ex}}A$. When the system expands through a distance dz against an external pressure p_{ex}, it follows that the work done is $\mathrm{d}w = -p_{\mathrm{ex}}A\mathrm{d}z$. But $A\mathrm{d}z$ is the change in volume, dV, in the course of the expansion. Therefore, the work done when the system expands by dV against a pressure p_{ex} is

$$\mathrm{d}w = -p_{\mathrm{ex}}\mathrm{d}V \qquad \text{Expansion work} \tag{55.6}$$

To obtain the total work done when the volume changes from V_{i} to V_{f} we integrate this expression between the initial and final volumes:

$$w = -\int_{V_{\mathrm{i}}}^{V_{\mathrm{f}}} p_{\mathrm{ex}}\mathrm{d}V \tag{55.7}$$

The force acting on the piston, $p_{\mathrm{ex}}A$, is equivalent to a weight that is raised as the system expands.

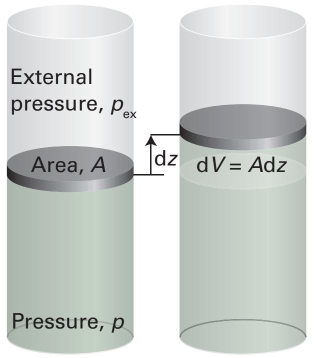

Figure 55.5 When a piston of area A moves out through a distance dz, it sweeps out a volume d$V = A$dz. The external pressure p_{ex} is equivalent to a weight pressing on the piston, and the force opposing expansion is $F = p_{\mathrm{ex}}A$.

If the system is compressed instead, then the same weight is lowered in the surroundings and eqn 55.7 can still be used, but now $V_{\mathrm{f}} < V_{\mathrm{i}}$. It is important to note that it is still the *external* pressure that determines the magnitude of the work. This somewhat perplexing conclusion seems to be inconsistent with the fact that the gas *inside* the container is opposing the compression. However, when a gas is compressed, the ability of the *surroundings* to do work is diminished by an amount determined by the weight that is lowered, and it is this energy that is transferred into the system.

Other types of work (for example, electrical work), which we shall call **non-expansion work**, have analogous expressions, with each one the product of an intensive factor (the pressure, for instance) and an extensive factor (the change in volume). Some are collected in Table 55.1. For the present we continue with the work associated with changing the volume, the expansion work, and see what we can extract from eqns 55.6 and 55.7.

Table 55.1 Varieties of work*

Type of work	dw	Comment	Units†
Expansion	$-p_{\mathrm{ex}}\mathrm{d}V$	p_{ex} is the external pressure dV is the change in volume	Pa m^3
Surface expansion	$\gamma\mathrm{d}\sigma$	γ is the surface tension dσ is the change in area	N m^{-1} m^2
Extension	$f\mathrm{d}l$	f is the tension dl is the change in length	N m
Electrical	$\phi\mathrm{d}Q$	ϕ is the electric potential dQ is the change in charge	V C

* In general, the work done on a system can be expressed in the form $\mathrm{d}w = -F\mathrm{d}z$, where F is a ‘generalized force’ and dz is a ‘generalized displacement’.

† For work in joules, note that 1 N m = 1 J, 1 Pa m^3 = 1 J, and 1 V C = 1 J.

Brief illustration 55.4 The work of extension

To establish an expression for the work of stretching an elastomer to an extension l given that the force opposing extension is proportional to the displacement from the resting state of the elastomer, we write $F = k_{\mathrm{f}}x$, where k_{f} is a constant and x is the displacement. It then follows from eqn 55.5 that, for an infinitesimal displacement from x to $x+\mathrm{d}x$, $\mathrm{d}w = -k_{\mathrm{f}}x\mathrm{d}x$. For the overall work of displacement from $x = 0$ to the final extension l,

$$w = -\int_0^l k_{\mathrm{f}}x\,\mathrm{d}x = -\frac{1}{2}k_{\mathrm{f}}l^2$$

Self-test 55.4 Suppose the restoring force weakens as the elastomer is stretched, and $k_{\mathrm{f}}(x) = a - bx^{1/2}$. Evaluate the work of extension to l.

Answer: $w = -\frac{1}{2}al^2 + \frac{2}{5}bl^{5/2}$

(b) Expansion against constant pressure

Now suppose that the external pressure is constant throughout the expansion. For example, the piston may be pressed on by the atmosphere, which exerts the same pressure throughout the expansion. A chemical example of this condition is the expansion of a gas formed in a chemical reaction. We can evaluate eqn 55.7 by taking the constant p_{ex} outside the integral:

$$w = -p_{ex}\int_{V_i}^{V_f} \mathrm{d}V = -p_{ex}(V_f - V_i)$$

Therefore, if we write the change in volume as $\Delta V = V_f - V_i$,

$$w = -p_{ex}\Delta V \qquad \textit{Constant external pressure} \qquad \text{Expansion work} \qquad (55.8)$$

This result, which is illustrated graphically in Fig. 55.6, makes use of the fact that an integral can be interpreted as an area. The magnitude of w, denoted $|w|$, is equal to the area beneath the horizontal line at $p = p_{ex}$ lying between the initial and final volumes.

When the external pressure is zero (as for expansion into a vacuum), the system undergoes **free expansion.** When $p_{ex} = 0$, eqn 55.8 implies that the expansion work is zero; that is,

$$w = 0 \qquad \textit{Free expansion } (p_{ex} = 0) \qquad \text{Expansion work} \qquad (55.9)$$

Brief illustration 55.5 The work of expansion

When a certain chemical reaction that produces gas takes place in a container of cross-sectional area 50 cm² (5.0×10^{-3} m²) a piston is pushed out through 15 cm (1.5×10^{-1} m) against an external pressure of 1.0 atm (1.0×10^{5} Pa). The work done by the system, eqn 55.8, is therefore

$$w = -(1.0\times10^{5}\,\text{Pa})\times(5.0\times10^{-3}\,\text{m}^2)\times(1.5\times10^{-1}\,\text{m}) = -75\,\text{J}$$

Note how we have converted the data to SI units (using 1 atm = 101.325 kPa) and base units and have used 1 J = 1 Pa m³.

Self-test 55.5 A reaction that consumes gas took place in a container of diameter 5.0 cm and in the process a piston moved in through 20 cm when the external pressure was 750 Torr. Evaluate the work done on the system.

Answer: +39 J

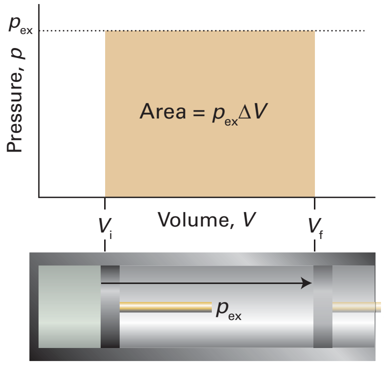

Figure 55.6 The work done by a gas when it expands against a constant external pressure, p_{ex}, is equal to the shaded area in this example of an indicator diagram.

(c) Reversible expansion

A **reversible change** in thermodynamics is a change that can be reversed by an infinitesimal modification of a variable. The key word 'infinitesimal' sharpens the everyday meaning of the word 'reversible' as something that can change direction. We say that a system is in **equilibrium** with its surroundings if an infinitesimal change in the conditions in opposite directions results in opposite changes in its state. One example of reversibility is the **thermal equilibrium** of two systems with the same temperature. The transfer of energy as heat between the two is reversible because, if the temperature of either system is lowered infinitesimally, then energy flows into the system with the lower temperature. If the temperature of either system at thermal equilibrium is raised infinitesimally, then energy flows out of the hotter (higher temperature) system.

Suppose a gas is confined by a piston and that the external pressure, p_{ex}, is set equal to the pressure, p, of the confined gas. Such a system is in **mechanical equilibrium** with its surroundings because an infinitesimal change in the external pressure in either direction causes changes in volume in the opposite direction. If the external pressure is reduced infinitesimally, then the gas expands slightly. If the external pressure is increased infinitesimally, then the gas contracts slightly. In either case the change is reversible in the thermodynamic sense. If, on the other hand, the external pressure is measurably greater than the internal pressure, then reducing p_{ex} infinitesimally will not decrease it below the pressure of the gas, so will not change the direction of the process. Such a system is not in mechanical equilibrium with its surroundings and the expansion is thermodynamically irreversible.

To achieve reversible expansion we set p_{ex} equal to p at each stage of the expansion. In practice, this equalization could be achieved by gradually removing weights from the piston so that the downward force due to the weights always matched the changing upward force due to the pressure of the gas. When we set $p_{ex} = p$, eqn 55.6 becomes

$$\mathrm{d}w = -p_{ex}\mathrm{d}V = -p\mathrm{d}V \qquad \textit{Reversible change} \qquad \text{Expansion work} \qquad (55.10)$$

Although the pressure inside the system appears in this expression for the work, it does so only because p_{ex} has been set equal to p to ensure reversibility. The total work of reversible expansion is therefore

$$w=-\int_{V_\mathrm{i}}^{V_\mathrm{f}} p\mathrm{d}V \tag{55.11}$$

We can evaluate the integral once we know how the pressure of the confined gas depends on its volume. Equation 55.11 is the link with the material covered in Topic 36, for if we know the equation of state of the gas, then we can express p in terms of V and evaluate the integral.

Consider the **isothermal** (constant-temperature), reversible expansion of a perfect gas. The expansion is made isothermal by keeping the system in thermal contact with its surroundings (which may be a constant-temperature bath). Because the equation of state is $pV=nRT$, we know that at each stage $p=nRT/V$, with V the volume at that stage of the expansion. The temperature T is constant in an isothermal expansion, so (together with n and R) it may be taken outside the integral. It follows that the work of reversible isothermal expansion of a perfect gas from V_i to V_f at a temperature T is

$$w=-\int_{V_\mathrm{i}}^{V_\mathrm{f}} \frac{nRT}{V}\mathrm{d}V=-nRT\int_{V_\mathrm{i}}^{V_\mathrm{f}} \frac{1}{V}\mathrm{d}V$$

Then, by using the standard integral of $1/x$ (Integral A.2 in the *Resource section*), we can write

$$w=-nRT\ln\frac{V_\mathrm{f}}{V_\mathrm{i}} \qquad \textit{Reversible, isothermal, perfect gas} \qquad \text{Expansion work} \tag{55.12}$$

Expressions that are valid only for perfect gases are labelled, as here, in blue.

Brief illustration 55.6 The work of isothermal, reversible expansion

When a sample of 1.00 mol Ar, regarded here as a perfect gas, undergoes an isothermal, reversible expansion at 20.0 °C from 10.0 dm³ to 30.0 dm³ the work done is

$$\begin{aligned} w&=-(1.00\,\mathrm{mol})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(293.2\,\mathrm{K})\ln\frac{30.0\,\mathrm{dm^3}}{10.0\,\mathrm{dm^3}}\\ &=-2.68\,\mathrm{kJ}\end{aligned}$$

Self-test 55.6 Suppose that attractions are important between gas molecules, and the equation of state is $p=nRT/V-n^2a/V^2$. Derive an expression for the reversible, isothermal expansion of this gas. Is more or less work done *on the surroundings* when it expands (compared with a perfect gas)?

Answer: $w=-nRT\ln(V_\mathrm{f}/V_\mathrm{i})-n^2a(1/V_\mathrm{f}-1/V_\mathrm{i})$; less

When the final volume is greater than the initial volume, as in an expansion, the logarithm in eqn 55.12 is positive and hence $w<0$. In this case, the system has done work on the surroundings and the internal energy of the system has decreased as a result. In Topic 58 we see that there is a compensating influx of energy as heat, so overall the internal energy is constant for the isothermal expansion of a perfect gas. The equations also show that more work is done for a given change of volume when the temperature is increased. The greater pressure of the confined gas then needs a higher opposing pressure to ensure reversibility. We cannot obtain more work than for the reversible process because increasing the external pressure even infinitesimally at any stage results in compression. We may infer from this discussion that, because some pushing power is wasted when $p>p_\mathrm{ex}$, the maximum work available from a system operating between specified initial and final states and passing along a specified path is obtained when the change takes place reversibly. As in the case of constant external pressure, the work done is equal to the area under the isotherm, in this case representing the balanced internal and external pressures (Fig. 55.7).

(d) The molecular interpretation of reversible expansion

The logarithmic term in eqn 55.12 can be explained in molecular terms by noting that, in general, an infinitesimal change in the total energy ($N\langle\varepsilon\rangle=\Sigma_i\varepsilon_iN_i$) of a collection of independent

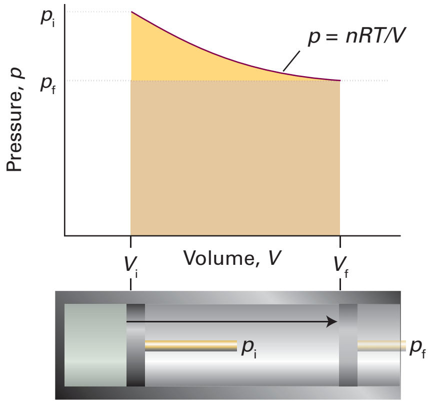

Figure 55.7 The work done by a perfect gas when it expands reversibly and isothermally is equal to the area under the isotherm $p=nRT/V$. The work done during the irreversible expansion against the same final pressure is equal to the rectangular area shown slightly darker. Note that the reversible work is greater than the irreversible work.

molecules arises from a change in the energy levels ε_i they occupy and a change in the populations N_i of those levels:

$$N\mathrm{d}\varepsilon=\sum_i \varepsilon_i \mathrm{d}N_i+\sum_i N_i \mathrm{d}\varepsilon_i \qquad (55.13)$$

We cannot in general identify one of the terms on the right with the work done by the system, except in the case of a *reversible* change, when the external force exerted against the system as it expands is matched to the force exerted by the molecules inside the system. In that case we can use the properties of the system to calculate the external opposing force (just as we replaced p_{ex} by p). Provided this expansion is both infinitesimal and isothermal, there is no change in the populations of the levels since the Boltzmann populations depend only on temperature, and therefore the first term on the right of eqn 55.13 is zero. Therefore, the work done by the system in the course of a reversible, isothermal expansion can be identified with the second term on the right:

$$\mathrm{d}w=\sum_i N_i \mathrm{d}\varepsilon_i \qquad \textit{Reversible, isothermal expansion} \qquad (55.14)$$

We show in Example 55.1 that when this expression is applied to a collection of independent molecules in a box, then we obtain the logarithmic term in eqn 55.12.

Example 55.1 Deriving the molecular expression for the work of isothermal, reversible expansion

Show that eqn 55.14 leads to the thermodynamic expression for the work when it is applied to the expansion of a box containing non-interacting molecules.

Method We know from Topic 9 that the energy levels of a particle in a box relative to its ground state (with the index i replaced by the quantum number n) are

$$\varepsilon_n=(n^2-1)\frac{h^2}{8mL^2}$$

Therefore, derive an expression for the change in this energy when the length of the box is increased infinitesimally and then use eqn 55.14. Integrate the resulting expression to obtain the work for a measurable change in length. At high temperature, use the equipartition value of the mean energy of the particles.

Answer The change in the energy of a level with quantum number n when the length of a one-dimensional box changes by $\mathrm{d}L$ is

$$\mathrm{d}\varepsilon_n=\left(\frac{\mathrm{d}\varepsilon_n}{\mathrm{d}L}\right)\mathrm{d}L=-2(n^2-1)\frac{h^2}{8mL^3}\mathrm{d}L=-2\varepsilon_n\frac{\mathrm{d}L}{L}$$

Equation 55.14 is therefore

$$\mathrm{d}w=\sum_n N_n\mathrm{d}\varepsilon_n=-2\frac{\mathrm{d}L}{L}\sum_n N_n\varepsilon_n=-2\langle\varepsilon\rangle N\frac{\mathrm{d}L}{L}$$

For this one-dimensional system, $\langle\varepsilon\rangle=\frac{1}{2}kT$. Provided the temperature is constant (so that $\langle\varepsilon\rangle$ is constant), we can integrate this expression between the initial and final lengths of the box:

$$w=-2\langle\varepsilon\rangle N\int_{L_\mathrm{i}}^{L_\mathrm{f}}\frac{\mathrm{d}L}{L}=-NkT\ln\frac{L_\mathrm{f}}{L_\mathrm{i}}=-nRT\ln\frac{L_\mathrm{f}}{L_\mathrm{i}}$$

We have used $N=nN_\mathrm{A}$ and $N_\mathrm{A}k=R$. In three dimensions, the ratio of lengths is replaced by the ratio of volumes, as in the classical calculation, and we recover eqn 55.12.

Self-test 55.7 Extend this calculation to a particle in a two-dimensional box.

Answer: $w=-nRT\ln(A_\mathrm{f}/A_\mathrm{i})$

55.4 Heat transactions

In general, the change in internal energy of a closed system is

$$\mathrm{d}U=\mathrm{d}q+\mathrm{d}w=\mathrm{d}q+\mathrm{d}w_{\mathrm{exp}}+\mathrm{d}w_\mathrm{e} \qquad (55.15)$$

where, as usual, $\mathrm{d}q$ is the energy transferred as heat and $\mathrm{d}w$ the energy transferred as work: $\mathrm{d}w_\mathrm{e}$ is non-expansion work, that is, work in addition (e for 'extra') to the expansion work, $\mathrm{d}w_{\mathrm{exp}}$. For instance, $\mathrm{d}w_\mathrm{e}$ might be the electrical work of driving a current through a circuit. A system kept at constant volume can do no expansion work, so $\mathrm{d}w_{\mathrm{exp}}=0$. If the system is also incapable of doing any other kind of work (if it is not, for instance, an electrochemical cell connected to an electric motor), then $\mathrm{d}w_\mathrm{e}=0$ too. Under these circumstances:

$$\mathrm{d}U=\mathrm{d}q \qquad \textit{Constant volume, no additional work} \qquad \text{Heat transaction} \qquad (55.16a)$$

We express this relation by writing $\mathrm{d}U=\mathrm{d}q_V$, where the subscript implies a change at constant volume. For a measurable change

$$\Delta U=q_V \qquad \textit{Constant volume, no additional work} \qquad \text{Heat transaction} \qquad (55.16b)$$

It follows that by measuring the energy supplied to a constant-volume system as heat ($q>0$) or obtained from it as heat ($q<0$) when it undergoes a change of state, we are in fact measuring the change in its internal energy.

Brief illustration 55.7 The change in internal energy

A combustion reaction took place in a rigid, sealed metal container, which was then allowed to reach thermal equilibrium with its surroundings, which consisted of a water bath with ice, all at 0 °C. At the end of the experiment it was found that some ice had melted, the amount corresponding to the transfer of 25 kJ of energy as heat to the water bath. We infer that $q_V = -25$ kJ, and therefore that the change in internal energy of the system in the course of the combustion is $\Delta U = -25$ kJ.

Self-test 55.8 Repeat the question for a chemical reaction for which it was observed that some water in the bath had frozen, corresponding to the removal of 30 kJ of energy as heat from the water bath.

Answer: $\Delta U = +30$ kJ

(a) Heat capacity

The internal energy of a substance increases when its temperature is raised and the Boltzmann distribution populates higher energy levels. The increase depends on the conditions under which the heating takes place and for the present we suppose that the sample is confined to a constant volume. For example, the sample may be a gas in a container of fixed volume.

If the internal energy is plotted against temperature, then a curve like that in Fig. 55.8 may be obtained. The slope of the tangent to the curve at any temperature is called the **heat capacity** of the system at that temperature. The **heat capacity at constant volume** (or 'isochoric heat capacity') is denoted C_V and is defined formally as

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad (55.17)$$

Definition Constant-volume heat capacity

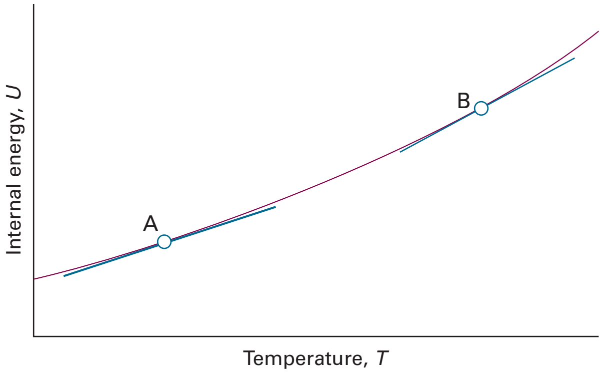

Figure 55.8 The internal energy of a system increases as the temperature is raised; this graph shows its variation as the system is heated at constant volume. The slope of the tangent to the curve at any temperature is the heat capacity at constant volume at that temperature. Note that, for the system illustrated, the heat capacity is greater at B than at A.

Brief illustration 55.8 The heat capacity of a gas

The heat capacity of a monatomic perfect gas can be calculated by inserting the expression for the internal energy, $U_m = U_m(0) + \frac{3}{2}RT$ (see *Brief illustration* 55.2); so from eqn 55.17

$$C_{V,m} = \left(\frac{\partial\left\{U_m(0) + \frac{3}{2}RT\right\}}{\partial T}\right)_V = \frac{3}{2}R$$

The numerical value is 12.47 J K^{-1} mol^{-1}.

Self-test 55.9 Estimate the molar heat capacity of a diatomic perfect gas free to rotate but not vibrate.

Answer: $C_{V,m} = \frac{5}{2}R$, 20.7947 J K^{-1} mol^{-1}

The heat capacity is used to relate a change in internal energy to a change in temperature of a constant-volume system. It follows from eqn 55.17 that

$$dU = C_V dT \qquad \textit{Constant volume} \qquad (55.18a)$$

That is, at constant volume, an infinitesimal change in temperature brings about an infinitesimal change in internal energy, and the constant of proportionality is C_V. If the heat capacity is independent of temperature over the range of temperatures of interest, a measurable change of temperature, ΔT, brings about a measurable increase in internal energy, ΔU, where

$$\Delta U = C_V \Delta T \qquad \textit{Constant volume} \qquad (55.18b)$$

Because a change in internal energy can be identified with the heat supplied at constant volume (eqn 55.16), the last equation can also be written

$$q_V = C_V \Delta T \qquad \textit{Constant volume} \qquad (55.18c)$$

This relation provides a simple way of measuring the heat capacity of a sample: a measured quantity of energy is transferred as heat to the sample (electrically, for example), and the resulting increase in temperature is monitored. The ratio of the energy transferred as heat to the temperature rise it causes ($q_V/\Delta T$) is the constant-volume heat capacity of the sample.

Brief illustration 55.9 The determination of a heat capacity

Suppose a 55 W electric heater immersed in a gas in a constant-volume adiabatic container was on for 120 s and it was found that the temperature of the gas rose by 5.0 °C (an increase equivalent to 5.0 K). The heat supplied is

$(55\,\text{W})\times(120\,\text{s})=6.6\,\text{kJ}$ (we have used $1\,\text{J}=1\,\text{W s}$), so the heat capacity of the sample is

$$C_V=\frac{6.6\,\text{kJ}}{5.0\,\text{K}}=1.3\,\text{kJ}\,\text{K}^{-1}$$

Self-test 55.10 When 229 J of energy is supplied as heat to 3.0 mol of a gas at constant volume, the temperature of the gas increases by 2.55 °C. Calculate C_V and the molar heat capacity at constant volume.

Answer: $89.8\,\text{J}\,\text{K}^{-1}$, $29.9\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$

(b) The molecular interpretation of heat transfer

In molecular terms, the influx of energy as heat does not change the energy levels of a system, but does modify their populations. That is, eqn 55.13 becomes

$$N\mathrm{d}\langle\varepsilon\rangle=\sum_i \varepsilon_i\,\mathrm{d}N_i \qquad \textit{Constant volume, no additional work} \qquad \text{Heat transaction} \qquad (55.19\text{a})$$

and for a measurable change

$$\Delta U=\sum_i \varepsilon_i\,\Delta N_i \qquad \textit{Constant volume, no additional work} \qquad \text{Heat transaction} \qquad (55.19\text{b})$$

The change in populations and therefore the internal energy is due to a change in temperature, which redistributes the molecules over the fixed energy levels. The relation of this discussion to the molecular basis of heat capacity is taken further in Topic 58.

Equation 55.19b is more general than at first it might look, for it applies to a chemical reaction as well as to a system composed of a single species. To interpret it in terms of the reaction $\text{A}\rightarrow\text{B}$, we imagine the energy levels of the molecules A and B as forming a single ladder of levels (Fig. 55.9). It should be recalled from Topic 51 that the principle of equal *a priori* probabilities, on which the Boltzmann distribution is based, ignores the specific types of energy levels, treating all kinds equally: that blindness applies to the energy levels of different species too. At the start of the reaction, only the levels belonging to A are occupied; at the end of a complete reaction, only the levels belonging to B are occupied (later we see that equilibrium corresponds to a Boltzmann distribution over both sets of levels). The redistribution of populations corresponds to the ΔN_i in eqn 55.19b:

$$\Delta U=\sum_i \varepsilon_i\,\Delta N_i=\sum_{i,\,\text{products}}\varepsilon_i N_i-\sum_{i,\,\text{reactants}}\varepsilon_i N_i \qquad (55.20)$$

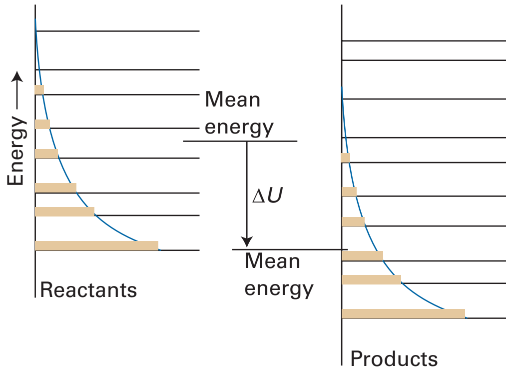

Figure 55.9 The change in internal energy when a chemical reaction takes place is equal to the change in mean energy between products and reactants, taking into account the Boltzmann distribution of populations. The blue lines are the distributions, and correspond to the same temperature.

Brief illustration 55.10 The difference in internal energy

Suppose that the reactant molecules lie at zero energy (in the sense that they define that energy level), and that the product molecules lie at an energy $120\,\text{kJ}\,\text{mol}^{-1}$ lower. To calculate ΔU when 1 mol of reactant molecules change into 1 mol of product molecules, we first write

$$\begin{aligned}U&=\varepsilon_{\text{products}}N_{\text{products}}-\varepsilon_{\text{reactants}}N_{\text{reactants}}=\varepsilon_{\text{products}}N_{\text{products}}\\&=\varepsilon_{\text{products}}n_{\text{products}}N_{\text{A}}\end{aligned}$$

where n_{products} is the chemical amount (in moles) of the product molecules and N_{A} is Avogadro's constant. Then, with $\varepsilon_{\text{products}}N_{\text{A}}=-120\,\text{kJ mol}^{-1}$ and $n_{\text{products}}=1\,\text{mol}$,

$$\Delta U=(-120\,\text{kJ}\,\text{mol}^{-1})\times\left(1\,\text{mol}\right)=-120\,\text{kJ}$$

Self-test 55.11 Suppose now that 80 per cent of the reactant molecules occupy the ground state (of zero energy), 20 per cent occupy a level $20\,\text{kJ}\,\text{mol}^{-1}$ above, and 70 per cent of the product molecules occupy a level of energy $120\,\text{kJ}\,\text{mol}^{-1}$ lower and 30 per cent occupy a level $40\,\text{kJ}\,\text{mol}^{-1}$ above that level. Calculate ΔU when 1 mol of reactant molecules change into 1 mol of product molecules.

Answer: $-112\,\text{kJ mol}^{-1}$

Changes in internal energy accompanying physical changes and chemical reactions are measured using a calorimeter: see Topic 57.

Checklist of concepts

☐ 1. **Thermodynamics** is the study of the transformations of energy.
☐ 2. The **system** is the part of the world in which we have a special interest. The **surroundings** is the region outside the system where we make our measurements.
☐ 3. An **open system** has a boundary through which matter can be transferred. A **closed system** has a boundary through which matter cannot be transferred. An **isolated system** has a boundary through which neither matter nor energy can be transferred.
☐ 4. **Energy** is the capacity to do work. The **internal energy** is the total energy of a system.
☐ 5. **Work** is the transfer of energy by motion against an opposing force. **Heat** is the transfer of energy as a result of a temperature difference between the system and the surroundings. In molecular terms, heating makes use of thermal motion, that is, disorderly molecular motion.
☐ 6. An **exothermic process** releases energy as heat; an **endothermic process** absorbs energy as heat.
☐ 7. A **state function** is a property that depends only on the current state of the system and is independent of how that state has been prepared.
☐ 8. The **First Law** of thermodynamics states that the internal energy of an isolated system is constant.
☐ 9. A **reversible change** is a change that can be reversed by an infinitesimal modification of a variable.
☐ 10. A system is in **equilibrium** with its surroundings if an infinitesimal change in conditions in an opposite direction results in an opposite change in state.
☐ 11. **Maximum work** is achieved in a reversible change.

Checklist of equations

Property	Equation	Comment	Equation number
First Law	$\Delta U = q + w$		55.3
	$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$	Infinitesimal change	55.4
Expansion work	$\mathrm{d}w = -p_{\mathrm{ex}}\mathrm{d}V$	In general	55.6
	$w = -p_{\mathrm{ex}}\Delta V$	Constant external pressure	55.8
	$w = -nRT\ln(V_{\mathrm{f}}/V_{\mathrm{i}})$	Perfect gas, isothermal, reversible	55.12
Heat capacity	$C_V = (\partial U/\partial T)_V$	Constant volume	55.17
Change in internal energy	$\Delta U = q_V$	Constant volume	55.18

TOPIC 56

Enthalpy

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➤ Why do you need to know this material?

The concept of enthalpy lies at the heart of the application of thermodynamics to chemistry, and in particular thermochemistry (Topic 57) and the discussion of physical and chemical equilibria (Topics 69 and 73). It is also central to the assessment of the energy resources of fuels and foods.

➤ What is the key idea?

A change in enthalpy of a system is equal to the energy supplied as heat at constant pressure.

➤ What do you need to know already?

You need to be familiar with the concepts relating to the First Law, particularly the internal energy, and the significance of the term 'state function' (Topic 55). You also need to be familiar with some of the manipulations of partial derivatives (*Mathematical background* 8).

When the system is free to change its volume, some of the energy supplied as heat to the system is returned to the surroundings as expansion work (Fig. 56.1), so $\mathrm{d}U$ is less than $\mathrm{d}q$. However, we shall now show that in this case the energy supplied as heat at constant pressure is equal to the change in another thermodynamic property of the system, the enthalpy.

56.1 The definition of enthalpy

The **enthalpy**, H, is defined as

$$H = U + pV$$

Definition Enthalpy (56.1)

where p is the pressure of the system and V is its volume. Because U, p, and V are all state functions, the enthalpy is a state function too. As is true of any state function, the change in enthalpy, ΔH, between any pair of initial and final states is independent of the path between them.

We show in the following *Justification* that eqn 56.1 implies that *the change in enthalpy is equal to the energy supplied as heat at constant pressure* (provided the system does no additional work):

$$\mathrm{d}H = \mathrm{d}q$$

Constant pressure, no additional work Enthalpy change (56.2a)

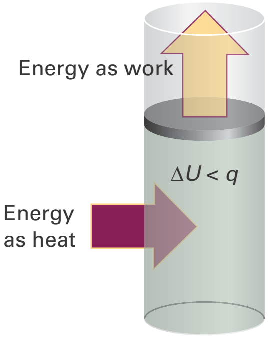

Figure 56.1 When a system is subjected to constant pressure and is free to change its volume, some of the energy supplied as heat may escape back into the surroundings as work. In such a case, the change in internal energy is smaller than the energy supplied as heat.

For a measurable change,

$$\Delta H = q_p \tag{56.2b}$$

Constant pressure, no additional work Enthalpy change

where the subscript p denotes constant pressure.

Justification 56.1 The relation $\Delta H = q_p$

For a general infinitesimal change in the state of the system, U changes to $U+\mathrm{d}U$, p changes to $p+\mathrm{d}p$, and V changes to $V+\mathrm{d}V$, so from the definition in eqn 56.1, H changes from $U+pV$ to

$$\begin{aligned} H+\mathrm{d}H &= (U+\mathrm{d}U)+(p+\mathrm{d}p)(V+\mathrm{d}V) \\ &= U+\mathrm{d}U+pV+p\mathrm{d}V+V\mathrm{d}p+\mathrm{d}p\mathrm{d}V \end{aligned}$$

The last term is the product of two infinitesimally small quantities and can therefore be neglected. As a result, after recognizing $U+pV=H$ on the right, we find that H changes to

$$H+\mathrm{d}H = H+\mathrm{d}U+p\mathrm{d}V+V\mathrm{d}p$$

and hence that

$$\mathrm{d}H = \mathrm{d}U+p\mathrm{d}V+V\mathrm{d}p$$

If we now substitute $\mathrm{d}U=\mathrm{d}q+\mathrm{d}w$ into this expression, we get

$$\mathrm{d}H = \mathrm{d}q+\mathrm{d}w+p\mathrm{d}V+V\mathrm{d}p$$

If the system is in mechanical equilibrium with its surroundings at a pressure p and does only expansion work, we can write $\mathrm{d}w=-p\mathrm{d}V$ and obtain

$$\mathrm{d}H = \mathrm{d}q+V\mathrm{d}p$$

Now we impose the condition that the heating occurs at constant pressure by writing $\mathrm{d}p=0$. Then

$$\mathrm{d}H = \mathrm{d}q \quad \text{(at constant pressure, no additional work)}$$

as in eqn 56.2a.

The result expressed in eqn 56.2 states that when a system is subjected to a constant pressure, and only expansion work can occur, the change in enthalpy is equal to the energy supplied as heat.

Brief illustration 56.1 The change in enthalpy

If we supply 36 kJ of energy through an electric heater immersed in an open beaker of water, then the enthalpy of the water increases by 36 kJ and we write +36 kJ. If a beaker of water cools to the temperature of its surroundings, and in the process loses 36 kJ of energy as heat, the enthalpy of the water decreases by 36 kJ and we write $\Delta H = -36$ kJ.

Self-test 56.1 What is the change of enthalpy when an exothermic reaction takes place in an adiabatic container fitted with a freely moving piston?

Answer: $\Delta H = 0$

56.2 Heat capacity at constant pressure

The enthalpy of a substance increases as its temperature is raised. The relation between the increase in enthalpy and the increase in temperature depends on the conditions (for example, constant pressure or constant volume). The most important condition is constant pressure, and the slope of the tangent to a plot of enthalpy against temperature at constant pressure is called the **heat capacity at constant pressure** (or 'isobaric heat capacity'), C_p, at a given temperature (Fig. 56.2). More formally:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{56.3}$$

Definition Heat capacity at constant pressure

The heat capacity at constant pressure is the analogue of the heat capacity at constant volume (Topic 55, eqn 55.17), and is an extensive property. As in the case of C_V, if the system can change its composition it is necessary to distinguish between equilibrium and fixed-composition values. All applications in this Topic refer to pure substances, so this complication can be ignored. The **molar heat capacity at constant pressure**, $C_{p,\mathrm{m}}$, is the heat capacity per mole of material; it is an intensive property.

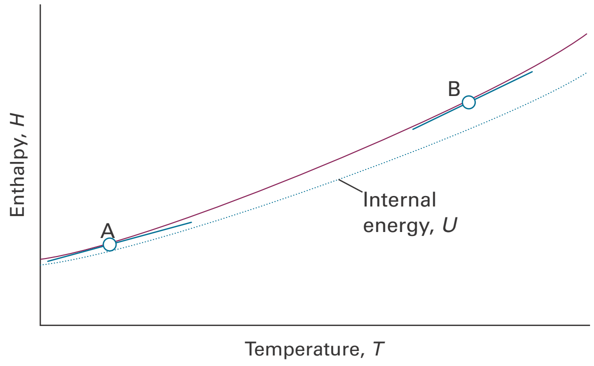

Figure 56.2 The slope of the tangent to a curve of the enthalpy of a system subjected to a constant pressure plotted against temperature is the constant-pressure heat capacity. The slope may change with temperature, in which case the heat capacity varies with temperature. Thus, the heat capacities at A and B are different. For gases, at a given temperature the slope of enthalpy versus temperature is steeper than that of internal energy versus temperature, and $C_{p,\mathrm{m}}$ is larger than $C_{V,\mathrm{m}}$.

The heat capacity at constant pressure is used to relate the change in enthalpy to a change in temperature. For infinitesimal changes of temperature,

$$\mathrm{d}H = C_p\mathrm{d}T$$

Constant pressure (56.4a)

If the heat capacity is constant over the range of temperatures of interest, then for a measurable increase in temperature

$$\Delta H = C_p\Delta T$$

Constant pressure, C_p constant (56.4b)

Because an increase in enthalpy can be equated to the energy supplied as heat at constant pressure, the practical form of the latter equation is

$$q_p = C_p\Delta T$$

Constant pressure, C_p constant (56.4c)

This expression shows us how to measure the heat capacity of a sample: a measured quantity of energy is supplied as heat under conditions of constant pressure (as in a sample exposed to the atmosphere and free to expand), and the temperature rise is monitored.

The variation of heat capacity with temperature can sometimes be ignored if the temperature range is small; this approximation is highly accurate for a monatomic perfect gas (for instance, one of the noble gases at low pressure). However, when it is necessary to take the variation into account, a convenient approximate empirical expression is

$$C_{p,\mathrm{m}} = a + bT + \frac{c}{T^2}$$

Empirical relation Heat capacity dependence on temperature (56.5)

The empirical parameters a, b, and c are independent of temperature (Table 56.1).

Table 56.1* Temperature variation of molar heat capacities, $C_{p,\mathrm{m}}/(\mathrm{J\,K^{-1}\,mol^{-1}}) = a + bT + c/T^2$

	a	$b/(10^{-3}\,\mathrm{K})$	$c/(10^5\,\mathrm{K}^2)$
C(s, graphite)	16.86	4.77	−8.54
CO_2(g)	44.22	8.79	−8.62
H_2O(l)	75.29	0	0
N_2(g)	28.58	3.77	−0.50

* More values are given in the *Resource section*.

Example 56.1 Evaluating an increase in enthalpy with temperature

What is the change in molar enthalpy of N_2 when it is heated from 25 °C to 100 °C? Use the heat capacity information in Table 56.1.

Method The heat capacity of N_2 changes with temperature, so we cannot use eqn 56.4c (which assumes that the heat capacity of the substance is constant). Therefore, we must use eqn 56.4a, substitute eqn 56.5 for the temperature dependence of the heat capacity, and integrate the resulting expression from 25 °C to 100 °C.

Answer For convenience, we denote the two temperatures T_1 (298 K) and T_2 (373 K). The integral we require is

$$\int_{H_\mathrm{m}(T_1)}^{H_\mathrm{m}(T_2)} \mathrm{d}H_\mathrm{m} = \int_{T_1}^{T_2}\left(a + bT + \frac{c}{T^2}\right)\mathrm{d}T$$

Now we use the integral of x^n (Integral A.1 of the *Resource section*) to obtain

$$H_\mathrm{m}(T_2) - H_\mathrm{m}(T_1) = a(T_2 - T_1) + \tfrac{1}{2}b(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Substitution of the numerical data results in

$$H_\mathrm{m}(373\,\mathrm{K}) = H_\mathrm{m}(298\,\mathrm{K}) + 2.20\,\mathrm{kJ\,mol^{-1}}$$

If we had assumed a constant heat capacity of 29.14 J K⁻¹ mol⁻¹ (the value given by eqn 56.5 at 25 °C), we would have found that the two enthalpies differed by 2.19 kJ mol⁻¹.

Self-test 56.2 At very low temperatures the heat capacity of a solid is proportional to T^3, and we can write $C_p = aT^3$. What is the change in enthalpy of such a substance when it is heated from 0 to a temperature T (with T close to 0)?

Answer: $\Delta H = \frac{1}{4}aT^4$

Most systems expand when heated at constant pressure. Such systems do work on the surroundings and therefore some of the energy supplied to them as heat escapes back to the surroundings. As a result, the temperature of the system rises less than when the heating occurs at constant volume. A smaller increase in temperature implies a larger heat capacity, so we conclude that in most cases the heat capacity at constant pressure of a system is larger than its heat capacity at constant volume. We show in Topics 58 and 66 that there is a simple relation between the two heat capacities of a perfect gas:

$$C_p - C_V = nR$$

Perfect gas Relation between heat capacities (56.6)

It follows that the molar heat capacity of a perfect gas is about 8 J K⁻¹ mol⁻¹ larger at constant pressure than at constant volume. Because the heat capacity at constant volume of a monatomic gas is about 12 J K⁻¹ mol⁻¹, the difference is highly significant and must be taken into account. For substances other than perfect gases, the forces between atoms play a role in determining the magnitude of the work of expansion and the expression for the difference between C_p and C_V is more complicated.[1]

56.3 Changes in enthalpy with pressure and temperature

It turns out that H is a useful thermodynamic function whenever the pressure is under our control: we saw a sign of that in the relation $\Delta H = q_p$ (eqn 56.2b). We shall therefore regard H as a function of p and T, and look for an expression for the variation of H with temperature and pressure. As set out in the following *Justification*, we find that, for a closed system of constant composition,

$$\mathrm{d}H = -\mu C_p \mathrm{d}p + C_p \mathrm{d}T \qquad \text{Variation of enthalpy} \qquad (56.7)$$

where the **Joule–Thomson coefficient**, μ (mu), is defined as

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H \qquad \textit{Definition} \quad \text{Joule–Thomson coefficient} \qquad (56.8)$$

As we shall see, this relation is useful for discussing the liquefaction of gases.

Brief illustration 56.2 The Joule–Thomson coefficient

When a sample of Freon gas used in refrigeration was allowed to expand at constant enthalpy from 32 atm at 0 °C to 1.00 atm, the temperature fell by 22 K. The Joule–Thomson coefficient is therefore

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H = \frac{-22\ \mathrm{K}}{-31\ \mathrm{atm}} = +0.71\ \mathrm{K\ atm^{-1}}$$

Self-test 56.3 Repeat the calculation for another experiment in which a gas expands from 22 atm to 1 atm, when the temperature fell by 10 K.

Answer: $\mu = +0.48\ \mathrm{K\ atm^{-1}}$

Justification 56.2 The variation of enthalpy with pressure and temperature

Because H may be regarded as a function of p and T, when these parameters change the enthalpy changes as follows:

$$\mathrm{d}H = \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p + \left(\frac{\partial H}{\partial T}\right)_p \mathrm{d}T$$

The second partial derivative is C_p; our task here is to express $(\partial H/\partial p)_T$ in terms of recognizable quantities. The chain relation (see *Mathematics background* 8) lets us write

$$\left(\frac{\partial H}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_p = -1$$

and therefore

$$\left(\frac{\partial H}{\partial p}\right)_T = -\frac{1}{\left(\frac{\partial p}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_p}$$

Both partial derivatives can be brought into the numerator by using the reciprocal identity $(\partial y/\partial x = 1/(\partial x/\partial y))$ twice:

$$\left(\frac{\partial H}{\partial p}\right)_T = -\left(\frac{\partial T}{\partial p}\right)_H \left(\frac{\partial H}{\partial T}\right)_p$$

We recognize the Joule–Thomson coefficient and the constant-pressure heat capacity, so this expression becomes

$$\left(\frac{\partial H}{\partial p}\right)_T = -\mu C_p$$

Equation 56.7 now follows directly.

56.4 The Joule–Thomson effect

The analysis of the Joule–Thomson coefficient is central to the technological problems associated with the liquefaction of gases. We need to be able to interpret it physically and to measure it.

As shown in the following *Justification*, the cunning required to impose the constraint of constant enthalpy, so that the process is **isenthalpic,** was supplied by Joule and William Thomson (later Lord Kelvin). They let a gas expand through a porous barrier from one constant pressure to another, and monitored the difference of temperature that arose from the expansion (Fig. 56.3). The whole apparatus was insulated so that the process was adiabatic. They observed a lower temperature on the low-pressure side, the difference in temperature being proportional to the pressure difference they maintained. This cooling by isenthalpic expansion is now called the **Joule–Thomson effect**.

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[1] For details, see our other *Physical chemistry* (2014).

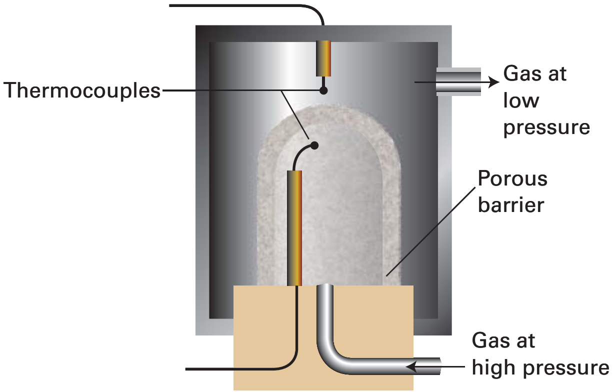

Figure 56.3 The apparatus used for measuring the Joule–Thomson effect. The gas expands through the porous barrier, which acts as a throttle, and the whole apparatus is thermally insulated. As explained in the text, this arrangement corresponds to an isenthalpic expansion (expansion at constant enthalpy). Whether the expansion results in a heating or a cooling of the gas depends on the conditions.

Justification 56.3 The Joule–Thomson effect

Here we show that the experimental arrangement results in expansion at constant enthalpy. Because all changes to the gas occur adiabatically,

$$q=0,\ \text{which implies } \Delta U=w$$

Consider the work done as the gas passes through the barrier. We focus on the passage of a fixed amount of gas from the high-pressure side, where the pressure is p_i, the temperature T_i, and the gas occupies a volume V_i (Fig. 56.4). The gas emerges on the low-pressure side, where the same amount of gas has a pressure p_f, a temperature T_f, and occupies a volume V_f. The gas on the left is compressed isothermally by the upstream gas acting as a piston. The relevant pressure is p_i and the volume changes from V_i to 0; therefore, the work done on the gas is

$$w_1=-p_i(0-V_i)=p_iV_i$$

The gas expands isothermally on the right of the barrier (but possibly at a different constant temperature) against the pressure p_f provided by the downstream gas acting as a piston to be driven out. The volume changes from 0 to V_f, so the work done on the gas in this stage is

$$w_2=-p_f(V_f-0)=-p_fV_f$$

The total work done on the gas is the sum of these two quantities, or

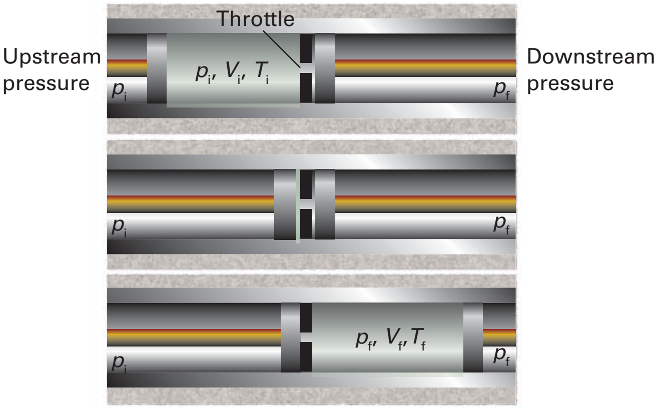

Figure 56.4 The thermodynamic basis of Joule–Thomson expansion. The pistons represent the upstream and downstream gases, which maintain constant pressures either side of the throttle. The transition from the top diagram to the bottom diagram, which represents the passage of a given amount of gas through the throttle, occurs without change of enthalpy.

$$w=w_1+w_2=p_iV_i-p_fV_f$$

It follows that the change of internal energy of the gas as it moves adiabatically from one side of the barrier to the other is

$$U_f-U_i=w=p_iV_i-p_fV_f$$

Reorganization of this expression gives

$$U_f+p_fV_f=U_i+p_iV_i,\quad \text{or}\quad H_f=H_i$$

Therefore, the expansion occurs without change of enthalpy.

The property measured in the experiment is the ratio of the temperature change to the change of pressure, $\Delta T/\Delta p$. Adding the constraint of constant enthalpy and taking the limit of small Δp implies that the thermodynamic quantity measured is $(\partial T/\partial p)_H$, which is the Joule–Thomson coefficient, μ. In other words, the physical interpretation of μ is that it is the ratio of the change in temperature to the change in pressure when a gas expands under conditions that ensure there is no change in enthalpy.

The modern method of measuring μ is indirect, and involves measuring the **isothermal Joule–Thomson coefficient**, the quantity

$$\mu_T=\left(\frac{\partial H}{\partial p}\right)_T \tag{56.9}$$

Definition Isothermal Joule–Thomson coefficient

which is the slope of a plot of enthalpy against pressure at constant temperature (Fig. 56.5). On comparing eqns 56.9 and the

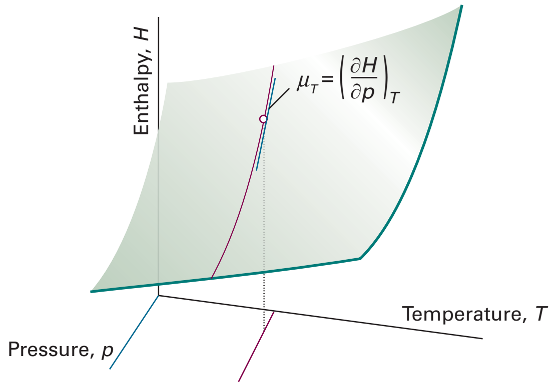

Figure 56.5 The isothermal Joule–Thomson coefficient is the slope of the enthalpy with respect to changing pressure, the temperature being held constant.

relation $(\partial H/\partial p)_T = -\mu C_p$ derived in *Justification* 56.2, we see that the two coefficients are related by

$$\mu_T = -C_p\mu \qquad \text{Relation between coefficients} \qquad (56.10)$$

Note that, whereas the Joule–Thomson coefficient is an intensive property, the *isothermal* Joule–Thomson coefficient depends on the heat capacity of the sample passing through the apparatus and is extensive.

To measure μ_T, the gas is pumped continuously at a steady pressure through a heat exchanger (which brings it to the required temperature), and then through a porous plug inside a thermally insulated container. The steep pressure drop is measured, and the cooling effect is exactly offset by an electric heater placed immediately after the plug (Fig. 56.6). The energy provided by the heater is monitored. Because the energy transferred as heat can be identified with the value of ΔH for the gas (because $\Delta H = q_p$), and the pressure change Δp is known, we can find μ_T from the limiting value of $\Delta H/\Delta p$ as $\Delta p \to 0$, and then convert it to μ. Table 56.2 lists some values obtained in this way.

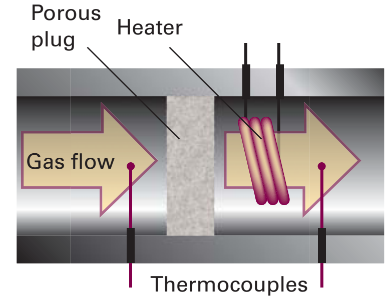

Figure 56.6 A schematic diagram of the apparatus used for measuring the isothermal Joule–Thomson coefficient. The electrical heating required to offset the cooling arising from expansion is interpreted as ΔH and used to calculate $(\partial H/\partial p)_T$, which is then converted to μ as explained in the text.

Table 56.2* Inversion temperatures, normal freezing and boiling points, and Joule–Thomson coefficients at 1 atm and 298 K

	T_I/K	T_f/K	T_b/K	μ/(K bar^{-1})
Ar	723	83.8	87.3	
CO_2	1500		194.7	+1.10
He	40		4.2	−0.062
N_2	621	63.3	77.4	+0.27

* More values are given in the *Resource section*.

Real gases have nonzero Joule–Thomson coefficients. Depending on the identity of the gas, the pressure, the relative magnitudes of the attractive and repulsive intermolecular forces, and the temperature, the sign of the coefficient may be either positive or negative (Fig. 56.7). A positive sign implies that dT is negative when dp is negative, in which case the gas cools on expansion. Gases that show a heating effect ($\mu < 0$) at one temperature show a cooling effect ($\mu > 0$) when the temperature passes through an **inversion temperature**, T_I (Table 56.2, Fig. 56.8). As indicated in Fig. 56.8, a gas typically has two inversion temperatures, one at high temperature and the other at low.

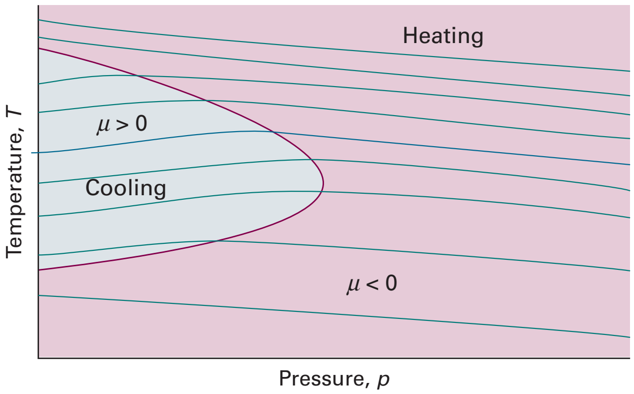

Figure 56.7 The sign of the Joule–Thomson coefficient, μ, depends on the conditions. Inside the boundary, the shaded area, it is positive and outside it is negative. The temperature corresponding to the boundary at a given pressure is the 'inversion temperature' of the gas at that pressure. For a given pressure, the temperature must be below a certain value if cooling is required, but if it becomes too low, the boundary is crossed again and heating occurs. Reduction of pressure under adiabatic conditions moves the system along one of the isenthalps, or curves of constant enthalpy. The inversion temperature curve runs through the points of the isenthalps where their slope changes from negative to positive.

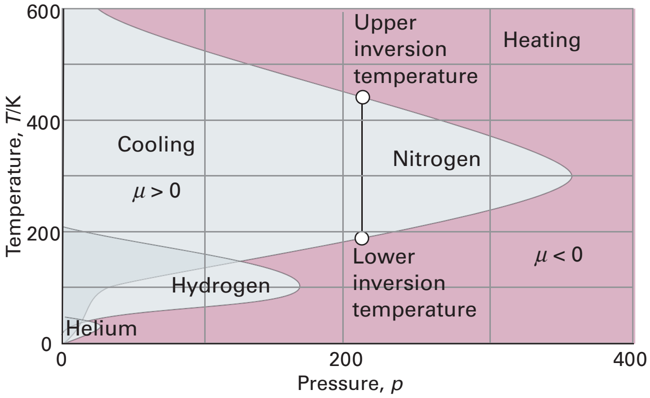

Figure 56.8 The inversion temperatures for three real gases, nitrogen, hydrogen, and helium.

Brief illustration 56.3 The isothermal Joule–Thomson coefficient

Suppose 2.00 mol of Freon gas molecules was used in the experiment described in *Brief illustration* 56.2. Given that the molar heat capacity of the Freon is 60.1 J K⁻¹ mol⁻¹, the heat capacity of the sample is 120.2 J K⁻¹, so the isothermal Joule–Thomson coefficient for the sample is

$$\mu_T = -C_p\mu = -(120.2\ \mathrm{J\ K^{-1}}) \times (0.71\ \mathrm{K\ atm^{-1}}) = -85\ \mathrm{J\ atm^{-1}}$$

Self-test 56.4 Repeat the calculation for the experiment described in Self-test 56.3 in which 1.50 mol of monatomic gas molecules was used.

Answer: $\mu_T = -15\ \mathrm{J\ atm^{-1}}$

The 'Linde refrigerator' makes use of Joule–Thomson expansion to liquefy gases (Fig. 56.9). The gas at high pressure is allowed to expand through a throttle, it cools, and is circulated past the incoming gas. That gas is cooled, and its subsequent expansion cools it still further. There comes a stage when the circulating gas becomes so cold that it condenses to a liquid.

As we show in the following *Justification*, for a perfect gas, $\mu = 0$; hence, the temperature of a perfect gas is unchanged by Joule–Thomson expansion. This characteristic points clearly to the involvement of intermolecular forces in determining the size of the effect. However, the Joule–Thomson coefficient of a real gas does not necessarily approach zero as the pressure is reduced even though the equation of state of the gas approaches that of a perfect gas. The coefficient behaves like the properties discussed Topic 36 in the sense that it depends on derivatives and not on p, V, and T themselves.

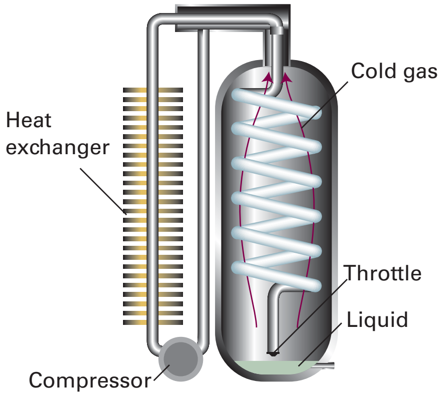

Figure 56.9 The principle of the Linde refrigerator is shown in this diagram. The gas is recirculated, and so long as it is beneath its inversion temperature it cools on expansion through the throttle. The cooled gas cools the high-pressure gas, which cools still further as it expands. Eventually liquefied gas drips from the throttle.

Justification 56.4 The Joule–Thomson coefficient of a perfect gas

For a perfect gas, $H = U + pV = U + nRT$. Therefore, the isothermal Joule–Thomson coefficient is

$$\mu_T = \left(\frac{\partial H}{\partial p}\right)_T = \left(\frac{\partial U}{\partial p}\right)_T$$

However, for a perfect gas, the internal energy depends only on the temperature (Topic 58), so the derivative and therefore μ_T is zero. Because $\mu_T = 0$, it follows from eqn 56.10 that $\mu = 0$ also.

The kinetic model of gases (Topic 78) and the equipartition theorem (Topic 53) imply that the mean kinetic energy of molecules in a gas is proportional to the temperature. It follows that reducing the average speed of the molecules is equivalent to cooling the gas. If the speed of the molecules can be reduced to the point that neighbours can capture each other by their intermolecular attractions, then the cooled gas will condense to a liquid. To slow the gas molecules, we make use of an effect similar to that seen when a ball is thrown into the air: as it rises it slows in response to the gravitational attraction of the Earth and its kinetic energy is converted into potential energy. Molecules in a real gas attract each other (the attraction is not gravitational, but the effect is the same). It follows that if we can cause the molecules to move apart from each other, like a ball rising from a planet, then they should slow.

It is very easy to move molecules apart from each other: we simply allow the gas to expand, which increases the average separation of the molecules. To cool a gas, therefore, we allow it to expand without allowing any energy to enter from outside as heat. As the gas expands, the molecules move apart to fill the available volume, struggling as they do so against the attraction of their neighbours. Because some kinetic energy must be converted into potential energy to reach greater separations, the molecules travel more slowly as their separation increases. This sequence of molecular events explains the Joule–Thomson effect: the cooling of a real gas by adiabatic expansion. The cooling effect, which corresponds to $\mu > 0$, is observed under conditions when attractive interactions are dominant, because the molecules have to climb apart against the attractive force in order for them to travel more slowly. For molecules under conditions when repulsions are dominant, the Joule–Thomson effect results in the gas becoming warmer, or $\mu < 0$.

Checklist of concepts

☐ 1. The **enthalpy change** of a system is equal to the energy transferred as heat at constant pressure.
☐ 2. The **heat capacity at constant pressure** is used to relate the change in enthalpy to a change in temperature.
☐ 3. The **Joule–Thomson effect** is the cooling of a real gas by isenthalpic expansion.
☐ 4. Gases that show a Joule–Thomson heating effect ($\mu < 0$) at one temperature show a cooling effect ($\mu > 0$) when the temperature passes through an inversion temperature.

Checklist of equations

Property	Equation	Comment	Equation number
Enthalpy	$H = U + pV$	Definition	56.1
Enthalpy change	$\Delta H = q_p$	At constant pressure, no additional work	56.2b
Heat capacity at constant pressure	$C_p = (\partial H/\partial T)_p$	Definition	56.3
Relation between heat capacities	$C_p - C_V = nR$	Perfect gas	56.6
Variation of enthalpy	$\mathrm{d}H = -\mu C_p \mathrm{d}p + C_p \mathrm{d}T$	Closed system	56.7
Joule–Thomson coefficient	$\mu = (\partial T/\partial p)_H$	Definition	56.8
Isothermal Joule–Thomson coefficient	$\mu_T = (\partial H/\partial p)_T$	Definition	56.9
Relation between coefficients	$\mu_T = -C_p \mu$		56.10

TOPIC 57

Thermochemistry

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➤ Why do you need to know this material?

Thermochemistry is one of the interfaces between formal thermodynamics and its practical application. You need to be familiar with thermochemistry if you want to assess the heat output of fuels and foods. Thermochemistry also provides a foundation for the quantitative discussion of chemical equilibrium (Topic 73).

➤ What is the key idea?

Because enthalpy is a state function, the enthalpy changes associated with physical and chemical processes can be combined to obtain the information about a real or hypothetical composite process.

➤ What do you need to know already?

This Topic is an extended application of the concept of enthalpy (Topic 56), and you need to be familiar with the concept of state function (Topic 55) and heat capacity (Topic 55). The Topic also draws on some aspects of the internal energy (Topic 55).

The study of the energy transferred as heat during the course of chemical reactions is called **thermochemistry**. Thermochemistry is a branch of thermodynamics because a reaction vessel and its contents form a system, and chemical reactions result in the exchange of energy between the system and the surroundings. Thus we can use calorimetry to measure the energy supplied or discarded as heat by a reaction, and can identify q with a change in internal energy if the reaction occurs at constant volume, and with a change in enthalpy if the reaction occurs at constant pressure. Conversely, if we know the ΔU or ΔH for a reaction, we can predict the energy (transferred as heat) that the reaction can produce.

57.1 Calorimetry

Calorimetry is the study of heat transfer during physical and chemical processes. A **calorimeter** is a device for measuring energy transferred as heat. The most common device for measuring ΔU (not ΔH without further analysis, as we describe below) is an **adiabatic bomb calorimeter** (Fig. 57.1). The process we wish to study—which may be a chemical reaction—is initiated inside a constant-volume container, the 'bomb'. The bomb is immersed in a stirred water bath, and the whole device is the calorimeter. The calorimeter is also immersed in an outer water bath. The water in the calorimeter and of the outer bath are both monitored and adjusted to the same temperature. This arrangement ensures that there is no net loss of heat from the calorimeter to the surroundings (the bath) and hence that the calorimeter is adiabatic. Changes in enthalpy and internal

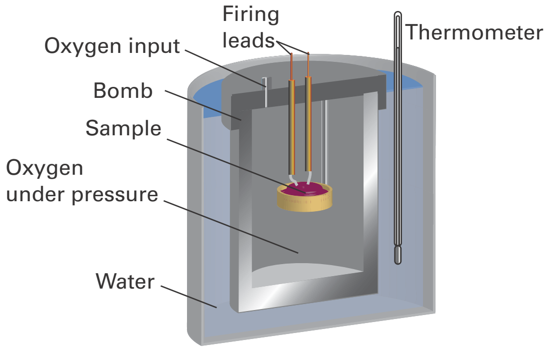


Figure 57.1 A constant-volume adiabatic bomb calorimeter. The 'bomb' is the central vessel, which is strong enough to withstand high pressures. The calorimeter (for which the heat capacity must be known) is the entire assembly shown here. To ensure adiabaticity, the calorimeter is immersed in a water bath with a temperature continuously readjusted to that of the calorimeter at each stage of the combustion.

energy may also be measured by non-calorimetric methods (Topic 75).

(a) Conventional calorimetry

The change in temperature, ΔT, of the calorimeter is proportional to the heat that the reaction releases or absorbs. Therefore, by measuring ΔT we can determine q_V and hence find ΔU. The conversion of ΔT to q_V is best achieved by calibrating the calorimeter using a process of known heat output, observing the temperature rise it produces, and determining the **calorimeter constant**, the constant C in the relation

$$q = C\Delta T \qquad \textit{Definition} \quad \text{Calorimeter constant} \tag{57.1}$$

The calorimeter constant may also be measured electrically by passing a constant current, I, from a source of known potential difference, $\mathcal{V}$, through a heater for a known period of time, t, for then (see *The chemist's toolkit* 57.1)

$$q = I\mathcal{V}t \qquad \text{Electrical heating} \tag{57.2}$$

The chemist's toolkit 57.1 Electrical quantities

Electric current, I, is measured in amperes (A), an SI base unit. A current of 1 A flowing for 1 s delivers a charge of 1 coulomb (1 C), so $1\,\mathrm{C} = 1\,\mathrm{A\,s}$. Because the fundamental charge is $1.602\times10^{-19}\,\mathrm{C}$, a current of 1 A corresponds to the passage of 6.24×10^{18} (10.4 µmol) of electrons per second.

According to *Ohm's law*, the current is proportional to the potential difference, $\mathcal{V}$ (in volts, $1\,\mathrm{V} = 1\,\mathrm{J\,A^{-1}}$), applied across the conductor. The constant of proportionality depends on the shape and constitution of the conductor and is written in terms of its resistance, R (in ohm, $1\,\Omega = 1\,\mathrm{V\,A^{-1}} = 1\,\mathrm{J\,A^{-2}}$). Ohm's law is then

$$I = \mathcal{V}/R \quad \text{or} \quad \mathcal{V} = IR$$

The power dissipated when a current I flows through a resistance R is

$$P = I^2R = I\mathcal{V}$$

Therefore, the energy generated as heat when the current passes for a time t is

$$q = Pt = I\mathcal{V}t$$

Brief illustration 57.1 The calorimeter constant

If a current of 10.0 A from a 12 V supply is passed for 300 s, then from eqn 57.2 the energy supplied as heat is

$$q = (10.0\,\mathrm{A})\times(12\,\mathrm{V})\times(300\,\mathrm{s}) = 3.6\times10^4\,\mathrm{A\,V\,s} = 36\,\mathrm{kJ}$$

because $1\,\mathrm{A\,V\,s} = 1\,\mathrm{J}$. If the observed rise in temperature is 5.5 K, then from eqn 57.1 the calorimeter constant is

$$C = (36\,\mathrm{kJ})/(5.5\,\mathrm{K}) = 6.5\,\mathrm{kJ\,K^{-1}}$$

Self-test 57.1 Calculate the calorimeter constant for a similar experiment in which the temperature rose by 6.3 K when a current of 11.5 A from a 12 V supply was passed for 450 s.

Answer: $9.9\,\mathrm{kJ\,K^{-1}}$

Alternatively, C may be determined by burning a known mass of substance (benzoic acid is often used) that has a known heat output. With C known, it is simple to interpret an observed temperature rise as a release of heat.

A calorimeter for studying processes at constant pressure is called an **isobaric calorimeter**. A simple example is a thermally insulated vessel open to the atmosphere: the heat released in the reaction is monitored by measuring the change in temperature of the contents. For a combustion reaction an **adiabatic flame calorimeter** may be used to measure ΔT when a given amount of substance burns in a supply of oxygen (Fig. 57.2). Another route to ΔH is to measure the internal energy change by using a bomb calorimeter, and then to convert ΔU to ΔH. Because solids and liquids have small molar volumes, for them pV_m is so small that the molar enthalpy and molar internal energy are almost identical ($H_\mathrm{m} = U_\mathrm{m} + pV_\mathrm{m} \approx U_\mathrm{m}$). Consequently, if a process involves only solids or liquids, the values of ΔH and ΔU are almost identical. Physically, such processes are accompanied by a very small change in volume, the system does negligible work on the surroundings when the process occurs, so the energy supplied as heat stays entirely within the system. If gases

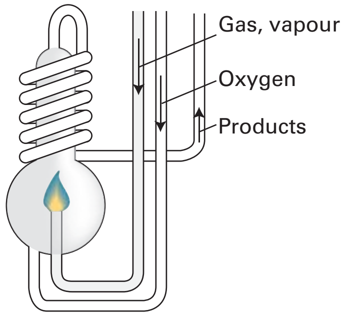


Figure 57.2 A constant-pressure flame calorimeter consists of this component immersed in a stirred water bath. Combustion occurs as a known amount of reactant is passed through to fuel the flame, and the rise of temperature is monitored.

are involved in the reaction, we treat them as perfect and use $H = U + nRT$, in which case

$$\Delta H = \Delta U + \Delta n_g RT \qquad \textit{Perfect gas} \qquad \text{Relation between } \Delta U \text{ and } \Delta H \qquad (57.3)$$

where Δn_g is the change in the amount of gas molecules in the reaction. Note that this expression applies to reactants and products at the same temperature. The temperature might rise or fall in the course of the reaction, but after it is over, the products are allowed to return to the same temperature as the reactants were initially.

Example 57.1 Calculating a change in enthalpy

Water is heated to boiling under a pressure of 1.0 atm. When an electric current of 0.50 A from a 12 V supply is passed for 300 s through a resistance in thermal contact with it, it is found that 0.798 g of water is vaporized. Calculate the molar internal energy and enthalpy changes at the boiling point (373.15 K).

Method Because the vaporization occurs at constant pressure, the enthalpy change is equal to the heat supplied by the heater. Therefore, the strategy is to calculate the energy supplied as heat (from $q = I\mathcal{V}t$), express that as an enthalpy change, and then convert the result to a molar enthalpy change by division by the amount of H_2O molecules vaporized. To convert from enthalpy change to internal energy change, we assume that the vapour is a perfect gas and use eqn 57.3.

Answer The enthalpy change is

$$\Delta H = q_p = (0.50\text{ A}) \times (12\text{ V}) \times (300\text{ s}) = +(0.50 \times 12 \times 300)\text{ J}$$

Here we have used 1 A V s = 1 J. Because 0.798 g of water is (0.798 g)/(18.02 g mol^{-1}) = (0.798/18.02) mol H_2O, the enthalpy of vaporization per mole of H_2O is

$$\Delta H_m = +\frac{0.50 \times 12 \times 300\text{ J}}{(0.798/18.02)\text{ mol}} = +41\text{ kJ mol}^{-1}$$

In the process $H_2O(l) \rightarrow H_2O(g)$ the change in the amount of gas molecules is $\Delta n_g = +1$ mol, so

$$\Delta U_m = \Delta H_m - RT = +38\text{ kJ mol}^{-1}$$

Notice that the internal energy change is smaller than the enthalpy change because energy has been used to drive back the surrounding atmosphere to make room for the vapour.

Self-test 57.2 The molar enthalpy of vaporization of benzene at its boiling point (353.25 K) is 30.8 kJ mol^{-1}. What is the molar internal energy change? For how long would the same 12 V source need to supply a 0.50 A current in order to vaporize a sample of mass 10.0 g?

Answer: +27.9 kJ mol^{-1}, 660 s

(b) Differential scanning calorimetry

A **differential scanning calorimeter** (DSC) measures the energy transferred as heat to or from a sample at constant pressure during a physical or chemical change. The term 'differential' refers to the fact that the behaviour of the sample is compared to that of a reference material which does not undergo a physical or chemical change during the analysis. The term 'scanning' refers to the fact that the temperatures of the sample and reference material are increased, or scanned, during the analysis.

A DSC consists of two small compartments that are heated electrically at a constant rate. The temperature, T, at time t during a linear scan is $T = T_0 + \alpha t$, where T_0 is the initial temperature and α is the temperature scan rate (in kelvin per second, K s^{-1}). A computer controls the electrical power output in order to maintain the same temperature in the sample and reference compartments throughout the analysis (Fig. 57.3).

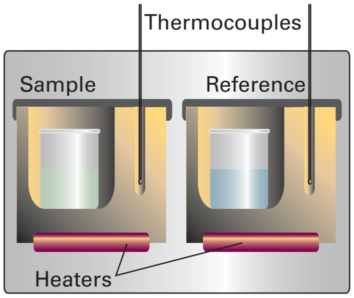


Figure 57.3 A differential scanning calorimeter. The sample and a reference material are heated in separate but identical metal heat sinks. The output is the difference in power needed to maintain the heat sinks at equal temperatures as the temperature rises.

The temperature of the sample changes significantly relative to that of the reference material if a chemical or physical process involving the transfer of energy as heat occurs in the sample during the scan. To maintain the same temperature in both compartments, excess energy is transferred as heat to or from the sample during the process. For example, an endothermic process lowers the temperature of the sample relative to that of the reference and, as a result, the sample must be heated more strongly than the reference in order to maintain equal temperatures.

If no physical or chemical change occurs in the sample at temperature T, we use eqn 57.1 to write the heat transferred to the sample as $q_p = C_p\Delta T$, where $\Delta T = T - T_0$ and we have assumed that C_p is independent of temperature. The chemical or physical process requires the transfer of $q_p + q_{p,\text{ex}}$, where $q_{p,\text{ex}}$ is excess energy transferred as heat, to attain the same change in temperature of the sample. We interpret $q_{p,\text{ex}}$ in terms of an apparent change in the heat capacity at constant pressure of the sample, C_p, during the temperature scan. Then we write the heat capacity of the sample as $C_p + C_{p,\text{ex}}$, and

$$q_p + q_{p,\text{ex}} = (C_p + C_{p,\text{ex}})\Delta T \qquad (57.4\text{a})$$

It follows that

$$C_{p,\text{ex}} = \frac{q_{p,\text{ex}}}{\Delta T} = \frac{q_{p,\text{ex}}}{\alpha t} = \frac{P_\text{ex}}{\alpha} \qquad (57.4\text{b})$$

where $P_\text{ex} = q_{p,\text{ex}}/t$ is the excess electrical power necessary to equalize the temperature of the sample and reference compartments.

A DSC trace, a **thermogram**, consists of a plot of P_ex or $C_{p,\text{ex}}$ against T (Fig. 57.4). Broad peaks in the thermogram indicate processes requiring transfer of energy as heat. From the relation $\mathrm{d}H = C_p\mathrm{d}T$, the enthalpy change associated with the process is

$$\Delta H = \int_{T_1}^{T_2} C_{p,\text{ex}}\,\mathrm{d}T \qquad (57.5)$$

where T_1 and T_2 are, respectively, the temperatures at which the process begins and ends. This relation shows that the enthalpy change is the area under the curve of $C_{p,\text{ex}}$ versus T. With a DSC, enthalpy changes may be determined in samples of masses as low as 0.5 mg, which is a significant advantage over bomb or flame calorimeters, which require several grams of material.

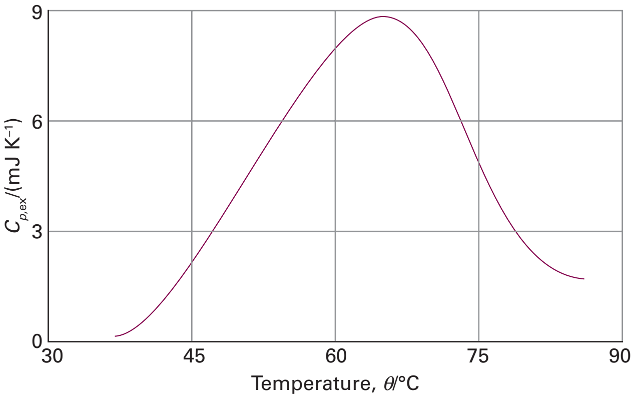


Figure 57.4 A thermogram for the protein ubiquitin at pH = 2.45. The protein retains its native structure up to about 45 °C and then undergoes an endothermic conformational change. (Adapted from B. Chowdhry and S. LeHarne, *J. Chem. Educ.* **74**, 236 (1997).)

57.2 Standard enthalpy changes

Changes in enthalpy are normally reported for processes taking place under a set of standard conditions. In most of our discussions we shall consider the **standard enthalpy change**, $\Delta H^\ominus$, the change in enthalpy for a process in which the initial and final substances are in their standard states:

> The **standard state** of a substance is its pure form at 1 bar.

(The standard state of substances in solution is described in Topic 72.) Standard enthalpy changes may be reported for any temperature. However, the conventional temperature for reporting thermodynamic data is 298.15 K (corresponding to 25.00 °C). Unless otherwise mentioned, all thermodynamic data in this text are for this conventional temperature.

(a) Enthalpies of physical change

The standard enthalpy change that accompanies a change of physical state is called the **standard enthalpy of transition** and is denoted $\Delta_\text{trs}H^\ominus$ (Table 57.1). The **standard enthalpy of vaporization**, $\Delta_\text{vap}H^\ominus$, is one example. Another is the **standard enthalpy of fusion**, $\Delta_\text{fus}H^\ominus$, the standard enthalpy change accompanying the conversion of a solid to a liquid, as in

$$\mathrm{H_2O(s)} \rightarrow \mathrm{H_2O(l)} \qquad \Delta_\text{fus}H^\ominus(273\text{ K}) = +6.01\text{ kJ mol}^{-1}$$

As in this case, it is sometimes convenient to know the standard enthalpy change at the transition temperature as well as at the conventional temperature. The different types of enthalpy changes encountered in thermochemistry are summarized in Table 57.1 and values for some processes are listed in Table 57.2. We shall meet them again in various locations throughout the text.

A note on good practice The attachment of the name of the transition to the symbol Δ, as in $\Delta_\text{trs}H$, is the modern

Table 57.1 Enthalpies of transition

Transition	Process	Symbol*
Transition	Phase α → phase β	$\Delta_{\rm trs}H$
Fusion	s → l	$\Delta_{\rm fus}H$
Vaporization	l → g	$\Delta_{\rm vap}H$
Sublimation	s → g	$\Delta_{\rm sub}H$
Mixing	Pure → mixture	$\Delta_{\rm mix}H$
Solution	Solute → solution	$\Delta_{\rm sol}H$
Hydration	$X^{\pm}(g) \rightarrow X^{\pm}(aq)$	$\Delta_{\rm hyd}H$
Atomization	Species(s, l, g) → atoms(g)	$\Delta_{\rm at}H$
Ionization	$X(g) \rightarrow X^{+}(g) + e^{-}(g)$	$\Delta_{\rm ion}H$
Electron gain	$X(g) + e^{-}(g) \rightarrow X^{-}(g)$	$\Delta_{\rm eg}H$
Reaction	Reactants → products	$\Delta_{\rm r}H$
Combustion	Compounds(s, l, g) + $O_2(g) \rightarrow CO_2(g), H_2O(l,g)$	$\Delta_{\rm c}H$
Formation	Elements → compound	$\Delta_{\rm f}H$
Activation	Reactants → activated complex	$\Delta^{\ddagger}H$

* IUPAC recommendations. In common usage, the transition subscript is often attached to ΔH, as in $\Delta H_{\rm trs}$.

Table 57.2* Standard enthalpies of fusion and vaporization at the transition temperature, $\Delta_{\rm trs}H^{\ominus}/(\rm kJ\ mol^{-1})$

	$T_{\rm f}/\rm K$	Fusion	$T_{\rm b}/\rm K$	Vaporization
Ar	83.8	1.188	87.29	6.506
C_6H_6	278.61	10.59	353.2	30.8
H_2O	273.15	6.008	373.15	40.656 44.016 at 298 K
He	3.5	0.021	4.22	0.084

* More values are given in the *Resource section*.

convention. However, the older convention, $\Delta H_{\rm trs}$, is still widely used. The new convention is more logical because the subscript identifies the type of change, not the physical observable related to the change.

Because enthalpy is a state function, a change in enthalpy is independent of the path between the specified initial and final states of the system. There are two immediate consequences of this path independence. One is that the enthalpy of an overall transition, such as sublimation (the direct conversion from solid to vapour), may be expressed as the sum of the enthalpies of fusion and vaporization (at the same temperature, **1**).

$$\Delta_{\rm sub}H^{\ominus}(T) = \Delta_{\rm fus}H^{\ominus}(T) + \Delta_{\rm vap}H^{\ominus}(T)$$

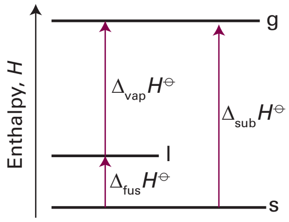
At same temperature Composition of changes (57.6)

An immediate conclusion is that, because almost all enthalpies of fusion are positive (helium is the exception), apart from helium the enthalpy of sublimation of a substance is always greater than its enthalpy of vaporization (at a given temperature). The second consequence is that the standard enthalpy changes of a forward process and its reverse differ only in sign (**2**):

$$\Delta H^{\ominus}(A \rightarrow B, T) = -\Delta H^{\ominus}(B \rightarrow A, T)$$

At same temperature Reverse change (57.7)

1



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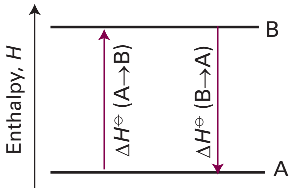


Brief illustration 57.2 Forward and reverse processes

Because the standard enthalpy of vaporization of water is $+44.01\ \rm kJ\ mol^{-1}$ at 298 K, its standard enthalpy of condensation at that temperature is $-44.01\ \rm kJ\ mol^{-1}$. The standard enthalpy of fusion of water at 298 K is close to $6\ \rm kJ\ mol^{-1}$ (an estimate). Therefore, the standard enthalpy of sublimation at this temperature is $6 + 44.01\ \rm kJ\ mol^{-1} = 50\ kJ\ mol^{-1}$.

Self-test 57.3 The standard enthalpy of fusion of solid ammonia is close to $5\ \rm kJ\ mol^{-1}$ and its standard enthalpy of vaporization is $23\ \rm kJ\ mol^{-1}$ at the same temperature. What is the standard enthalpy of vapour deposition at that temperature?

Answer: $-28\ \rm kJ\ mol^{-1}$

(b) Enthalpies of chemical change

The **standard enthalpy of reaction** (or 'standard reaction enthalpy'), $\Delta_{\rm r}H^{\ominus}$, is the difference in standard molar enthalpies of the products and reactants weighted by their stoichiometric coefficients in the chemical equation. Thus, for the reaction

$$2\,A + B \rightarrow 3\,C + D$$

the standard reaction enthalpy is

$$\Delta_{\rm r}H^{\ominus} = \{3H_{\rm m}^{\ominus}(C) + H_{\rm m}^{\ominus}(D)\} - \{2H_{\rm m}^{\ominus}(A) + H_{\rm m}^{\ominus}(B)\}$$

and in general

$$\Delta_{r}H^{\ominus} = \sum_{\rm Products} \nu H_{\rm m}^{\ominus} - \sum_{\rm Reactants} \nu H_{\rm m}^{\ominus}$$

Definition Standard reaction enthalpy (57.8a)

corresponding to the process

Reactants in their standard states →
products in their standard states

Except in the case of ionic reactions in solution, the enthalpy changes accompanying mixing of the pure reactants and separation of the products into their pure form (as implied by 'standard state') are insignificant in comparison with the contribution from the reaction itself.

> *A note on good practice* The units of the standard reaction enthalpy $\Delta_r H^\ominus$ are kilojoules per mole. The 'per mole' refers to 'per mole of reaction events' of the reaction as written, such as per 2 mol A or per mol B that are consumed, or per 3 mol C or per mol D that are formed.

Equation 57.8a may be written in a more compact manner by adopting the convention that the stoichiometric coefficients of products are positive and those of reactants are negative. For instance, in the reaction 2 A + B → 3 C + D, the coefficients are $\nu_A = -2$, $\nu_B = -1$, $\nu_C = 3$, and $\nu_D = 1$. Then eqn 57.8a becomes

$$\Delta_r H^\ominus = \sum_J \nu_J H_m^\ominus(J) \qquad (57.8b)$$

Compact definition Standard reaction enthalpy

It will be familiar from introductory chemistry that, just as standard enthalpies of transition may be combined, standard enthalpies of reactions can also be combined to obtain the enthalpy of another reaction. This application, which is a direct consequence of the fact that enthalpy is a state function, is called **Hess's law**:

> The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided.

The individual steps need not be realizable in practice: they may be hypothetical reactions, the only requirement being that their chemical equations should balance and that all numerical values should refer to the same temperature.

Example 57.2 Using Hess's law

Use the following data to determine the standard reaction enthalpy of $2\,B(s) + 3\,H_2(g) \rightarrow B_2H_6(g)$.

(1) $B_2H_6(g) + 3\,O_2(g) \rightarrow B_2O_3(s) + 3\,H_2O(g)$
$\Delta_r H^\ominus = -1941\ \text{kJ mol}^{-1}$

(2) $2\,B(s) + \frac{3}{2}O_2(g) \rightarrow B_2O_3(s)$ $\Delta_r H^\ominus = -2368\ \text{kJ mol}^{-1}$

(3) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$ $\Delta_r H^\ominus = -242\ \text{kJ mol}^{-1}$

Method Find a combination (sum or difference) of the three chemical equations that is equal to the chemical equation of interest, and combine the standard reaction enthalpies in the same way. Subtracting an equation is the same as adding its reverse.

Answer The difference (2) – (1) is

$$\begin{aligned}
&(2): && 2\,B(s) + \tfrac{3}{2}O_2(g) \rightarrow B_2O_3(s)\\
&-(1): && B_2O_3(s) + 3\,H_2O(g) \rightarrow B_2H_6(g) + 3\,O_2(g)\\
&(2)-(1) && 2\,B(s) + \tfrac{3}{2}O_2(g) + B_2O_3(s) + 3\,H_2O(g) \rightarrow\\
& && \quad B_2O_3(s) + B_2H_6(g) + 3\,O_2(g)\\
&\text{Or:} && 2\,B(s) + 3\,H_2O(g) \rightarrow B_2H_6(g) + \tfrac{3}{2}O_2(g)
\end{aligned}$$

Now add 3×(3) to remove the H_2O from the left-hand side:

$$\begin{aligned}
&(2)-(1): && 2\,B(s) + 3\,H_2O(g) \rightarrow B_2H_6(g) + \tfrac{3}{2}O_2(g)\\
&3(3): && 3\,H_2(g) + \tfrac{3}{2}O_2(g) \rightarrow 3\,H_2O(g)\\
&(2)-(1)+3(3): && 2\,B(s) + 3\,H_2O(g) + 3\,H_2(g) + \tfrac{3}{2}O_2(g)\\
& && \quad \rightarrow B_2H_6(g) + \tfrac{3}{2}O_2(g) + 3\,H_2O(g)\\
&\text{Or:} && 2\,B(s) + 3\,H_2(g) \rightarrow B_2H_6(g)
\end{aligned}$$

Finally, combine the standard reaction enthalpies in the same way:

$$\begin{aligned}
\Delta_r H^\ominus &= \Delta_r H^\ominus(2) - \Delta_r H^\ominus(1) + 3\Delta_r H^\ominus(3)\\
&= -2368 - (-1941) + 3(-242)\ \text{kJ mol}^{-1}\\
&= -1153\ \text{kJ mol}^{-1}
\end{aligned}$$

Self-test 57.4 From the following data, calculate the standard reaction enthalpy for the isomerization of cyclopropane to propene.

(1) *cyclo*-$C_3H_6(g) + \frac{9}{2}O_2(g) \rightarrow 3\,CO_2(g) + 3\,H_2O(g)$
$\Delta_r H^\ominus = -2091\ \text{kJ mol}^{-1}$

(2) $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta_r H^\ominus = -394\ \text{kJ mol}^{-1}$

(3) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$ $\Delta_r H^\ominus = -242\ \text{kJ mol}^{-1}$

(4) $3\,C(s) + 3\,H_2(g) \rightarrow CH_3CH{=}CH_2(g)$ $\Delta_r H^\ominus = +20\ \text{kJ mol}^{-1}$

Answer: $-163\ \text{kJ mol}^{-1}$

57.3 Standard enthalpies of formation

The **standard enthalpy of formation**, $\Delta_f H^\ominus$, of a substance is the standard reaction enthalpy for the formation of the compound from its elements in their reference states. The **reference state** of an element is its most stable state at the specified temperature and 1 bar. For example, at 298 K the reference state of nitrogen is a gas of N_2 molecules, that of mercury is liquid mercury, that of carbon is graphite, and that of tin is the white (metallic) form. There is one exception to this general prescription: the reference state of phosphorus is taken to be white phosphorus despite this allotrope not being the most stable form but simply the most reproducible form of the element. Standard enthalpies of formation are expressed as enthalpies per mole of molecules or (for ionic substances) formula units of the compound. The standard enthalpy of formation of liquid benzene at 298 K, for example, refers to the reaction

$$6\,C(s, graphite) + 3\,H_2(g) \rightarrow C_6H_6(l)$$

and is +49.0 kJ mol⁻¹. The standard enthalpies of formation of elements in their reference states are zero at all temperatures because they are the enthalpies of such 'null' reactions as $N_2(g) \rightarrow N_2(g)$. Some enthalpies of formation are listed in Tables 57.3 and 57.4.

The standard enthalpy of formation of ions in solution poses a special problem because it is impossible to prepare a solution of cations alone or of anions alone. This problem is solved by defining one ion, conventionally the hydrogen ion, to have zero standard enthalpy of formation at all temperatures:

$$\Delta_f H^\ominus(H^+, aq) = 0 \qquad \textit{Definition} \qquad (57.9)$$

Thus, if the enthalpy of formation of HBr(aq) is found to be −122 kJ mol⁻¹, then the whole of that value is ascribed to the formation of $Br^-(aq)$, and we write $\Delta_f H^\ominus(Br^-, aq) = -122$ kJ mol⁻¹. That value may then be combined with, for instance, the enthalpy of formation of AgBr(aq) to determine the value of $\Delta_f H^\ominus(Ag^+, aq)$, and so on. In essence, this definition adjusts the actual values of the enthalpies of formation of ions by a fixed amount, which is chosen so that the standard value for one of them, $H^+(aq)$, has the value zero. Tabulated values are based on a set of experimental values and adjusted to give the best fit to the entire set rather than just isolated pairs of measurements.

Table 57.3* Standard enthalpies of formation and combustion of organic compounds at 298 K

	$\Delta_f H^\ominus$/(kJ mol⁻¹)	$\Delta_c H^\ominus$/(kJ mol⁻¹)
Benzene, $C_6H_6(l)$	+49.0	−3268
Ethane, $C_2H_6(g)$	−84.7	−1560
Glucose, $C_6H_{12}O_6(s)$	−1274	−2808
Methane, $CH_4(g)$	−74.8	−890
Methanol, $CH_3OH(l)$	−238.7	−726

* More values are given in the *Resource section*.

Table 57.4* Standard enthalpies of formation of inorganic compounds at 298 K

	$\Delta_f H^\ominus$/(kJ mol⁻¹)
$H_2O(l)$	−285.83
$H_2O(g)$	−241.82
$NH_3(g)$	−46.11
$N_2H_4(l)$	+50.63
$NO_2(g)$	33.18
$N_2O_4(g)$	+9.16
NaCl(s)	−411.15
KCl(s)	−436.75

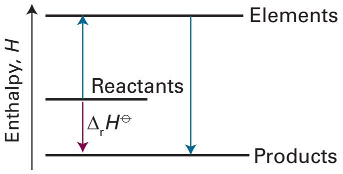
* More values are given in the *Resource section*.

(a) The reaction enthalpy in terms of enthalpies of formation

Conceptually, we can regard a reaction as proceeding by decomposing the reactants into their elements and then forming those elements into the products. The value of $\Delta_r H^\ominus$ for the overall reaction is the sum of these 'unforming' and forming enthalpies. Because 'unforming' is the reverse of forming, the enthalpy of an unforming step is the negative of the enthalpy of formation (**3**). Hence, in the enthalpies of formation of substances, we have enough information to calculate the enthalpy of any reaction by using

$$\Delta_r H^\ominus = \sum_J \nu_J \Delta_f H^\ominus(J) \qquad \textit{Practical implementation} \qquad (57.10)$$

Standard reaction enthalpy



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Brief illustration 57.3 The standard reaction enthalpy

The standard reaction enthalpy of $2\,HN_3(l) + 2\,NO(g) \rightarrow H_2O_2(l) + 4\,N_2(g)$ is calculated as follows:

$$\begin{aligned}\Delta_r H^\ominus &= \Delta_f H^\ominus(H_2O_2, l) + 4\Delta_f H^\ominus(N_2, g) - 2\Delta_f H^\ominus(HN_3, l) \\ &\quad -2\Delta_f H^\ominus(NO, g) \\ &= \{-187.78 + 4(0) - 2(264.0) - 2(90.25)\}\ \text{kJ mol}^{-1} \\ &= -896.3\ \text{kJ mol}^{-1}\end{aligned}$$

Therefore, 896.3 kJ of energy is transferred to the surroundings as heat at constant pressure per mole of reaction events, that is, per 2 mol HN_3 or per 2 mol NO that are consumed or per mol H_2O_2 or per 4 mol N_2 that are formed.

Self-test 57.5 From the data in Tables 57.3 and 57.4, calculate $\Delta_r H^\ominus$ at 298 K for the reaction C(graphite) + H_2O(g) → CO(g) + H_2(g).

Answer: +131.29 kJ mol^{-1}

(b) Enthalpies of formation and molecular modelling

We have seen how to construct standard reaction enthalpies by combining standard enthalpies of formation. The question that now arises is whether we can construct standard enthalpies of formation from a knowledge of the chemical constitution of the species. The short answer is that there is no thermodynamically exact way of expressing enthalpies of formation in terms of contributions from individual atoms and bonds. In the past, approximate procedures based on **mean bond enthalpies**, ΔH(A–B), the average molar enthalpy change associated with the breaking of a specific A–B bond,

$$\mathrm{A{-}B(g)} \rightarrow \mathrm{A(g)} + \mathrm{B(g)}$$

have been used. However, this procedure is notoriously unreliable, in part because the ΔH(A–B) are average values for a series of related compounds. Nor does the approach distinguish between geometrical isomers, where the same atoms and bonds may be present but experimentally the enthalpies of formation might be significantly different.

Computer-aided molecular modelling has largely displaced this more primitive approach. Commercial software packages use the principles developed in Topics 27–30 to calculate the standard enthalpy of formation of a molecule drawn on the computer screen. As pointed out there, the parameters used in a variety of semi-empirical approaches are optimized for the computation of enthalpies of formation. The techniques can be applied to different conformations of the same molecule. In the case of methylcyclohexane, for instance, the calculated conformational energy difference ranges from 5.9 to 7.9 kJ mol^{-1}, with the equatorial conformer having the lower standard enthalpy of formation. These estimates compare favourably with the experimental value of 7.5 kJ mol^{-1}. However, good agreement between calculated and experimental values is relatively rare. Computational methods almost always predict correctly which conformer is more stable but do not always predict the correct magnitude of the conformational energy difference.

Brief illustration 57.4 Molecular modelling software

Each software package has its own procedures; the general approach, though, is the same in most cases: the structure of the molecule is specified and the nature of the calculation selected. When the procedure is applied to the axial and equatorial isomers of methylcyclohexane, a typical value for the standard enthalpy of formation of equatorial isomer in the gas phase is −183 kJ mol^{-1} (using the AM1 semi-empirical procedure) whereas that for the axial isomer is −177 kJ mol^{-1}, a difference of 6 kJ mol^{-1}. The experimental difference is 7.5 kJ mol^{-1}.

Self-test 57.6 If you have access to modelling software, repeat this calculation for the two isomers of cyclohexanol.

Answer: Using AM1: eq: −345 kJ mol^{-1}; ax: −349 kJ mol^{-1}

57.4 The temperature dependence of reaction enthalpies

The standard enthalpies of many important reactions have been measured at different temperatures. However, in the absence of this information, standard reaction enthalpies at different temperatures may be calculated from heat capacities and the reaction enthalpy at some other temperature (Fig. 57.5). In many cases heat capacity data are more accurate than reaction enthalpies, so, providing the information is available, the procedure we are about to describe is more accurate that a direct measurement of a reaction enthalpy at an elevated temperature.

It follows from eqn 56.4a ($\mathrm{d}H = C_p\mathrm{d}T$) that when a substance is heated from T_1 to T_2, its enthalpy changes from $H(T_1)$ to

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p \mathrm{d}T \qquad (57.11)$$

(We have assumed that no phase transition takes place in the temperature range of interest.) Because this equation applies to

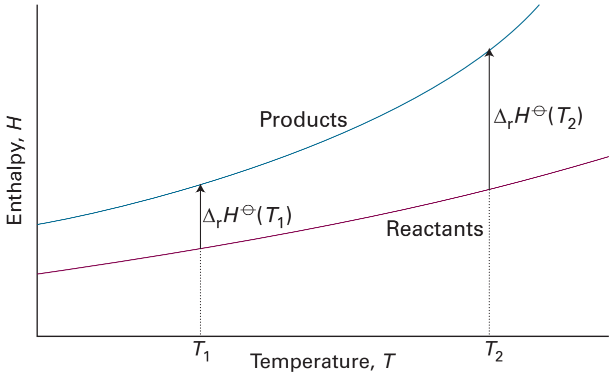

Figure 57.5 An illustration of the content of Kirchhoff's law. When the temperature is increased, the enthalpy of the products and the reactants both increase, but may do so to different extents. In each case, the change in enthalpy depends on the heat capacities of the substances. The change in reaction enthalpy reflects the difference in the changes of the enthalpies.

each substance in the reaction, the standard reaction enthalpy changes from $\Delta_r H^{\ominus}(T_1)$ to

$$\Delta_r H^{\ominus}(T_2)=\Delta_r H^{\ominus}(T_1)+\int_{T_1}^{T_2}\Delta_r C_p^{\ominus}\,\mathrm{d}T \quad \text{Kirchhoff's law} \quad (57.12)$$

where $\Delta_r C_p^{\ominus}$ is the difference of the molar constant-pressure heat capacities of products and reactants under standard conditions weighted by the stoichiometric coefficients that appear in the chemical equation:

$$\Delta_r C_p^{\ominus}=\sum_J \nu_J C_{p,\mathrm{m}}^{\ominus}(\mathrm{J}) \quad (57.13)$$

Equation 57.12 is known as **Kirchhoff's law**. It is normally a good approximation to assume that $\Delta_r C_p$ is independent of the temperature, at least over reasonably limited ranges: although the individual heat capacities may vary, their difference varies less significantly. When $\Delta C_p^{\ominus}$ is independent of temperature in the range T_1 to T_2, the integral in eqn 57.12 evaluates to $(T_2 - T_1)\Delta_r C_p^{\ominus}$. Therefore,

$$\begin{aligned}\Delta_r H^{\ominus}(T_2)={}&\Delta_r H^{\ominus}(T_1)\\&+(T_2-T_1)\Delta_r C_p^{\ominus}\end{aligned} \quad \begin{array}{l}\Delta_r C_p^{\ominus}\\ \textit{independent of}\\ \textit{temperature}\end{array} \quad \begin{array}{l}\text{Approximate}\\ \text{form of}\\ \text{Kirchhoff's law}\end{array} \quad (57.14)$$

In some cases the temperature dependence of heat capacities is taken into account by using eqn 56.5 (that $C_{p,\mathrm{m}}=a+bT+c/T^2$).

Brief illustration 57.5 Kirchhoff's law

The standard enthalpy of formation of gaseous H_2O at 298 K, $H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(g)$, is -241.82 kJ mol^{-1}. To estimate its value at 100 °C, given the following values of the molar heat capacities at constant pressure:

$H_2O(g)$: 33.58 J K^{-1} mol^{-1}; $H_2(g)$: 28.84 J K^{-1} mol^{-1}; $O_2(g)$: 29.37 J K^{-1} mol^{-1}

we assume that the heat capacities are independent of temperature and calculate $\Delta_r C_p^{\ominus}$ from the data:

$$\begin{aligned}\Delta_r C_p^{\ominus}&=C_{p,\mathrm{m}}^{\ominus}(\mathrm{H_2O,g})-C_{p,\mathrm{m}}^{\ominus}(\mathrm{H_2,g})-\tfrac{1}{2}C_{p,\mathrm{m}}^{\ominus}(\mathrm{O_2,g})\\&=-9.94\ \mathrm{J\,K^{-1}mol^{-1}}\end{aligned}$$

(Notice: joules not kilojoules.) It then follows that

$$\begin{aligned}\Delta_f H^{\ominus}(373\ \mathrm{K})&=-241.82\ \mathrm{kJ\,mol^{-1}}+(75\ \mathrm{K})\times(-9.94\ \mathrm{J\,K^{-1}mol^{-1}})\\&=-242.6\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

Self-test 57.7 Estimate the standard enthalpy of formation of cyclohexene at 400 K from the data in Table 57.3.

Answer: −163 kJ mol^{-1}

Checklist of concepts

☐ **1.** The **standard enthalpy change** is the change in enthalpy for a process in which the initial and final substances are in their standard states.

☐ **2.** The **standard state** is the pure substance at 1 bar.

☐ **3.** **Hess's law** states that the standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided.

☐ **4.** The **standard enthalpy of formation** ($\Delta_f H^{\ominus}$) is the standard reaction enthalpy for the formation per mole of the compound from its elements in their reference states.

☐ **5.** The **reference state** is the most stable state of an element at the specified temperature and 1 bar.

☐ **6.** The temperature dependence of the reaction enthalpy is given by **Kirchhoff's law**.

Checklist of equations

Property	Equation	Comment	Equation number
Calorimeter constant	$C=q/\Delta T$	Definition	57.1
Electrical heating	$q=I\mathcal{V}t$		57.2
Relation between ΔH and ΔU	$\Delta H=\Delta U+\Delta n_g RT$	Gases are perfect	57.3

Property	Equation	Comment	Equation number
Standard reaction enthalpy	$\Delta_r H^{\ominus} = \sum_{\text{Products}} \nu H_m^{\ominus} - \sum_{\text{Reactants}} \nu H_m^{\ominus} = \sum_J \nu_J H_m^{\ominus}(J)$	Definition	57.8
	$\Delta_r H^{\ominus} = \sum_J \nu_J \Delta_f H^{\ominus}(J)$	Practical implementation	57.10
Kirchhoff's law	$\Delta_r H^{\ominus}(T_2) = \Delta_r H^{\ominus}(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^{\ominus} \mathrm{d}T$		57.12
	$\Delta_r C_p^{\ominus} = \sum_J \nu_J C_{p,m}^{\ominus}(J)$	Definition	57.13
	$\Delta_r H^{\ominus}(T_2) = \Delta_r H^{\ominus}(T_1) + (T_2 - T_1)\Delta_r C_p^{\ominus}$	Approximate form; $\Delta_r C_p^{\ominus}$ constant	57.14

TOPIC 58

Internal energy

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➤ Why do you need to know this material?

This Topic introduces you to the way that thermodynamics acquires power and gives insight by showing how the changes in the internal energy are related to a variety of bulk and molecular properties. Other Topics focus on isothermal changes; this Topic also shows how to use internal energy and heat capacity to discuss another great class of processes, adiabatic changes.

➤ What is the key idea?

Changes in the internal energy are related to the heat capacity and internal pressure, and the heat capacity is related to the spread of populations over the available energy levels.

➤ What do you need to know already?

You need to be familiar with the definition of internal energy in terms of transfers of energy as work and heat, and the definition and significance of the heat capacity at constant volume (Topic 55). For the molecular interpretation sections, you need to be familiar with the relation between the mean energy in terms of the molecular partition function and the equipartition theorem (Topic 53).

The internal energy, U, of a system of constant composition can be regarded as a function of V, T, and p; but because there is an equation of state, stating the values of two of the variables fixes the value of the third (for instance, $p=nRT/V$ for a perfect gas). Therefore, it is possible to write U in terms of just two independent variables: V and T, p and T, or p and V. Expressing U as a function of volume and temperature fits the purpose of our discussion.

58.1 Changes in internal energy

The internal energy depends on parameters under our control, such as the volume, pressure, and temperature. The simplest expressions are obtained by treating U as a function of V and T.

(a) The effect of changing temperature and volume

When V changes by $\mathrm{d}V$ and T changes by $\mathrm{d}T$, the internal energy changes by

$$\mathrm{d}U=\left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V+\left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T \qquad (58.1)$$

The quantity $(\partial U/\partial T)_V$ is introduced in Topic 53 as the constant-volume heat capacity, C_V:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad \textit{Definition} \quad \text{Constant-volume heat capacity} \tag{58.2}$$

It follows from eqn 58.1 that the change in internal energy when the temperature is changed by $\mathrm{d}T$ at constant volume $(\mathrm{d}V=0)$ is

$$\mathrm{d}U = C_V\,\mathrm{d}T \qquad \textit{Constant volume} \tag{58.3}$$

The other coefficient, $(\partial U/\partial V)_T$, plays a major role in thermodynamics because it is a measure of the variation of the internal energy of a substance as its volume is changed at constant temperature (Fig. 58.1). We denote it π_T and, because it has the same dimensions as pressure, call it the **internal pressure**:

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T \qquad \textit{Definition} \quad \text{Internal pressure} \tag{58.4}$$

It follows from eqn 58.1 that the change in internal energy when the volume is changed by $\mathrm{d}V$ at constant temperature $(\mathrm{d}T=0)$ is

$$\mathrm{d}U = \pi_T\,\mathrm{d}V \qquad \textit{Constant temperature} \tag{58.5}$$

When there are no interactions between the molecules, the internal energy is independent of their separation and hence independent of the volume of the sample. Therefore, for a perfect gas we can write $\pi_T=0$. This conclusion is put on a more formal basis in Topic 66. The statement $\pi_T=0$ (that is, the internal energy is independent of the volume occupied by the sample) can be taken to be the definition of a perfect gas, for in Topic 66 we see that it implies the equation of state $pV=nRT$. In terms of the notation C_V and π_T, eqn 58.1 becomes

$$\mathrm{d}U = \pi_T\,\mathrm{d}V + C_V\,\mathrm{d}T \tag{58.6}$$

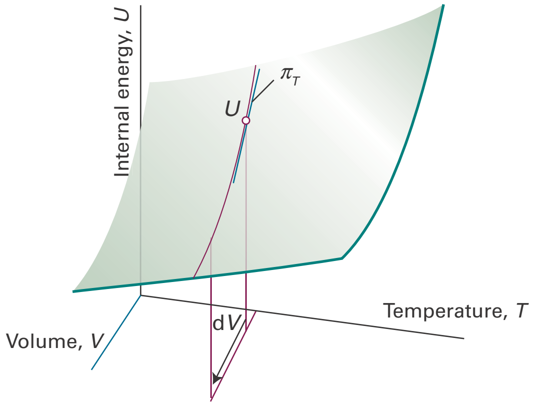

Figure 58.1 The internal pressure, π_T, is the slope of U with respect to V with the temperature T held constant.

Brief illustration 58.1 Changes in internal energy

For a gas that obeys the van der Waals equation of state, $\pi_T = n^2a/V^2$ (see Topic 66) and we can take $C_{V,\mathrm{m}} = \frac{3}{2}R$, a value that applies strictly to monatomic perfect gases (see Topic 55) but is a good approximation in this calculation. Suppose that 1.0 mol Ar, for which $a = 0.1337\,\mathrm{Pa\,m^6\,mol^{-2}}$, occupies $10\,\mathrm{dm^3}$. The internal pressure is

$$\pi_T = \frac{(1.0\,\mathrm{mol})^2 \times (0.1337\,\mathrm{Pa\,m^6\,mol^{-2}})}{(10\times10^{-3}\,\mathrm{m^3})^2} = 1.33\ldots\,\mathrm{kPa}$$

When its volume is increased by $100\,\mathrm{cm^3}$ and its temperature raised by 5.0 °C the change in internal energy is approximately

$$\begin{aligned}\Delta U &= (1.33\ldots\,\mathrm{kPa})\times(1.00\times10^{-4}\,\mathrm{m^3}) + \tfrac{3}{2}(1.0\,\mathrm{mol})\\ &\quad\times(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(5.0\,\mathrm{K})\\ &= 0.133\ldots\,\mathrm{Pa\,m^3} + 62\ldots\,\mathrm{J} \approx +62\,\mathrm{J}\end{aligned}$$

We have used $1\,\mathrm{Pa\,m^3} = 1\,\mathrm{J}$. Notice how the effect of the increase in temperature dominates the effect of the increase in volume.

Self-test 58.1 Repeat the calculation for Cl_2(g) (refer to Table 36.3 for *a*).

Answer: +104 J

(b) Changes at constant pressure

Partial derivatives have many useful properties and some that we shall draw on frequently are reviewed in *Mathematical background* 8. Skilful use of them can often turn some unfamiliar quantity into a quantity that can be recognized, interpreted, and measured.

As an example, suppose you want to find out how the internal energy varies with temperature when the pressure of the system is kept constant. If we divide both sides of eqn 58.6 by $\mathrm{d}T$ and impose the condition of constant pressure on the resulting differentials, so $\mathrm{d}U/\mathrm{d}T$ on the left becomes $(\partial U/\partial T)_p$, we obtain

$$\left(\frac{\partial U}{\partial T}\right)_p = \pi_T\left(\frac{\partial V}{\partial T}\right)_p + C_V$$

It is usually sensible in thermodynamics to inspect the output of a manipulation like this to see if it contains any recognizable physical quantity. The partial derivative on the right in this expression is the slope of the plot of volume against temperature (at constant pressure). This property is normally tabulated as the (cubic) **expansion coefficient**, α, of a substance, which is defined as

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \qquad \textit{Definition} \quad \text{Expansion coefficient} \tag{58.7}$$

and physically is the fractional change in volume that accompanies a rise in temperature. A large value of α means that the volume of the sample responds strongly to changes in temperature. Table 58.1 lists some experimental values of α and also of the **isothermal compressibility**, κ_T (kappa), which is defined as

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \qquad \textit{Definition} \qquad \text{Isothermal compressibility} \qquad (58.8)$$

The isothermal compressibility is a measure of the fractional change in volume when the pressure is increased by a small amount; the negative sign in the definition ensures that the compressibility is a positive quantity, because an increase of pressure, implying a positive dp, brings about a reduction of volume, a negative dV.

Table 58.1* Expansion coefficients (α) and isothermal compressibilities (κ_T) at 298 K

	$\alpha/(10^{-4}\ \mathrm{K}^{-1})$	$\kappa_T/(10^{-6}\ \mathrm{bar}^{-1})$
Benzene	12.4	90.9
Diamond	0.030	0.185
Lead	0.861	2.18
Water	2.1	49.0

* More values are given in the *Resource section*.

Example 58.1 Calculating the expansion coefficient of a gas

Derive an expression for the expansion coefficient of a perfect gas.

Method The expansion coefficient is defined in eqn 58.7. To use this expression, substitute the expression for V in terms of T obtained from the equation of state for the gas. As implied by the subscript in eqn 58.7, the pressure, p, is treated as a constant.

Answer Because $pV = nRT$, we can write

$$\alpha = \frac{1}{V}\left(\frac{\partial(nRT/p)}{\partial T}\right)_p = \frac{nR}{pV} = \frac{1}{T}$$

The higher the temperature, the less responsive is the volume of a perfect gas to a change in temperature.

Self-test 58.2 Derive an expression for the isothermal compressibility of a perfect gas.

Answer: $\kappa_T = 1/p$

When we introduce the definition of α into the equation for $(\partial U/\partial T)_p$, it becomes

$$\left(\frac{\partial U}{\partial T}\right)_p = \alpha\pi_T V + C_V \qquad (58.9)$$

This equation is entirely general (provided the system is closed and its composition is constant). It expresses the dependence of the internal energy on the temperature at constant pressure in terms of C_V, which can be measured in one experiment, in terms of α, which can be measured in another, and in terms of the quantity π_T. For a perfect gas, $\pi_T = 0$, so then

$$\left(\frac{\partial U}{\partial T}\right)_p = C_V \qquad \textit{Perfect gas} \qquad (58.10)$$

That is, although the constant-volume heat capacity is *defined* as the slope of a plot of internal energy against temperature at constant volume, for a perfect gas C_V is *also* the slope at constant pressure.

In Topic 56 we encounter the enthalpy, $H = U + pV$, and the constant-pressure heat capacity, $C_p = (\partial H/\partial T)_p$. Equation 58.10 provides an easy way to derive the relation between C_p and C_V for a perfect gas. Thus, we use it to express both heat capacities in terms of derivatives at constant pressure:

$$C_p - C_V = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_p \qquad \textit{Perfect gas} \qquad (58.11)$$

Then we replace the pV in $H = U + pV$ by nRT and substitute $H = U + nRT$ into the first term, which results in

$$C_p - C_V = \left(\frac{\partial U}{\partial T}\right)_p + nR - \left(\frac{\partial U}{\partial T}\right)_p = nR \qquad \textit{Perfect gas} \qquad (58.12)$$

This relation is used and discussed in Topic 57.

58.2 The molecular basis of heat capacity

The molecular interpretation of heat capacity provides considerable insight into this important property. We proceed in two steps. First we show in the following *Justification* that the heat capacity is proportional to the spread of occupied energy levels, in the sense that

$$C_V = \frac{N\Delta\varepsilon^2}{kT^2} \qquad \Delta\varepsilon^2 = \langle\varepsilon^2\rangle - \langle\varepsilon\rangle^2 \qquad (58.13)$$

Then we show how the heat capacity may be calculated from a knowledge of the structure of molecules.

Justification 58.1 The heat capacity and the width of a population distribution

Because differentiation with respect to $\beta = 1/kT$ is often much simpler than differentiation with respect to T, we form

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial \beta}\right)_V \frac{\mathrm{d}\beta}{\mathrm{d}T} = -\frac{1}{kT^2}\left(\frac{\partial U}{\partial \beta}\right)_V$$

Then, because the only change occurring to the energy levels is their populations, from eqn 53.1 ($\langle\varepsilon\rangle = (1/N)\sum_i N_i\varepsilon_i$ in the form $\langle E\rangle = \sum_i \varepsilon_i N_i$) write

$$\left(\frac{\partial U}{\partial \beta}\right)_V = \sum_i \varepsilon_i \frac{\mathrm{d}N_i}{\mathrm{d}\beta}$$

It then follows from the Boltzmann distribution (eqn 51.6, $N_i = N\mathrm{e}^{-\beta\varepsilon_i}/q$, where q is the partition function) that

$$\frac{\mathrm{d}N_i}{\mathrm{d}\beta} = N\frac{\mathrm{d}}{\mathrm{d}\beta}\frac{\mathrm{e}^{-\beta\varepsilon_i}}{q} = -N\varepsilon_i\frac{\mathrm{e}^{-\beta\varepsilon_i}}{q} - N\left(\frac{\mathrm{d}q}{\mathrm{d}\beta}\right)\frac{\mathrm{e}^{-\beta\varepsilon_i}}{q^2}$$

Because $N_i = N\mathrm{e}^{-\beta\varepsilon_i}/q$ and $-(1/q)(\mathrm{d}q/\mathrm{d}\beta) = \langle\varepsilon\rangle$, it follows that

$$\frac{\mathrm{d}N_i}{\mathrm{d}\beta} = -N_i\varepsilon_i + N_i\langle\varepsilon\rangle$$

Therefore,

$$\begin{aligned}\left(\frac{\partial U}{\partial \beta}\right)_V &= -\sum_i N_i\varepsilon_i^2 + \langle\varepsilon\rangle\sum_i N_i\varepsilon_i \\ &= -N\langle\varepsilon^2\rangle + N\langle\varepsilon\rangle^2\end{aligned}$$

That is, provided the volume is constant and the system is closed (so that there is no change in its composition), the change in its internal energy with temperature is found by substituting this expression into the first equation of this *Justification*, and results in eqn 58.13.

Equation 58.13 shows that the heat capacity rises as the spread in occupied energy levels increases. When all the molecules occupy the ground state, there is no difference between the mean of the square of the energies and the square of the mean energy, so the heat capacity is then zero. As the system is heated, this equality no longer holds, and provided the numerator in eqn 58.13 increases more rapidly than the denominator, the heat capacity rises. In certain cases, the numerator increases as T^2, in which case C_V is independent of temperature (provided $T > 0$).

Example 58.2 Calculating the mean square deviation of energies of a perfect gas

Calculate the value of $\langle\varepsilon^2\rangle$ for a one-dimensional monatomic perfect gas and then show that its heat capacity is independent of temperature.

Method For a one-dimensional monatomic perfect gas, we know from the equipartition theorem (Topic 53) that $\langle\varepsilon\rangle = \frac{1}{2}kT$, and can evaluate the mean square energy by using the same approximations used to derive the translational partition function in Topic 52. As before, we interpret the state index i as the quantum number n.

Answer To evaluate the mean square energy, we write

$$\langle\varepsilon^2\rangle = \frac{1}{N}\sum_n N_n\varepsilon_n^2 = \frac{1}{q^{\mathrm{T}}}\sum_n \varepsilon_n^2\mathrm{e}^{-\beta\varepsilon_n} \approx \frac{1}{q^{\mathrm{T}}}\int_0^\infty \left(\frac{n^2h^2}{8mL^2}\right)^2 \mathrm{e}^{-n^2\beta h^2/8mL^2}\mathrm{d}n$$

As in *Justification* 52.1, we have replaced $n^2 - 1$ by n^2 in the expression for the energy relative to the ground state, because most occupied levels have $n \gg 1$. We now make the substitution

$$n = \left(\frac{8mL^2}{\beta h^2}\right)^{1/2} x$$

to obtain

$$\langle\varepsilon^2\rangle = \frac{1}{q^{\mathrm{T}}}\frac{1}{\beta^2}\left(\frac{8mL^2}{\beta h^2}\right)^{1/2} \overbrace{\int_0^\infty x^4\mathrm{e}^{-x^2}\mathrm{d}x}^{\frac{3}{8}\pi^{1/2}}$$

Now use Integral G.5 in the *Resource section* and the translational partition function (eqn 52.7)

$$q^{\mathrm{T}} = \left(\frac{2\pi m}{\beta h^2}\right)^{1/2} L$$

to obtain

$$\langle\varepsilon^2\rangle = \frac{1}{L\beta^2}\left(\frac{\beta h^2}{2\pi m}\right)^{1/2}\left(\frac{8mL^2}{\beta h^2}\right)^{1/2}\left(\frac{3}{8}\pi^{1/2}\right) = \frac{3}{4\beta^2} = \frac{3}{4}k^2T^2$$

The mean energy is $\frac{1}{2}kT$, so

$$C_V = \frac{N\left(\frac{3}{4}k^2T^2 - \frac{1}{4}k^2T^2\right)}{kT^2} = \frac{1}{2}Nk = \frac{1}{2}nR$$

where once again we have used $N = nN_{\mathrm{A}}$ and $N_{\mathrm{A}}k = R$.

Self-test 58.3 Use eqn 58.13 to show that the heat capacity of a two-level system is zero at infinite temperature.

Answer: $C_V \propto 1/T^2 \to 0$ as $T \to \infty$

Although eqn 58.13 gives some insight into the origin of heat capacities, it is not the easiest route to their calculation. To calculate the heat capacity at constant volume, all we need do is to evaluate the internal energy as a function of temperature and then form the derivative. In most cases it is easier to evaluate the derivative with respect to β, and therefore to evaluate (as shown in the preceding *Justification*)

$$C_V = -\frac{1}{kT^2}\left(\frac{\partial U}{\partial \beta}\right)_V = -\frac{N}{kT^2}\left(\frac{\partial \langle \varepsilon \rangle}{\partial \beta}\right)_V = \frac{N}{kT^2}\left(\frac{\partial^2 \ln q}{\partial \beta^2}\right)_V \qquad (58.14)$$

We have used $\mathrm{d}\beta/\mathrm{d}T = -1/kT^2$, $\mathrm{d}U = N\mathrm{d}\langle\varepsilon\rangle$, and $\langle\varepsilon\rangle = -(\partial \ln q/\partial\beta)_V$. In Problem 58.9 you are invited to confirm that this expression can be converted into eqn 58.13. Once we know the partition function, all we need to do is to evaluate its second derivative with respect to β.

Example 58.3 Deriving the vibrational contribution to the heat capacity

Derive an expression for the heat capacity of a harmonic oscillator. At the same time derive an expression for the spread of energies ($\Delta\varepsilon^2$) and plot both functions against temperature.

Method The partition function is given in eqn 52.15 and the expression derived for the mean energy is given in eqn 53.8. It is simplest to differentiate the latter expression with respect to β, and express the resulting expression as a function of T. Compare that expression with eqn 58.13 to identify $\Delta\varepsilon^2$.

Answer The mean energy of a harmonic oscillator (relative to its ground state, eqn 53.8) is

$$\langle \varepsilon^{\mathrm{V}} \rangle = \frac{hc\tilde{\nu}}{\mathrm{e}^{\beta hc\tilde{\nu}} - 1}$$

Therefore,

$$\frac{\mathrm{d}\langle \varepsilon^{\mathrm{V}} \rangle}{\mathrm{d}\beta} = -\frac{(hc\tilde{\nu})^2 \mathrm{e}^{\beta hc\tilde{\nu}}}{(\mathrm{e}^{\beta hc\tilde{\nu}} - 1)^2}$$

and consequently, by using eqn 58.14 in the form $C_V = -Nk(1/kT)^2(\partial\langle\varepsilon\rangle/\partial\beta)_V$,

$$C_V = Nk\left(\frac{hc\tilde{\nu}}{kT}\right)^2 \frac{\mathrm{e}^{\beta hc\tilde{\nu}}}{(\mathrm{e}^{\beta hc\tilde{\nu}} - 1)^2} = Nk\left(\frac{hc\tilde{\nu}}{kT}\right)^2 \frac{\mathrm{e}^{hc\tilde{\nu}/kT}}{(\mathrm{e}^{hc\tilde{\nu}/kT} - 1)^2}$$

This function is plotted in Fig. 58.2. Comparison with eqn 58.13 lets us infer that

$$\Delta\varepsilon^2 = \frac{(hc\tilde{\nu})^2 \mathrm{e}^{hc\tilde{\nu}/kT}}{(\mathrm{e}^{hc\tilde{\nu}/kT} - 1)^2}$$

This function is plotted in Fig. 58.3. Note that at high temperatures ($T \gg hc\tilde{\nu}/k$) the spread is

$$\Delta\varepsilon^2 = \frac{(hc\tilde{\nu})^2(1 + hc\tilde{\nu}/kT + \cdots)}{(1 + hc\tilde{\nu}/kT + \cdots - 1)^2} = \frac{(hc\tilde{\nu})^2}{(hc\tilde{\nu}/kT)^2} = (kT)^2$$

and the spread increases quadratically as the temperature rises. That dependence is cancelled by the T^2 in the denominator of eqn 58.13, and the heat capacity approaches a constant value (of Nk) at high temperatures, as expected from the equipartition theorem.

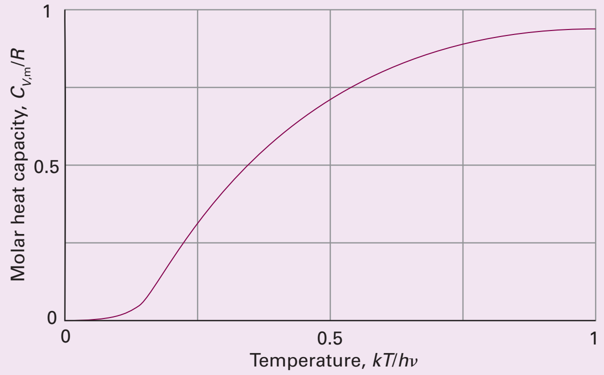

Figure 58.2 The heat capacity of a collection of harmonic oscillators as a function of temperature.

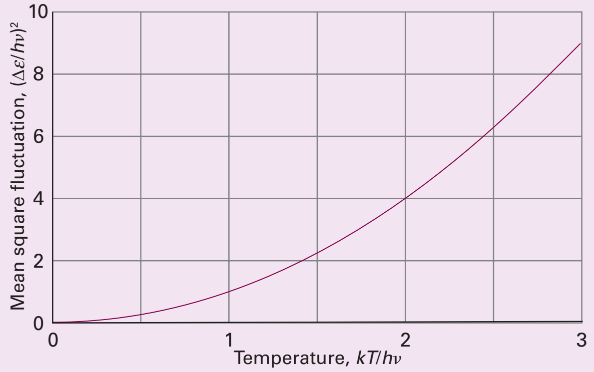

Figure 58.3 The mean square fluctuations in the energy of a collection of harmonic oscillators as a function of temperature.

Self-test 58.4 Repeat the analysis for a two-level system.

Answer: $C_V = Nkf \to 0$, $\Delta\varepsilon^2 = (kT)^2 f \to \frac{1}{4}\varepsilon^2$, where $f = (\varepsilon/kT)^2 \mathrm{e}^{\varepsilon/kT}/(\mathrm{e}^{\varepsilon/kT} + 1)^2$, see Fig. 58.4

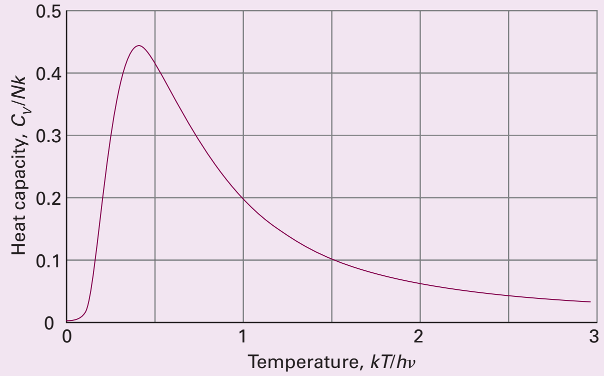

Figure 58.4 The heat capacity of a collection of two-level systems as a function of temperature.

When the temperature is high enough for the rotations of the molecules to be highly excited (when $T \gg \theta^{\mathrm{R}}$, where the rotational temperature θ^{R} is defined in Topic 52 as $\theta^{\mathrm{R}} = hc\tilde{B}/k$), we can use the equipartition value kT for the mean rotational energy (for a linear rotor) and $N_{\mathrm{A}}k = R$ to obtain $C_{V,\mathrm{m}} = R$. For nonlinear molecules, the mean rotational energy rises to $\frac{3}{2}kT$, so the molar rotational heat capacity rises to $\frac{3}{2}R$ when $T \gg \theta^{\mathrm{R}}$. Only the lowest rotational state is occupied when the temperature is very low, and then rotation does not contribute to the heat capacity. We can calculate the rotational heat capacity at intermediate temperatures by differentiating the equation for the mean rotational energy (eqn 53.6a). The resulting (untidy) expression, which is plotted in Fig. 58.5, shows that the contribution rises from zero (when $T = 0$) to the equipartition value (when $T \gg \theta^{\mathrm{R}}$). Because the translational contribution is always present, we can expect the molar heat capacity of a gas of diatomic molecules ($C^{T}_{V,\mathrm{m}} + C^{R}_{V,\mathrm{m}}$) to rise from $\frac{3}{2}R$ to $\frac{5}{2}R$ as the temperature is increased above θ^{R}. Problem 58.18 explores how the overall shape of the curve can be traced to the sum of thermal excitations between all the available rotational energy levels (Fig. 58.6).

Molecular vibrations contribute to the heat capacity, but only when the temperature is high enough for them to be significantly excited. The equipartition mean energy is kT for each mode, so the maximum contribution to the molar heat capacity is R. However, it is very unusual for the vibrations to be so highly excited that equipartition is valid, and it is more appropriate to use the full expression for the vibrational heat capacity, which was derived in Example 58.3. The curve in Fig. 58.7 shows how the vibrational heat capacity depends on temperature. Note that even when the temperature is only slightly above the characteristic vibrational temperature $\theta^{\mathrm{V}} = hc\tilde{\nu}/k$ of the normal mode, the heat capacity is close to its equipartition value.

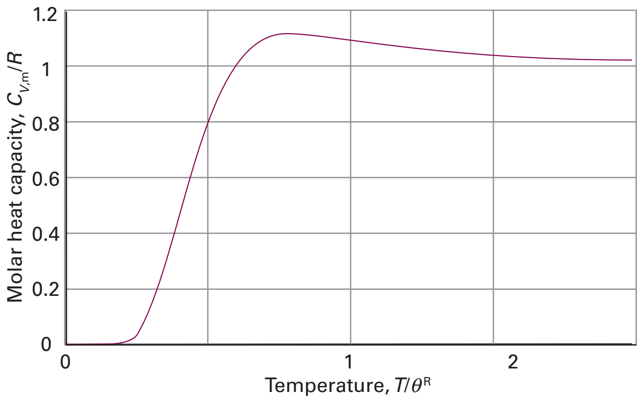

Figure 58.5 The temperature dependence of the rotational contribution to the heat capacity of a linear molecule.

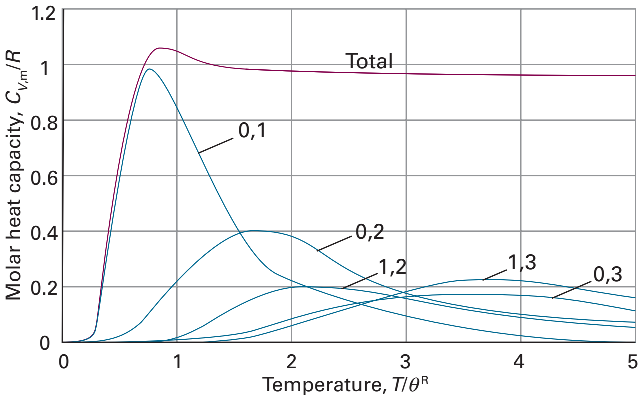

Figure 58.6 The rotational heat capacity of a linear molecule can be regarded as the sum of contributions from a collection of two-level systems, in which the rise in temperature stimulates transitions between *J* levels, some of which are shown here. The calculation on which this illustration is based is the topic of Problem 58.18.

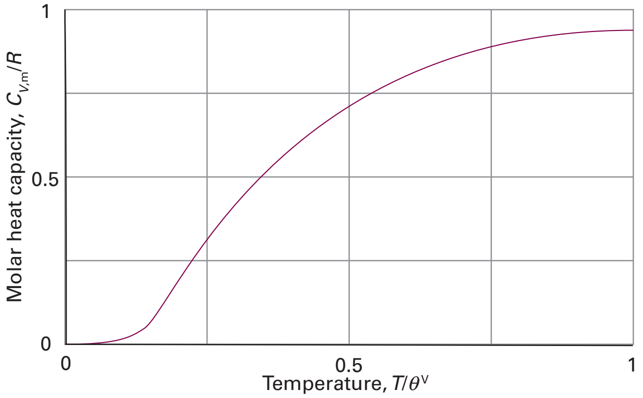

Figure 58.7 The temperature dependence of the vibrational contribution to the heat capacity of a molecule in the harmonic approximation calculated by using the full expression derived in Example 58.3 but expressed in terms of the vibrational temperature. Note that the heat capacity is within 10 per cent of its classical value for temperatures greater than θ^{V}.

The total heat capacity of a molecular substance is the sum of each contribution (Fig. 58.8). When equipartition is valid (almost always for translation and when the temperature is well above the characteristic temperature of the mode M = R or V; that is, $T \gg \theta^{\mathrm{M}}$) we can estimate the heat capacity by counting the numbers of modes that are active. In gases, all three translational modes are always active and contribute $\frac{3}{2}R$ to the molar heat capacity. If we denote the number of active rotational modes by ν_{R}^{*} (so for most molecules at normal temperatures $\nu_{\mathrm{R}}^{*} = 2$ for linear molecules, and $\nu_{\mathrm{R}}^{*} = 3$ for nonlinear molecules), then the rotational contribution is $\frac{1}{2}\nu_{\mathrm{R}}^{*}R$. If the temperature is high enough for ν_{V}^{*} vibrational modes to be active, the vibrational contribution to the molar heat capacity

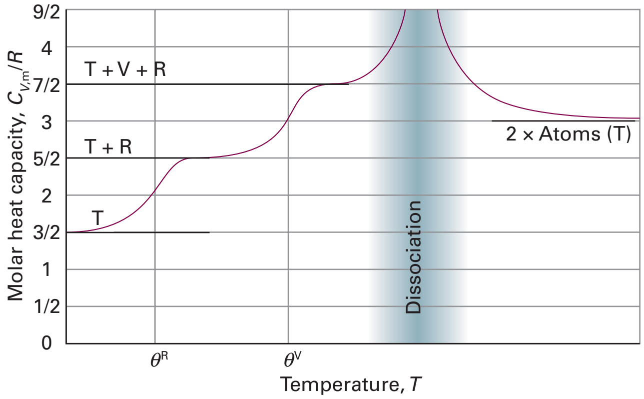

Figure 58.8 The general features of the temperature dependence of the heat capacity of diatomic molecules are as shown here. Each mode becomes active when its characteristic temperature is exceeded. The heat capacity becomes very large when the molecule dissociates because the energy is used to cause dissociation and not to raise the temperature. Then it falls back to the translation-only value of the atoms.

is $\nu_V^* R$. In most cases $\nu_V^* \approx 0$. It follows that the total molar heat capacity is

$$C_{V,\mathrm{m}}=\tfrac{1}{2}(3+\nu_\mathrm{R}^*+2\nu_\mathrm{V}^*)R \qquad \textit{High temperature, } T\gg\theta^\mathrm{M} \qquad \text{Molar heat capacity} \tag{58.15}$$

Example 58.4 Estimating the molar heat capacity of a gas

Estimate the molar constant-volume heat capacity of water vapour at 100 °C. The vibrational wavenumbers of H_2O are 3656.7 cm^{-1}, 1594.8 cm^{-1}, and 3755.8 cm^{-1} and the rotational constants are 27.9, 33.5, and 9.3 cm^{-1}.

Method We need to assess whether the rotational and vibrational modes are active by computing their characteristic temperatures from the data (to do so, use $hc/k=1.439$ cm K).

Answer The characteristic temperatures (in round numbers) of the vibrations are 5300 K, 2300 K, and 5400 K; the vibrations are therefore not significantly excited at 373 K. The three rotational modes have characteristic temperatures 40 K, 21 K, and 13 K, so they are fully excited, like the three translational modes. The translational contribution is $\frac{3}{2}R=12.5\,\mathrm{J\,K^{-1}\,mol^{-1}}$. Fully excited rotations ($\nu_\mathrm{R}^*=3$) contribute a further $\frac{3}{2}R=12.5\,\mathrm{J\,K^{-1}\,mol^{-1}}$. Therefore, a value close to 25 J K^{-1} mol^{-1} is predicted. The experimental value is 26.1 J K^{-1} mol^{-1}. The discrepancy is probably due to deviations from perfect gas behaviour.

Self-test 58.5 Estimate the molar constant-volume heat capacity of gaseous I_2 at 25 °C ($\tilde{\nu}=0.037\,\mathrm{cm^{-1}}$ and $\tilde{\nu}=214.5\,\mathrm{cm^{-1}}$).

Answer: 29 J K^{-1} mol^{-1}

58.3 Adiabatic processes

Work is done when a perfect gas expands adiabatically (without a transfer of energy as heat) but because no heat enters the system, the internal energy falls and therefore the temperature of the working gas also falls. In molecular terms, the kinetic energy of the molecules falls as work is done, so their average speed decreases, and hence the temperature falls.

(a) The work of adiabatic expansion

The change in internal energy of a perfect gas when the temperature is changed from T_i to T_f and the volume is changed from V_i to V_f can be expressed as the sum of two steps (Fig. 58.9). In the first step, only the volume changes and the temperature is held constant at its initial value. However, because the internal energy of a perfect gas is independent of the volume the molecules occupy, the overall change in internal energy arises solely from the second step, the change in temperature at constant volume. Provided the heat capacity is independent of temperature, this change is

$$\Delta U=C_V(T_\mathrm{f}-T_\mathrm{i})=C_V\Delta T$$

Because the expansion is adiabatic, we know that $q=0$; because $\Delta U=q+w$, it then follows that $\Delta U=w_\mathrm{ad}$. The subscript 'ad' denotes an adiabatic process. Therefore,

$$w_\mathrm{ad}=C_V\Delta T \qquad \textit{Perfect gas} \qquad \text{Adiabatic change} \tag{58.16}$$

That is, the work done during an adiabatic expansion of a perfect gas is proportional to the temperature difference between the initial and final states. That is exactly what we expect on molecular grounds, because the mean kinetic energy is proportional to T, so a change in internal energy arising from temperature alone is also expected to be proportional to ΔT. In the following *Justification* we show that the initial and final temperatures of a perfect gas that undergoes reversible adiabatic expansion (reversible expansion in a thermally insulated container) can be calculated from

$$T_\mathrm{f}=\left(\frac{V_\mathrm{i}}{V_\mathrm{f}}\right)^{1/c}T_\mathrm{i} \qquad \textit{Perfect gas, reversible change} \tag{58.17a}$$

where $c=C_{V,\mathrm{m}}/R$, or equivalently

$$V_\mathrm{i}T_\mathrm{i}^c=V_\mathrm{f}T_\mathrm{f}^c \qquad \textit{Perfect gas, reversible change} \tag{58.17b}$$

This result is often summarized in the form $VT^c=$constant.

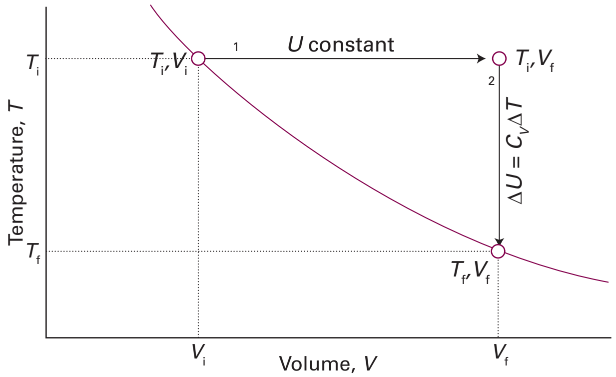

Figure 58.9 To achieve a change of state from one temperature and volume to another temperature and volume, we may consider the overall change as composed of two steps. In the first step, the system expands at constant temperature; there is no change in internal energy if the system consists of a perfect gas. In the second step, the temperature of the system is reduced at constant volume. The overall change in internal energy is the sum of the changes for the two steps.

Brief illustration 58.2 Adiabatic expansion 1

Consider the adiabatic, reversible expansion of 0.020 mol Ar, initially at 25 °C, from 0.50 dm³ to 1.00 dm³. The molar heat capacity of argon at constant volume is 12.48 J K⁻¹ mol⁻¹, so $c = 1.501$. Therefore, from eqn 58.17a,

$$T_f = \left(\frac{0.50\,\mathrm{dm}^3}{1.00\,\mathrm{dm}^3}\right)^{1/1.501} \times (298\,\mathrm{K}) = 188\,\mathrm{K}$$

It follows that $\Delta T = -110$ K, and therefore, from eqn 58.16, that

$$w = \{(0.020\ \mathrm{mol}) \times (12.48\ \mathrm{J\ K^{-1} mol^{-1}})\} \times (-110\ \mathrm{K}) = -27\ \mathrm{J}$$

Note that the temperature change is independent of the amount of gas but the work is not.

Self-test 58.6 Calculate the final temperature, the work done, and the change of internal energy when ammonia is used in a reversible adiabatic expansion from 0.50 dm³ to 2.00 dm³, the other initial conditions being the same. Use Table 57.4.

Answer: 194 K, −56 J, −56 J

(b) Adiabats

We show in the following *Justification* that the pressure of a perfect gas that undergoes reversible adiabatic expansion from a volume V_i to a volume V_f is related to its initial pressure by

$$p_f V_f^{\gamma} = p_i V_i^{\gamma} \quad \gamma = C_{p,\mathrm{m}}/C_{V,\mathrm{m}} \qquad (58.18)$$

Perfect gas, reversible change

Adiabatic expansion

This result is commonly summarized in the form $pV^{\gamma} = \text{constant}$. For a monatomic perfect gas, $C_{V,\mathrm{m}} = \frac{3}{2}R$, and from eqn 58.12 $C_{p,\mathrm{m}} = \frac{5}{2}R$; so $\gamma = \frac{5}{3}$. For a gas of nonlinear polyatomic molecules (which can rotate as well as translate), $C_{V,\mathrm{m}} = 3R$, so $\gamma = \frac{4}{3}$.

Justification 58.2 Adiabatic processes

Consider a stage in a reversible adiabatic expansion when the pressure inside and out is p. The work done when the gas expands by $\mathrm{d}V$ is $\mathrm{d}w = -p\mathrm{d}V$; therefore, from eqn 58.6 ($\mathrm{d}U = \pi_T \mathrm{d}V + C_V \mathrm{d}T$ with $\pi_T = 0$ for a perfect gas and $\mathrm{d}U = \mathrm{d}w$ for an adiabatic change)

$$C_V \mathrm{d}T = -p\mathrm{d}V$$

We are dealing with a perfect gas, so we can replace p by nRT/V and obtain

$$\frac{C_V \mathrm{d}T}{T} = -\frac{nR\mathrm{d}V}{V}$$

To integrate this expression we note that T is equal to T_i when V is equal to V_i, and is equal to T_f when V is equal to V_f at the end of the expansion. Therefore,

$$C_V \int_{T_i}^{T_f} \frac{\mathrm{d}T}{T} = -nR \int_{V_i}^{V_f} \frac{\mathrm{d}V}{V}$$

(We are taking C_V to be independent of temperature.) Then, because $\int \mathrm{d}x/x = \ln x + \text{constant}$, we obtain

$$C_V \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i}$$

Because $\ln(x/y) = -\ln(y/x)$, this expression rearranges to

$$\frac{C_V}{nR} \ln \frac{T_f}{T_i} = \ln \frac{V_i}{V_f}$$

With $c = C_V/nR$ we obtain (because $\ln x^a = a \ln x$)

$$\ln \left(\frac{T_f}{T_i}\right)^c = \ln \frac{V_i}{V_f}$$

which implies that $(T_f/T_i)^c = (V_i/V_f)$ and, upon rearrangement, eqn 58.17.

The initial and final states of a perfect gas satisfy the perfect gas law regardless of how the change of state takes place, so we can use $pV = nRT$ to write

$$\frac{T_f}{T_i} = \frac{p_f V_f}{p_i V_i}, \text{ and therefore } \left(\frac{p_f V_f}{p_i V_i}\right)^c = \frac{V_i}{V_f}$$

By taking the $1/c$ root of each side of this expression and combining terms we obtain

$$\frac{p_f V_f}{p_i V_i} = \left(\frac{V_i}{V_f}\right)^{1/c} = \left(\frac{V_f}{V_i}\right)^{-1/c} \text{ and therefore } \frac{p_f V_f^{1+1/c}}{p_i V_i^{1+1/c}} = 1$$

However, because, for a perfect gas, $C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = R$,

$$1 + \frac{1}{c} = \frac{c+1}{c} = \frac{C_V/nR + 1}{C_V/nR} = \frac{C_{V,\mathrm{m}} + R}{C_{V,\mathrm{m}}} = \frac{C_{p,\mathrm{m}}}{C_{V,\mathrm{m}}}$$

and we recognize the heat capacity ratio $\gamma = C_{p,\mathrm{m}}/C_{V,\mathrm{m}}$. It follows that

$$\frac{p_\mathrm{f} V_\mathrm{f}^\gamma}{p_\mathrm{i} V_\mathrm{i}^\gamma} = 1$$

which rearranges to $p_\mathrm{i} V_\mathrm{i}^\gamma = p_\mathrm{f} V_\mathrm{f}^\gamma$, which is eqn 58.18.

The curves of pressure versus volume for adiabatic change are known as **adiabats**, and one for a reversible path is illustrated in Fig. 58.10. Because $\gamma > 1$, an adiabat falls more steeply ($p \propto 1/V^\gamma$) than the corresponding isotherm ($p \propto 1/V$). The physical reason for the difference is that in an isothermal expansion, energy flows into the system as heat and maintains the temperature; as a result, the pressure does not fall as much as in an adiabatic expansion.

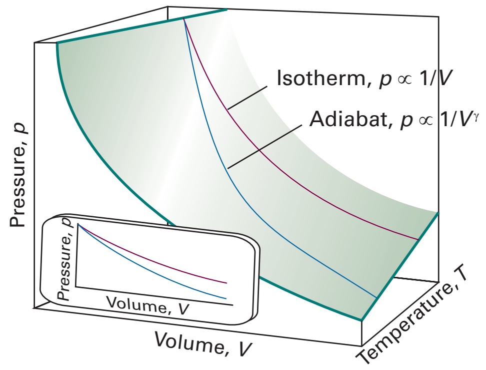

Figure 58.10 An adiabat depicts the variation of pressure with volume when a gas expands adiabatically (and, in this case, reversibly). Note from the insert that the pressure declines more steeply for an adiabat than it does for an isotherm because the temperature also decreases during an adiabatic expansion.

Brief illustration 58.3 Adiabatic expansion 2

When a sample of argon (for which $\gamma = \frac{5}{3}$) at 100 kPa expands reversibly and adiabatically to twice its initial volume the final pressure will be

$$p_\mathrm{f} = \left(\frac{V_\mathrm{i}}{V_\mathrm{f}}\right)^\gamma p_\mathrm{i} = \left(\frac{1}{2}\right)^{5/3} \times (100\,\mathrm{kPa}) = 31.5\,\mathrm{kPa}$$

For an isothermal doubling of volume, the final pressure would be 50 kPa.

Self-test 58.7 Calculate the final pressure of a sample of carbon dioxide that expands reversibly and adiabatically from 67.4 kPa and 0.50 dm^3 to a final volume of 2.00 dm^3. Take $\gamma = 1.4$.

Answer: 9.7 kPa

(c) The molecular interpretation of adiabatic change

We can get some insight into the origin of the temperature dependence expressed by eqn 58.17 and understand adiabatic changes at a molecular level by considering the reversible, adiabatic expansion of particles in a one-dimensional box. In quantum mechanics, an **adiabatic process** is one that occurs so slowly that the system follows a single evolving state of a system and, in contrast to an impulsive change, does not jump into a linear combination of other states. We can explore the consequence of this model in statistical mechanics by supposing that the molecules that occupy a given level of the box all remain in that level as the box expands reversibly and adiabatically (Fig. 58.11). That is, we suppose that all the N_i remain constant even though the energy levels are changing. For the populations to remain the same even though the energy levels are getting closer together, the temperature must fall, so our task is to see how that changing temperature must vary with the length of the box. In other words, we must look for a solution of

$$\frac{\mathrm{d}N_n}{\mathrm{d}L} = \frac{\mathrm{d}}{\mathrm{d}L}\left(\frac{Ne^{-\beta\varepsilon_n}}{q}\right) = 0 \qquad (58.19)$$

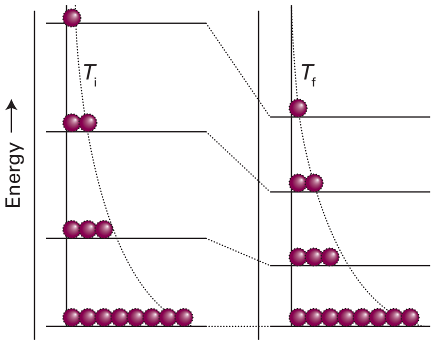

Figure 58.11 In a reversible adiabatic expansion, the populations of the quantum states remain constant, which corresponds to a lowering of the temperature if the Boltzmann distribution is to continue to match the same distribution but now over the changed energy levels.

with β and ε_n, and therefore q too, functions of L. Because $\beta\varepsilon_n = n^2h^2/8mkL^2T$, the value of $\beta\varepsilon_n$ and therefore the population N_n is independent of the length if at all stages of the expansion

$$LT^{1/2} = \text{constant} \tag{58.20}$$

However, for a one-dimensional system, the molar heat capacity is $\frac{1}{2}R$, so this solution is the one-dimensional version of eqn 58.17.

Another way to appreciate the conclusion in eqn 58.20 is to consider the relative populations of the states with quantum numbers n and 1 (the ground state), with energies $E_n = n^2h^2/8mL^2$ and $E_1 = h^2/8mL^2$, respectively. This ratio is

$$\frac{N_n}{N_1} = \mathrm{e}^{-(E_n - E_1)/kT} = \mathrm{e}^{-(n^2-1)h^2/8mkL^2T} \tag{58.21}$$

and is a constant for a given value of n provided that T adjusts as L changes such that L^2T (and therefore $LT^{1/2}$) is a constant.

Brief illustration 58.4 The preservation of populations

Although gases are normally considered to occupy laboratory-sized vessels, we can illustrate the content of eqn 58.21 and the relation in eqn 58.20 by considering a tiny vessel of length 100 nm and the relative population of the state with n such that $(n^2-1)h^{-2}/8mk = 10^6\ \text{nm}^2\ \text{K}$. At 300 K the relative populations are

$$\frac{N_n}{N_1} = \mathrm{e}^{-(10^6\ \text{nm}^2\ \text{K})/(100\ \text{nm})^2 \times (300\ \text{K})} = 0.716\ldots$$

When the length of the vessel is increased to 110 nm, the same relative population is achieved provided the temperature is adjusted to 248 K:

$$\frac{N_n}{N_1} = \mathrm{e}^{-(10^6\ \text{nm}^2\ \text{K})/(110\ \text{nm})^2 \times (248\ \text{K})} = 0.716\ldots$$

Self-test 58.8 What temperature is needed to preserve this ratio when the length is increased adiabatically to 120 nm?

Answer: 208 K

The result we have obtained shows what to imagine is happening at a molecular level during a reversible adiabatic expansion of a perfect gas. As shown in Fig. 58.11, the populations of each level remain constant as the levels fall in energy. However, for that to be the case the temperature must fall. The precise dependence of the temperature that guarantees this constancy is exactly the condition expressed in eqn 58.17.

Checklist of concepts

☐ 1. Changes in the internal energy of a system may be expressed in terms of the constant-volume heat capacity and the internal pressure (see below).
☐ 2. The heat capacity is proportional to the spread of occupied energy levels.
☐ 3. The equipartition theorem may be used to estimate the heat capacity of a gas.
☐ 4. In an **adiabatic expansion**, the temperature falls as a perfect gas does work, and the pressure/volume relation is known as an adiabat.
☐ 5. In quantum mechanics, an adiabatic process is one that occurs so slowly that the system remains in its initial but evolving state.
☐ 6. In the adiabatic, reversible expansion of a perfect gas, the populations of each level remain constant as the levels fall in energy.

Checklist of equations

Property	Equation	Comment	Equation number
Constant-volume heat capacity	$C_V = (\partial U/\partial T)_V$	Definition	58.2
Internal pressure	$\pi_T = (\partial U/\partial V)_T$	Definition; for a perfect gas, $\pi_T = 0$	58.4
Change of internal energy	$\mathrm{d}U = \pi_T \mathrm{d}V + C_V \mathrm{d}T$	Closed, constant-composition system	58.6
Expansion coefficient	$\alpha = (1/V)(\partial V/\partial T)_p$	Definition; for a perfect gas, $\alpha = 1/T$	58.7

Property	Equation	Comment	Equation number
Isothermal compressibility	$\kappa_T = -(1/V)(\partial V/\partial p)_T$	Definition; for a perfect gas $\kappa_T = 1/p$	58.8
	$(\partial U/\partial T)_p = C_V$	Perfect gas	58.10
Relation between heat capacities	$C_p - C_V = nR$	Perfect gas	58.12
Molecular origin of heat capacity	$C_V = N\Delta\varepsilon^2/kT^2$ $\Delta\varepsilon^2 = \langle\varepsilon^2\rangle - \langle\varepsilon\rangle^2$	Independent molecules	58.13
	$C_V = (N/kT^2)(\partial^2 \ln q/\partial\beta^2)_V$	Independent molecules	58.14
	$C_{V,\mathrm{m}} = \frac{1}{2}(3 + \nu_\mathrm{R}^* + 2\nu_\mathrm{V}^*)R$	Perfect gas, $T \gg \theta^\mathrm{M}$	58.15
Work of adiabatic expansion	$w_\mathrm{ad} = C_V\Delta T$	Perfect gas	58.16
Volume and temperature	$V_\mathrm{i}T_\mathrm{i}^c = V_\mathrm{f}T_\mathrm{f}^c$, $c = C_{V,\mathrm{m}}/R$	Reversible change; perfect gas	58.17
Pressure and volume	$p_\mathrm{f}V_\mathrm{f}^\gamma = p_\mathrm{i}V_\mathrm{i}^\gamma$, $\gamma = C_{p,\mathrm{m}}/C_{V,\mathrm{m}}$	Reversible change; perfect gas	58.18

Focus 12 on The First Law of thermodynamics

Assume all gases are perfect unless stated otherwise. Unless otherwise stated, thermochemical data are for 298.15 K.

Topic 55 The First Law

Discussion questions

55.1 Describe and distinguish the various uses of the words 'system' and 'state' in physical chemistry.

55.2 Describe the distinction between heat and work in thermodynamic and molecular terms, the latter in terms of populations and energy levels.

55.3 Give examples of state functions and discuss why they play a critical role in thermodynamics.

Exercises

55.1(a) Use the equipartition theorem to estimate the molar internal energy of (a) I_2, (b) CH_4, (c) C_6H_6 in the gas phase at 25 °C.
55.1(b) Use the equipartition theorem to estimate the molar internal energy of (a) O_3, (b) C_2H_6, (c) SO_2 in the gas phase at 25 °C.

55.2(a) Which of (a) pressure, (b) temperature, (c) work, (d) enthalpy are state functions?
55.2(b) Which of (a) volume, (b) heat, (c) internal energy, (d) density are state functions?

55.3(a) Calculate the work needed for a 60 kg person to climb through 6.0 m (a) on the surface of the Earth and (b) on the Moon ($g = 1.60\,\mathrm{m\,s^{-2}}$).
55.3(b) Calculate the work needed for a bird of mass 150 g to fly to a height of 75 m from the surface of the Earth.

55.4(a) A chemical reaction takes place in a container of cross-sectional area 50 cm². As a result of the reaction, a piston is pushed out through 15 cm against an external pressure of 1.0 atm. Calculate the work done by the system.
55.4(b) A chemical reaction takes place in a container of cross-sectional area 75.0 cm². As a result of the reaction, a piston is pushed out through 25.0 cm against an external pressure of 150 kPa. Calculate the work done by the system.

55.5(a) A sample consisting of 1.00 mol Ar is expanded isothermally at 20 °C from 10.0 dm³ to 30.0 dm³ (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q, w, and ΔU.
55.5(b) A sample consisting of 2.00 mol He is expanded isothermally at 0 °C from 5.0 dm³ to 20.0 dm³ (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q, w, and ΔU.

55.6(a) A sample consisting of 1.00 mol of perfect gas atoms, for which $C_{V,\mathrm{m}} = \frac{3}{2}R$, initially at $p_1 = 1.00$ atm and $T_1 = 300$ K, is heated reversibly to 400 K at constant volume. Calculate the final pressure, ΔU, q, and w.
55.6(b) A sample consisting of 2.00 mol of perfect gas molecules, for which $C_{V,\mathrm{m}} = \frac{5}{2}R$, initially at $p_1 = 111$ kPa and $T_1 = 277$ K, is heated reversibly to 356 K at constant volume. Calculate the final pressure, ΔU, q, and w.

Problems

55.1 Calculate the work done during the isothermal, reversible expansion of a van der Waals gas (Topic 36). Plot on the same graph the indicator diagrams (graphs of pressure against volume) for the isothermal reversible expansion of (a) a perfect gas, (b) a van der Waals gas in which $a = 0$ and $b = 5.11 \times 10^{-2}\,\mathrm{dm^3\,mol^{-1}}$, and (c) $a = 4.2\,\mathrm{dm^6\,atm\,mol^{-2}}$ and $b = 0$. The values selected exaggerate the imperfections but give rise to significant effects on the indicator diagrams. Take $V_\mathrm{i} = 1.0\,\mathrm{dm^3}$, $n = 1.0$ mol, and $T = 298$ K.

55.2 It is possible to see with the aid of a powerful microscope that a long piece of double-stranded DNA is flexible, with the distance between the ends of the chain adopting a wide range of values. This flexibility is important because it allows DNA to adopt very compact conformations as it is packaged in a chromosome. It is convenient to visualize a long piece of DNA as a 'freely jointed chain', a chain of N small, rigid units of length l that are free to make any angle with respect to each other. The length l, the *persistence length*, is approximately 45 nm, corresponding to approximately 130 base pairs. You will now explore the work associated with extending a DNA molecule. (a) Suppose that a DNA molecule resists being extended from an equilibrium, more compact conformation with a restoring force $F = -k_\mathrm{F}x$, where x is the difference in the end-to-end distance of the chain from an equilibrium value and k_F is the force constant. Use this model to write an expression for the work that must be done to extend a DNA molecule by a distance x. Draw a graph of your conclusion. (b) A better model of a DNA molecule is the 'one-dimensional freely jointed chain', in which a rigid unit of length l can only make an angle of 0° or 180° with an adjacent unit. In this case, the restoring force of a chain extended by $x = nl$ is given by

$$F = \frac{kT}{2l}\ln\left(\frac{1+\nu}{1-\nu}\right) \qquad \nu = \frac{n}{N}$$

where k is Boltzmann's constant. (i) What is the magnitude of the force that must be applied to extend a DNA molecule with $N = 200$ by 90 nm? (ii) Plot the restoring force against ν, noting that ν can be either positive or negative. How is the variation of the restoring force with end-to-end distance different from that predicted by Hooke's law? (iii) Keep in mind that the difference in end-to-end distance from an equilibrium value is $x = nl$ and, consequently, $dx = ldn = Nld\nu$, and write an expression for the work of extending a DNA molecule. (iv) Calculate the work of extending a DNA molecule from $\nu = 0$ to $\nu = 1.0$. *Hint*: You must integrate the expression for w. The task can be accomplished easily with mathematical software. (c) Show that for small extensions of the chain, when $\nu \ll 1$, the restoring force is given by

$$F \approx \frac{\nu kT}{l} = \frac{nkT}{Nl}$$

(d) Is the variation of the restoring force with extension of the chain given in part (c) different from that predicted by Hooke's law? Explain your answer.

Topic 56 Enthalpy

Discussion questions

56.1 Explain why a perfect gas does not have an inversion temperature.

56.2 Explain why in most cases the constant-pressure heat capacity is larger than the constant-volume heat capacity.

56.3 Describe how the Joule–Thomson effect is used in the liquefaction of gases.

Exercises

56.1(a) When 229 J of energy is supplied as heat to 3.0 mol Ar(g), the temperature of the sample increases by 2.55 K. Calculate the molar heat capacities at constant volume and constant pressure of the gas.
56.1(b) When 178 J of energy is supplied as heat to 1.9 mol of gas molecules, the temperature of the sample increases by 1.78 K. Calculate the molar heat capacities at constant volume and constant pressure of the gas.

56.2(a) The constant-pressure heat capacity of a sample of a perfect gas was found to vary with temperature according to the expression $C_p/(\mathrm{J\,K^{-1}}) = 20.17 + 0.3665(T/\mathrm{K})$. Calculate q, w, and ΔU when the temperature is raised from 25 °C to 100 °C (a) at constant pressure, (b) at constant volume.
56.2(b) The constant-pressure heat capacity of a sample of a perfect gas was found to vary with temperature according to the expression $C_p/(\mathrm{J\,K^{-1}}) = 20.17 + 0.4001(T/\mathrm{K})$. Calculate q, w, and ΔU when the temperature is raised from 0 °C to 200 °C (a) at constant pressure, (b) at constant volume.

56.3(a) When 3.0 mol O_2 is heated at a constant pressure of 3.25 atm, its temperature increases from 260 K to 285 K. Given that the molar heat capacity of O_2 at constant pressure is $29.4\,\mathrm{J\,K^{-1}\,mol^{-1}}$, calculate q, ΔH, and ΔU.
56.3(b) When 2.0 mol CO_2 is heated at a constant pressure of 1.25 atm, its temperature increases from 250 K to 277 K. Given that the molar heat capacity of CO_2 at constant pressure is $37.11\,\mathrm{J\,K^{-1}\,mol^{-1}}$, calculate q, ΔH, and ΔU.

56.4(a) Given that $\mu = 0.25\,\mathrm{K\,atm^{-1}}$ for nitrogen, calculate the value of its isothermal Joule–Thomson coefficient. Calculate the energy that must be supplied as heat to maintain constant temperature when 10.0 mol N_2 flows through a throttle in an isothermal Joule–Thomson experiment and the pressure drop is 85 atm.
56.4(b) Given that $\mu = 1.11\,\mathrm{K\,atm^{-1}}$ for carbon dioxide, calculate the value of its isothermal Joule–Thomson coefficient. Calculate the energy that must be supplied as heat to maintain constant temperature when 10.0 mol CO_2 flows through a throttle in an isothermal Joule–Thomson experiment and the pressure drop is 75 atm.

Problems

56.1 The following data show how the standard molar constant-pressure heat capacity of sulfur dioxide varies with temperature. By how much does the standard molar enthalpy of SO_2(g) increase when the temperature is raised from 298.15 K to 1500 K?

56.2 The following data show how the standard molar constant-pressure heat capacity of ammonia depends on the temperature. Use mathematical software to fit an expression of the form of eqn 56.5 to the data and determine the values of a, b, and c. Explore whether it would be better to express the data as $C_{p,\mathrm{m}} = \alpha + \beta T + \gamma T^2$, and determine the values of these coefficients.

T/K	300	500	700	900	1100	1300	1500
$C^{\ominus}_{p,\mathrm{m}}/(\mathrm{J\,K^{-1}\,mol^{-1}})$	39.909	46.490	50.829	53.407	54.993	56.033	56.759

56.3 A sample consisting of 2.0 mol CO_2 occupies a fixed volume of 15.0 dm³ at 300 K. When it is supplied with 2.35 kJ of energy as heat its temperature increases to 341 K. Assume that CO_2 is described by the van der Waals equation of state (Topic 36) and calculate w, ΔU, and ΔH.

T/K	300	400	500	600	700	800	900	1000
$C^{\ominus}_{p,\mathrm{m}}/(\mathrm{J\,K^{-1}\,mol^{-1}})$	35.678	38.674	41.994	45.229	48.269	51.112	53.769	56.244

56.4 (a) Express (i) $(\partial C_V/\partial V)_T$ as a second derivative of U and find its relation to $(\partial U/\partial V)_T$, and (ii) $(\partial C_p/\partial p)_T$ as a second derivative of H and find its relation to $(\partial H/\partial p)_T$. (b) From these relations show that $(\partial C_V/\partial V)_T = 0$ and $(\partial C_p/\partial p)_T = 0$ for a perfect gas.

56.5‡ A gas obeying the equation of state $p(V - nb) = nRT$ is subjected to a Joule–Thomson expansion. Will the temperature increase, decrease, or remain the same?

56.6 Use the fact that $(\partial U/\partial V)_T = a/V_\mathrm{m}^2$ for a van der Waals gas (Topic 36) to show that $\mu C_{p,\mathrm{m}} \approx (2a/RT) - b$ by using the definition of μ and appropriate relations between partial derivatives. *Hint*: Use the approximation $pV_\mathrm{m} \approx RT$ when it is justifiable to do so.

56.7‡ Concerns over the harmful effects of chlorofluorocarbons on stratospheric ozone have motivated a search for new refrigerants. One such alternative is 2,2-dichloro-1,1,1-trifluoroethane (refrigerant 123). Younglove and McLinden published a compendium of thermophysical properties of this substance (B.A. Younglove and M. McLinden, *J. Phys. Chem. Ref. Data* **23**, 7 (1994)), from which properties such as the Joule–Thomson

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‡ These problems were supplied by Charles Trapp and Carmen Giunta.

coefficient μ can be computed. (a) Compute μ at 1.00 bar and 50 °C given that $(\partial H/\partial p)_T = -3.29 \times 10^3\ \mathrm{J\ MPa^{-1}\ mol^{-1}}$ and $C_{p,\mathrm{m}} = 110.0\ \mathrm{J\ K^{-1}\ mol^{-1}}$. (b) Compute the temperature change which would accompany adiabatic expansion of 2.0 mol of this refrigerant from 1.5 bar to 0.5 bar at 50 °C.

56.8‡ Another alternative refrigerant (see preceding problem) is 1,1,1,2-tetrafluoroethane (refrigerant HFC-134a). A compendium of thermophysical properties of this substance has been published (R. Tillner-Roth and H.D. Baehr, *J. Phys. Chem. Ref. Data* **23**, 657 (1994)) from which properties such as the Joule–Thomson coefficient μ can be computed. (a) Compute μ at 0.100 MPa and 300 K from the following data (all referring to 300 K):

p/MPa	0.080	0.100	0.12
Specific enthalpy/(kJ kg^{-1})	426.48	426.12	425.76

(The specific constant-pressure heat capacity is $0.7649\ \mathrm{kJ\ K^{-1}\ kg^{-1}}$.) (b) Compute μ at 1.00 MPa and 350 K from the following data (all referring to 350 K):

p/MPa	0.80	1.00	1.2
Specific enthalpy/(kJ kg^{-1})	461.93	459.12	456.15

(The specific constant-pressure heat capacity is $1.0392\ \mathrm{kJ\ K^{-1}\ kg^{-1}}$.)

Topic 57 Thermochemistry

Discussion questions

57.1 Describe two calorimetric methods for the determination of enthalpy changes that accompany chemical processes.

57.2 Distinguish between 'standard state' and 'reference state', and indicate their applications.

Exercises

57.1(a) For tetrachloromethane, $\Delta_{\mathrm{vap}}H^{\ominus} = 30.0\ \mathrm{kJ\ mol^{-1}}$. Calculate q, w, ΔH, and ΔU when 0.75 mol $CCl_4(l)$ is vaporized at 250 K and 750 Torr.

57.1(b) For ethanol, $\Delta_{\mathrm{vap}}H^{\ominus} = 43.5\ \mathrm{kJ\ mol^{-1}}$. Calculate q, w, ΔH, and ΔU when 1.75 mol $C_2H_5OH(l)$ is vaporized at 260 K and 765 Torr.

57.2(a) The standard enthalpy of formation of ethylbenzene is $-12.5\ \mathrm{kJ\ mol^{-1}}$. Calculate its standard enthalpy of combustion.

57.2(b) The standard enthalpy of formation of phenol is $-165.0\ \mathrm{kJ\ mol^{-1}}$. Calculate its standard enthalpy of combustion.

57.3(a) The standard enthalpy of combustion of cyclopropane is $-2091\ \mathrm{kJ\ mol^{-1}}$ at 25 °C. From this information and enthalpy of formation data for $CO_2(g)$ and $H_2O(g)$, calculate the enthalpy of formation of cyclopropane. The enthalpy of formation of propene is $+20.42\ \mathrm{kJ\ mol^{-1}}$. Calculate the enthalpy of isomerization of cyclopropane to propene.

57.3(b) From the following data, determine $\Delta_f H^{\ominus}$ for diborane, $B_2H_6(g)$, at 298 K:

(1) $B_2H_6(g) + 3\ O_2(g) \rightarrow B_2O_3(s) + 3\ H_2O(g)$ $\quad \Delta_r H^{\ominus} = -1941\ \mathrm{kJ\ mol^{-1}}$

(2) $2\,B(s) + \frac{3}{2} O_2(g) \rightarrow B_2O_3(s)$ $\quad \Delta_r H^{\ominus} = 2368\ \mathrm{kJ\ mol^{-1}}$

(3) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(g)$ $\quad \Delta_r H^{\ominus} = -241.8\ \mathrm{kJ\ mol^{-1}}$

57.4(a) Given that the standard enthalpy of formation of HCl(aq) is $-167\ \mathrm{kJ\ mol^{-1}}$, what is the value of $\Delta_f H^{\ominus}(Cl^-, aq)$?

57.4(b) Given that the standard enthalpy of formation of HI(aq) is $-55\ \mathrm{kJ\ mol^{-1}}$, what is the value of $\Delta_f H^{\ominus}(I^-, aq)$?

57.5(a) When 120 mg of naphthalene, $C_{10}H_8(s)$, was burned in a bomb calorimeter the temperature rose by 3.05 K. Calculate the calorimeter constant. By how much will the temperature rise when 150 mg of phenol, $C_6H_5OH(s)$, is burned in the calorimeter under the same conditions?

57.5(b) When 2.25 mg of anthracene, $C_{14}H_{10}(s)$, was burned in a bomb calorimeter the temperature rose by 1.75 K. Calculate the calorimeter constant. By how much will the temperature rise when 125 mg of phenol, $C_6H_5OH(s)$, is burned in the calorimeter under the same conditions? ($\Delta_c H^{\ominus}(C_{14}H_{10}, s) = -7061\ \mathrm{kJ\ mol^{-1}}$.)

57.6(a) Given the reactions (1) and (2) below, determine (i) $\Delta_r H^{\ominus}$ and $\Delta_r U^{\ominus}$ for reaction (3), (ii) $\Delta_f H^{\ominus}$ for both HCl(g) and $H_2O(g)$, all at 298 K.

(1) $H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$ $\quad \Delta_r H^{\ominus} = -184.62\ \mathrm{kJ\ mol^{-1}}$

(2) $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$ $\quad \Delta_r H^{\ominus} = -483.64\ \mathrm{kJ\ mol^{-1}}$

(3) $4\ HCl(g) + O_2(g) \rightarrow 2\ Cl_2(g) + 2\ H_2O(g)$

57.6(b) Given the reactions (1) and (2) below, determine (i) $\Delta_r H^{\ominus}$ and $\Delta_r U^{\ominus}$ for reaction (3), (ii) $\Delta_f H^{\ominus}$ for both HI(g) and $H_2O(g)$, all at 298 K.

(1) $H_2(g) + I_2(s) \rightarrow 2\ HI(g)$ $\quad \Delta_r H^{\ominus} = +52.96\ \mathrm{kJ\ mol^{-1}}$

(2) $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$ $\quad \Delta_r H^{\ominus} = -483.64\ \mathrm{kJ\ mol^{-1}}$

(3) $4\ HI(g) + O_2(g) \rightarrow 2\ I_2(s) + 2\ H_2O(g)$

57.7(a) For the reaction $C_2H_5OH(l) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(g)$, $\Delta_r U^{\ominus} = -1373\ \mathrm{kJ\ mol^{-1}}$ at 298 K. Calculate $\Delta_r H^{\ominus}$.

57.7(b) For the reaction $2\ C_6H_5COOH(s) + 15\ O_2(g) \rightarrow 14\ CO_2(g) + 6\ H_2O(g)$, $\Delta_r U^{\ominus} = -772.7\ \mathrm{kJ\ mol^{-1}}$ at 298 K. Calculate $\Delta_r H^{\ominus}$.

57.8(a) From the data in Tables 57.3 and 57.4, calculate $\Delta_r H^{\ominus}$ and $\Delta_r U^{\ominus}$ at (a) 298 K, (b) 478 K for the reaction $C(\text{graphite}) + H_2O(g) \rightarrow CO(g) + H_2(g)$. Assume all heat capacities to be constant over the temperature range of interest.

57.8(b) Calculate $\Delta_r H^{\ominus}$ and $\Delta_r U^{\ominus}$ at 298 K and $\Delta_r H^{\ominus}$ at 427 K for the hydrogenation of ethyne (acetylene) to ethene (ethylene) from the enthalpy of combustion and heat capacity data in Tables 57.3 and 57.4. Assume the heat capacities to be constant over the temperature range involved.

57.9(a) Estimate $\Delta_r H^{\ominus}(500\ \mathrm{K})$ for the combustion of methane, $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$, by using the data on the temperature dependence of heat capacities in Table 56.1 (and Tables 57.3 and 57.4 for any species not in Table 56.1).

57.9(b) Estimate $\Delta_r H^\ominus(478\,\text{K})$ for the combustion of naphthalene, $C_{10}H_8(l) + 12\,O_2(g) \rightarrow 10\,CO_2(g) + 4\,H_2O(g)$, by using the data on the temperature dependence of heat capacities in Table 56.1 (and Tables 57.3 and 57.4 for any species not in Table 56.1).

57.10(a) Set up a thermodynamic cycle for determining the enthalpy of hydration of Mg^{2+} ions using the following data: enthalpy of sublimation of Mg(s), +167.2 kJ mol^{-1}; first and second ionization enthalpies of Mg(g), 7.646 eV and 15.035 eV, respectively dissociation enthalpy of $Cl_2(g)$, +241.6 kJ mol^{-1}; electron gain enthalpy of Cl(g), −3.78 eV; enthalpy of solution of $MgCl_2(s)$, −150.5 kJ mol^{-1}; enthalpy of hydration of $Cl^-(g)$, −383.7 kJ mol^{-1}.

57.10(b) Set up a thermodynamic cycle for determining the enthalpy of hydration of Ca^{2+} ions using the following data: enthalpy of sublimation of Ca(s), +178.2 kJ mol^{-1}; first and second ionization enthalpies of Ca(g), 589.7 kJ mol^{-1} and 1145 kJ mol^{-1}, respectively enthalpy of vaporization of bromine, +30.91 kJ mol^{-1}; dissociation enthalpy of $Br_2(g)$, +192.9 kJ mol^{-1}; electron gain enthalpy of Br(g), −331.0 kJ mol^{-1}; enthalpy of solution of $CaBr_2(s)$, −103.1 kJ mol^{-1}; enthalpy of hydration of $Br^-(g)$, +97.5 kJ mol^{-1}.

Problems

57.1 A sample of the sugar D-ribose ($C_5H_{10}O_5$) of mass 0.727 g was placed in a calorimeter and then ignited in the presence of excess oxygen. The temperature rose by 0.910 K. In a separate experiment in the same calorimeter, the combustion of 0.825 g of benzoic acid, for which the internal energy of combustion is −3251 kJ mol^{-1}, gave a temperature rise of 1.940 K. Calculate the enthalpy of formation of D-ribose.

57.2 The standard enthalpy of formation of bis(benzene)chromium was measured in a calorimeter. It was found for the reaction $Cr(C_6H_6)_2(s) \rightarrow Cr(s) + 2\,C_6H_6(g)$ that $\Delta_r U^\ominus(583\,\text{K}) = +8.0\,\text{kJ mol}^{-1}$. Find the corresponding reaction enthalpy and estimate the standard enthalpy of formation of the compound at 583 K. The constant-pressure molar heat capacity of benzene is 136.1 J K^{-1} mol^{-1} in its liquid state and 81.67 J K^{-1} mol^{-1} as a gas.

57.3‡ From the enthalpy of combustion data in Table 57.3 for the alkanes methane through octane, test the extent to which the relation $\Delta_c H^\ominus = k\{(M/(\text{g mol}^{-1})\}^n$ holds and find the numerical values for k and n. Predict $\Delta_c H^\ominus$ for decane and compare to the known value.

57.4‡ Kolesov, et al. reported the standard enthalpy of combustion and of formation of crystalline C_{60} based on calorimetric measurements (V.P. Kolesov, et al., *J. Chem. Thermodynamics* **28**, 1121 (1996)). In one of their runs, they found the standard specific internal energy of combustion to be −36.0334 kJ g^{-1} at 298.15 K Compute $\Delta_c H^\ominus$ and $\Delta_f H^\ominus$ of C_{60}.

57.5‡ A thermodynamic study of $DyCl_3$ (E.H.P. Cordfunke, et al., *J. Chem. Thermodynamics* **28**, 1387 (1996)) determined its standard enthalpy of formation from the following information

$$\text{(1) } DyCl_3(s) \rightarrow DyCl_3(aq,\ \text{in } 4.0\ \text{M HCl}) \quad \Delta_r H^\ominus = -180.06\,\text{kJ mol}^{-1}$$

$$\text{(2) } Dy(s) + 3\,HCl(aq, 4.0\,\text{M}) \rightarrow DyCl_3(aq, \text{in } 4.0\,\text{M HCl(aq)}) + \tfrac{3}{2}H_2(g) \quad \Delta_r H^\ominus = -699.43\,\text{kJ mol}^{-1}$$

$$\text{(3) } \tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \rightarrow HCl(aq, 4.0\,\text{M}) \quad \Delta_r H^\ominus = -158.31\,\text{kJ mol}^{-1}$$

Determine $\Delta_f H^\ominus(DyCl_3, s)$ from these data.

57.6‡ Silylene (SiH_2) is a key intermediate in the thermal decomposition of silicon hydrides such as silane (SiH_4) and disilane (Si_2H_6). H.K. Moffat, et al. (*J. Phys. Chem.* **95**, 145 (1991)) report $\Delta_f H^\ominus(SiH_2) = +274\,\text{kJ mol}^{-1}$. If $\Delta_f H^\ominus(SiH_4) = +34.3\,\text{kJ mol}^{-1}$ and $\Delta_f H^\ominus(Si_2H_6) = +80.3\,\text{kJ mol}^{-1}$, compute the standard enthalpies of the following reactions:

(a) $SiH_4(g) \rightarrow SiH_2(g) + H_2(g)$

(b) $Si_2H_6(g) \rightarrow SiH_2(g) + SiH_4(g)$

57.7 As remarked in Problem 56.2, it is sometimes appropriate to express the temperature dependence of the heat capacity by the empirical expression $C_{p,\text{m}} = \alpha + \beta T + \gamma T^2$. Use this expression to estimate the standard enthalpy of combustion of methane at 350 K. Use the following data:

	$\alpha/(\text{J K}^{-1}\,\text{mol}^{-1})$	$\beta/(\text{mJ K}^{-2}\,\text{mol}^{-1})$	$\gamma/(\mu\text{J K}^{-3}\,\text{mol}^{-1})$
$CH_4(g)$	14.16	75.5	−17.99
$CO_2(g)$	26.86	6.97	−0.82
$O_2(g)$	25.72	12.98	−3.862
$H_2O(g)$	30.36	9.61	1.184

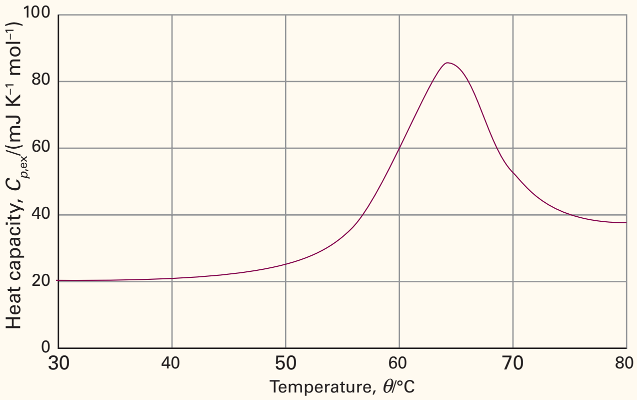

Figure F12.1 An experimental DSC scan of hen white lysozyme.

57.8 Figure F12.1 shows the experimental DSC scan of hen white lysozyme (G. Privalov, et al., *Anal. Biochem.* **79**, 232 (1995)) converted to joules (from calories). Determine the enthalpy of unfolding of this protein by integration of the curve and the change in heat capacity accompanying the transition.

57.9 An average human produces about 10 MJ of heat each day through metabolic activity. If a human body were an isolated system of mass 65 kg with the heat capacity of water, what temperature rise would the body experience? Human bodies are actually open systems, and the main mechanism of heat loss is through the evaporation of water. What mass of water should be evaporated each day to maintain constant temperature?

57.10 In biological cells that have a plentiful supply of oxygen, glucose is oxidized completely to CO_2 and H_2O by a process called *aerobic oxidation*. Muscle cells may be deprived of O_2 during vigorous exercise and, in that case, one molecule of glucose is converted to two molecules of lactic acid, $CH_3CH(OH)COOH$, by a process called *anaerobic glycolysis*. (a) When 0.3212 g of glucose was burned in a bomb calorimeter of calorimeter constant 641 J K^{-1} the temperature rose by 7.793 K. Calculate (i) the standard molar enthalpy of combustion, (ii) the standard internal energy of combustion, and (iii) the standard enthalpy of formation of glucose. (b) What is the biological advantage (in kilojoules per mole of energy released as heat) of complete aerobic oxidation compared with anaerobic glycolysis to lactic acid?

Topic 58 Internal energy

Discussion questions

58.1 Suggest (with explanation) how the internal energy of a van der Waals gas should vary with volume at constant temperature.

58.2 Use concepts of statistical thermodynamics to describe the molecular features that determine the magnitude of the constant-volume molar heat capacity of a molecular substance.

58.3 Use concepts of statistical thermodynamics to describe the molecular features that lead to the equations of state of perfect and real gases.

Exercises

58.1(a) The ground level of Cl is $^2P_{3/2}$ and a $^2P_{1/2}$ level lies 881 cm^{-1} above it. Calculate the electronic contribution to the molar constant-volume heat capacity of Cl atoms at (a) 500 K and (b) 900 K.
58.1(b) The first electronically excited state of O_2 is $^1\Delta_g$ and lies 7918.1 cm^{-1} above the ground state, which is $^3\Sigma_g^-$. Calculate the electronic contribution to the molar constant-volume heat capacity of O_2 at 400 K.

58.2(a) Use the equipartition principle to estimate the values of $\gamma = C_p/C_V$ for gaseous ammonia and methane. Do this calculation with and without the vibrational contribution to the energy. Which is closer to the expected experimental value at 25 °C?
58.2(b) Use the equipartition principle to estimate the value of $\gamma = C_p/C_V$ for carbon dioxide. Do this calculation with and without the vibrational contribution to the energy. Which is closer to the expected experimental value at 25 °C?

58.3(a) What is the root mean square deviation of the molecular energy of argon atoms at 298 K?
58.3(b) What is the root mean square deviation of the molecular energy of carbon dioxide molecules at 298 K?

58.4(a) Calculate the final temperature of a sample of argon of mass 12.0 g that is expanded reversibly and adiabatically from 1.0 dm^3 at 273.15 K to 3.0 dm^3.
58.4(b) Calculate the final temperature of a sample of carbon dioxide of mass 16.0 g that is expanded reversibly and adiabatically from 500 cm^3 at 298.15 K to 2.00 dm^3.

58.5(a) A sample consisting of 1.0 mol of perfect gas molecules with $C_V = 20.8$ J K^{-1} is initially at 4.25 atm and 300 K. It undergoes reversible, adiabatic expansion until its pressure reaches 2.50 atm. Calculate the final volume and temperature and the work done.
58.5(b) A sample consisting of 2.5 mol of perfect gas molecules with $C_{p,m} = 20.8$ J K^{-1} mol^{-1} is initially at 240 kPa and 325 K. It undergoes reversible, adiabatic expansion until its pressure reaches 150 kPa. Calculate the final volume and temperature and the work done.

58.6(a) A sample of carbon dioxide of mass 2.45 g at 27.0 °C is allowed to expand reversibly and adiabatically from 500 cm^3 to 3.00 dm^3. What is the work done by the gas?
58.6(b) A sample of nitrogen of mass 3.12 g at 23.0 °C is allowed to expand reversibly and adiabatically from 400 cm^3 to 2.00 dm^3. What is the work done by the gas?

58.7(a) Calculate the final pressure of a sample of carbon dioxide that expands reversibly and adiabatically from 67.4 kPa and 0.50 dm^3 to a final volume of 2.00 dm^3. Take $\gamma = 1.4$.
58.7(b) Calculate the final pressure of a sample of water vapour that expands reversibly and adiabatically from 97.3 Torr and 400 cm^3 to a final volume of 5.0 dm^3. Take $\gamma = 1.3$.

58.8(a) Estimate the internal pressure, π_T, of water vapour at 1.00 bar and 400 K, treating it as a van der Waals gas (Topic 36). *Hint*: Simplify the approach by estimating the molar volume by treating the gas as perfect.
58.8(b) Estimate the internal pressure, π_T, of sulfur dioxide at 1.00 bar and 298 K, treating it as a van der Waals gas (Topic 36). *Hint*: Simplify the approach by estimating the molar volume by treating the gas as perfect.

58.9(a) For a van der Waals gas (Topic 36), $\pi_T = a/V_m^2$. Calculate ΔU_m for the isothermal expansion of nitrogen gas from an initial volume of 1.00 dm^3 to 20.00 dm^3 at 298 K. What are the values of q and w?
58.9(b) Repeat Exercise 58.9a. for argon, from an initial volume of 1.00 dm^3 to 30.00 dm^3 at 298 K.

58.10(a) The volume of a certain liquid varies with temperature as

$$V = V'\{0.75 + 3.9 \times 10^{-4}(T/\text{K}) + 1.48 \times 10^{-6}(T/\text{K})^2\}$$

where V' is its volume at 300 K. Calculate its expansion coefficient, α, at 320 K.

58.10(b) The volume of a certain liquid varies with temperature as

$$V = V'\{0.77 + 3.7 \times 10^{-4}(T/\text{K}) + 1.52 \times 10^{-6}(T/\text{K})^2\}$$

where V' is its volume at 298 K. Calculate its expansion coefficient, α, at 310 K.

58.11(a) The isothermal compressibility of water at 293 K is 4.96×10^{-5} atm^{-1}. Calculate the pressure that must be applied in order to increase its density by 0.10 per cent.
58.11(b) The isothermal compressibility of lead at 293 K is 2.21×10^{-6} atm^{-1}. Calculate the pressure that must be applied in order to increase its density by 0.10 per cent.

Problems

58.1‡ In 2006, the Intergovernmental Panel on Climate Change (IPCC) considered a global average temperature rise of 1.0–3.5 °C likely by the year 2100, with 2.0 °C its best estimate. Predict the average rise in sea level due to thermal expansion of seawater based on temperature rises of 1.0 °C, 2.0 °C, and 3.5 °C, given that the volume of the Earth's oceans is 1.37×10^9 km^3 and their surface area is 361×10^6 km^2, and state the approximations which go into the estimates.

58.2 The constant-volume heat capacity of a gas can be measured by observing the decrease in temperature when it expands adiabatically and reversibly. The value of $\gamma = C_p/C_V$ can be inferred if the decrease in pressure is also measured and the constant-pressure heat capacity deduced by combining the two values. A fluorocarbon gas was allowed to expand reversibly and adiabatically to twice its volume; as a result, the temperature fell from 298.15 K to 248.44 K and its pressure fell from 202.94 kPa to 81.840 kPa. Evaluate C_p.

58.3 The NO molecule has a doubly degenerate electronic ground state and a doubly degenerate excited state at 121.1 cm^{-1}. Calculate the electronic contribution to the molar heat capacity of the molecule at (a) 100 K, (b) 298 K, and (c) 600 K.

58.4 The energy levels of a CH_3 group attached to a larger fragment are given by the expression for a particle on a ring (Topic 13), provided the group is rotating freely. What is the high-temperature contribution to the heat capacity of such a freely rotating group at 25 °C? The moment of inertia of CH_3 about its threefold rotation axis (the axis that passes through the C atom and the centre of the equilateral triangle formed by the H atoms) is $5.341 \times 10^{-47}\,\text{kg}\,\text{m}^2$.

58.5 Calculate the temperature dependence of the heat capacity of p-H_2 (in which only rotational states with even values of J are populated) at low temperatures on the basis that its rotational levels $J = 0$ and $J = 2$ constitute a system that resembles a two-level system except for the degeneracy of the upper level. Use $\tilde{B} = 60.864\,\text{cm}^{-1}$ and sketch the heat capacity curve. The experimental heat capacity of p-H_2 does in fact show a peak at low temperatures.

58.6‡ In a spectroscopic study of buckminsterfullerene, C_{60}, F. Negri, et al. (*J. Phys. Chem.* **100**, 10849 (1996)) reviewed the wavenumbers of all the vibrational modes of the molecule. The wavenumber for the single A_u mode is 976 cm^{-1}; wavenumbers for the four threefold degenerate T_{1u} modes are 525, 578, 1180, and 1430 cm^{-1}; wavenumbers for the five threefold degenerate T_{2u} modes are 354, 715, 1037, 1190, and 1540 cm^{-1}; wavenumbers for the six fourfold degenerate G_u modes are 345, 757, 776, 963, 1315, and 1410 cm^{-1}; and wavenumbers for the seven fivefold degenerate H_u modes are 403, 525, 667, 738, 1215, 1342, and 1566 cm^{-1}. How many modes have a vibrational temperature θ^{V} below 1000 K? Estimate the molar constant-volume heat capacity of C_{60} at 1000 K, counting as active all modes with θ^{V} below this temperature.

58.7‡ Treat carbon monoxide as a perfect gas and apply equilibrium statistical thermodynamics to the study of its properties, as specified below, in the temperature range 100–1000 K at 1 bar. $\tilde{\nu} = 2169.8\,\text{cm}^{-1}$, $\tilde{B} = 1.931\,\text{cm}^{-1}$, and $hc\tilde{D}_0 = 11.09\,\text{eV}$; neglect anharmonicity and centrifugal distortion. (a) Examine the probability distribution of molecules over available rotational and vibrational states. (b) Explore numerically the differences, if any, between the rotational molecular partition function as calculated with the discrete energy distribution and that calculated with the classical, continuous energy distribution. (c) Calculate the individual contributions to $U_m(T) - U_m(100\,\text{K})$ and $C_{V,m}(T)$ made by the translational, rotational, and vibrational degrees of freedom.

58.8 In the realm of nanotechnology, even translational quantization may have significant consequences. Suppose an electron is trapped in a tiny one-dimensional well, where only about 10 states are thermally accessible. Derive an expression for (a) the heat capacity, (b) the root mean square spread in energies ($\Delta\varepsilon$) at such low temperatures (without making the 'continuum' approximation), and plot the heat capacity as a function of temperature. Can you identify a 'characteristic temperature' for the system?

58.9 Show that eqn 58.14 can be converted into eqn 58.13.

58.10 The energies of the first six levels of a particle in a spherical cavity are specified in Problem 53.1. Suppose that these levels are the only ones that are thermally accessible, and derive an expression for (a) the heat capacity, (b) the root mean square spread in energies ($\Delta\varepsilon$), and plot the former as a function of temperature.

58.11 Derive an expression for the rotational contribution to the heat capacity of a linear rotor without making the high-temperature approximation, and plot $C_{V,m}$ against T/θ^{R}, where the 'rotational temperature' is $\theta^{R} = hc\tilde{B}/k$. Ignore the role of nuclear statistics.

58.12 Are there thermal consequences of nuclear statistics that even the Victorians might have noticed? Explore the consequences, by direct summation of energy levels, of nuclear statistics for the molar heat capacities of *ortho*- and *para*-hydrogen.

58.13 In one of the earliest applications of quantum theory, Einstein sought to account for the decrease in heat capacity with decreasing temperature that had been observed. He supposed that each of the atoms in a monatomic solid could vibrate in three dimensions with a frequency ν. Deduce the Einstein formula and plot $C_{V,m}$ against T/θ^{E}, where the 'Einstein temperature' is $\theta^{E} = h\nu/k$.

58.14 Debye improved on Einstein's model by considering the *collective* modes of the atoms in the solid. Why would that lead to a higher heat capacity at all temperatures? He took the Einstein formula (Problem 58.13), multiplied it by a factor that represents the number of vibrational modes in the range ν to $\nu + d\nu$, and then integrated the resulting expression from $\nu = 0$ up to a maximum value ν_{max}. The result is

$$C_{V,m} = 9R\left(\frac{T}{\theta^{D}}\right)^{3}\int_{0}^{\theta^{D}/T}\frac{x^4 e^x}{\left(e^x - 1\right)^2}\,dx$$

where the 'Debye temperature' is $\theta^{D} = h\nu_{\text{max}}/k$. Use mathematical software to plot $C_{V,m}$ against T/θ^{D}. Show that when $T \ll \theta^{D}$, the heat capacity follows the 'Debye T^3 law' (see Self-test 56.2). You will need Integral E.2 in the *Resource section*.

58.15‡ For H_2 at very low temperatures, only translational motion contributes to the heat capacity. At temperatures above $\theta^{R} = hc\tilde{B}/k$, the rotational contribution to the heat capacity becomes significant. At still higher temperatures, above $\theta^{V} = h\nu/k$, the vibrations contribute. But at this latter temperature, dissociation of the molecule into the atoms must be considered. (a) Explain the origin of the expressions for θ^{R} and θ^{V}, and calculate their values for hydrogen. (b) Obtain an expression for the molar constant-pressure heat capacity of hydrogen at all temperatures, taking into account the dissociation of hydrogen. (c) Make a plot of the molar constant-pressure heat capacity as a function of temperature in the high temperature region where dissociation of the molecule is significant.

58.16 Although expressions like $\varepsilon = -d \ln q/d\beta$ are useful for formal manipulations in statistical thermodynamics, and for expressing thermodynamic functions in neat formulas, they are sometimes more trouble than they are worth in practical applications. When presented with a table of energy levels, it is often much more convenient to evaluate the following sums directly:

$$q = \sum_j e^{-\beta\varepsilon_j} \qquad \dot{q} = \sum_j \beta\varepsilon_j e^{-\beta\varepsilon_j} \qquad \ddot{q} = \sum_j (\beta\varepsilon_j)^2 e^{-\beta\varepsilon_j}$$

where $\dot{q}$ and $\ddot{q}$ are related to the first and second derivatives of q with respect to β. (a) Derive expressions for the internal energy and heat capacity in terms of these three functions. (b) Apply the technique to the calculation of the electronic contribution to the constant-volume molar heat capacity of magnesium vapour at 5000 K using the following data:

Term	^1S	$^3P_0$	$^3P_1$	$^3P_2$	$^1P_1$	^3S
Degeneracy	1	1	3	5	3	3
$\tilde{\nu}/\text{cm}^{-1}$	0	21850	21870	21911	35051	41197

58.17 Calculate the values of q, $\dot{q}$ and $\ddot{q}$ (Problem 58.16) for the rotational states of (a) HCl ($\tilde{B} = 10.593\,\text{cm}^{-1}$) and (b) CCl_4 ($\tilde{B} = 5.797\,\text{m}^{-1}$). (Be alert to the units!)

58.18 Show how the heat capacity of a linear rotor is related to the following sum:

$$\zeta(\beta)=\frac{1}{q^2}\sum_{J,J'}\{\varepsilon(J)-\varepsilon(J')\}^2 g(J)g(J')\mathrm{e}^{-\beta\{\varepsilon(J)+\varepsilon(J')\}}$$

by

$$C=\frac{1}{2}k\beta^2\zeta(\beta)$$

where the $\varepsilon(J)$ are the rotational energy levels and $g(J)$ their degeneracies. Then go on to show graphically that the total contribution to the heat capacity of a linear rotor can be regarded as a sum of contributions due to transitions $0\rightarrow1$, $0\rightarrow2$, $1\rightarrow2$, $1\rightarrow3$, etc. In this way, construct Fig. 58.6 for the rotational heat capacities of a linear molecule.

58.19 The 'bump' in the low-temperature variation of the heat capacity with temperature seen in Fig. 58.6 is more pronounced in the case of *para*-hydrogen, where only even values of J are allowed. Adapt the expression derived in Problem 58.18 to the cases of *ortho*- and *para*-hydrogen, and construct graphs of their heat capacities.

58.20 Set up a calculation like that in Problem 58.18 to analyse the vibrational contribution to the heat capacity in terms of excitations between levels and illustrate your results graphically in terms of a diagram like that in Fig. 58.6.

58.21 Equation 58.19 in the form

$$\frac{\mathrm{d}}{\mathrm{d}L}\frac{\mathrm{e}^{-\beta\varepsilon_i}}{q(\beta)}=0$$

is a differential equation for β (and therefore T) as a function of L, but we solved it there by inspection. Solve the equation formally and confirm that eqn 58.20 is a solution.

58.22 The heat capacity ratio of a gas determines the speed of sound in it through the formula $c_s=(\gamma RT/M)^{1/2}$, where $\gamma=C_p/C_V$ and M is the molar mass of the gas. Deduce an expression for the speed of sound in a perfect gas of (a) diatomic, (b) linear triatomic, (c) nonlinear triatomic molecules at high temperatures (with translation and rotation active). Estimate the speed of sound in air at 25 °C.

58.23 Starting from the expression $C_p-C_V=T(\partial p/\partial T)_V(\partial V/\partial T)_p$, use the appropriate relations between partial derivatives to show that

$$C_p-C_V=\frac{T(\partial V/\partial T)_p^2}{(\partial V/\partial p)_T}$$

Evaluate C_p-C_V for a perfect gas.

58.24 (a) Write expressions for $\mathrm{d}V$ and $\mathrm{d}p$ given that V is a function of p and T and that p is a function of V and T. (b) Deduce expressions for d ln V and d ln p in terms of the expansion coefficient and the isothermal compressibility.

58.25 Rearrange the van der Waals equation of state (Topic 36), $p=nRT/(V-nb)-n^2a/V^2$, to give an expression for T as a function of p and V (with n constant). Calculate $(\partial T/\partial p)_V$ and confirm that $(\partial T/\partial p)_V=1/(\partial p/\partial T)_V$. Go on to confirm Euler's chain relation (*Mathematical background* 8).

58.26 Calculate the isothermal compressibility and the expansion coefficient of a van der Waals gas (see Problem 58.25). Show, using Euler's chain relation (*Mathematical background* 8), that $\kappa_T R=\alpha(V_m-b)$.

58.27 The speed of sound, c_s, in a gas of molar mass M is related to the ratio of heat capacities γ by $c_s=(\gamma RT/M)^{1/2}$. Show that $c_s=(\gamma p/\rho)^{1/2}$, where ρ is the mass density of the gas. Calculate the speed of sound in argon at 25 °C.

58.28 The statistical properties of a two-level system enable us to give formal significance to negative thermodynamic temperatures. From the Boltzmann distribution for such a system, show that the temperature may be defined as

$$T=\frac{\varepsilon/k}{\ln(N_-/N_+)}$$

where ε is the energy separation and N_+ and N_- are the populations of the upper and lower states, respectively. Find the corresponding expression for $\beta=1/kT$. It follows that if the system can be contrived to have $N_-<N_+$, then $T<0$. Go on to plot graphs of the partition function, internal energy, and heat capacity of the system in the range $-\infty<kT/\varepsilon<\infty$. Observe that there are discontinuities in the graphs. These discontinuities are eliminated by plotting the properties against β in the range $-\infty<\varepsilon\beta<\infty$: do so.

Integrated activities

F12.1 Explore whether a magnetic field can influence the heat capacity of a paramagnetic molecule by calculating the electronic contribution to the heat capacity of an NO_2 molecule in a magnetic field. Estimate the total constant-volume heat capacity by using equipartition, and calculate the percentage change in heat capacity brought about by a 10.0 T magnetic field at (a) 100 K, (b) 298 K.

F12.2 The thermochemical properties of hydrocarbons are commonly investigated by using molecular modelling methods. (a) Use software to predict $\Delta_c H^\ominus$ values for the alkanes methane through pentane. To calculate $\Delta_c H^\ominus$ values, estimate the standard enthalpy of formation of C_nH_{2n+2}(g) by performing semi-empirical calculations (for example, AM1 or PM3 methods) and use experimental standard enthalpy of formation values for CO_2(g) and H_2O(l). (b) Compare your estimated values with the experimental values of $\Delta_c H^\ominus$ (Table 57.3) and comment on the reliability of the molecular modelling method. (c) Test the extent to which the relation $\Delta_c H^\ominus=\text{constant}\times\{(M/(\text{g mol}^{-1})\}^n$ holds and determine the numerical values of the constant and n. Compare to the results of Problem 57.3.

F12.3 Explain the difference between the change in internal energy and the change in enthalpy accompanying a chemical or physical process.

F12.4 Glucose and fructose are simple sugars with the molecular formula $C_6H_{12}O_6$. Sucrose, or table sugar, is a complex sugar with molecular formula $C_{12}H_{22}O_{11}$ that consists of a glucose unit covalently bound to a fructose unit (a water molecule is eliminated as a result of the reaction between glucose and fructose to form sucrose). (a) Calculate the energy released as heat when a typical table sugar cube of mass 1.5 g is burned in air. (b) To what height could you climb on the energy a table sugar cube provides, assuming 25 per cent of the energy is available for work? (c) The mass of a typical glucose tablet is 2.5 g. Calculate the energy released as heat when a glucose tablet is burned in air. (d) To what height could you climb on the energy a glucose tablet provides assuming 25 per cent of the energy is available for work?

F12.5 (a) Derive the relation $C_V=-(\partial U/\partial V)_T(\partial V/\partial T)_U$ from the expression for the total differential of $U(T,V)$ and (b) starting from the expression for the total differential of $H(T,p)$, express $(\partial H/\partial p)_T$ in terms of C_p and the Joule–Thomson coefficient, μ.

F12.6 (a) By direct differentiation of $H = U + pV$, obtain a relation between $(\partial H/\partial U)_p$ and $(\partial U/\partial V)_p$. (b) Confirm that $(\partial H/\partial U)_p = 1 + p(\partial V/\partial U)_p$ by expressing $(\partial H/\partial U)_p$ as the ratio of two derivatives with respect to volume and then using the definition of enthalpy.

F12.7‡ A gas obeys the equation of state $V_m = RT/p + aT^2$ and its constant-pressure heat capacity is given by $C_{p,m} = A + BT + Cp$, where a, A, B, and C are constants independent of T and p. Obtain expressions for (a) the Joule–Thomson coefficient and its constant-volume heat capacity.

F12.8 Use mathematical software, a spreadsheet, or the *Living graphs* (labelled $^{\mathrm{LG}}$) on the website of this book for the following exercises.

(a) Calculate the work of isothermal reversible expansion of 1.0 mol $CO_2(g)$ at 298 K from 1.0 dm^3 to 3.0 dm^3 on the basis that it obeys the van der Waals equation of state.

(b)$^{\mathrm{LG}}$ Explore the effect of the rotational constant on the plot of $C^{\mathrm{R}}_{V,\mathrm{m}}$ against T.

(c)$^{\mathrm{LG}}$ Explore the effect of the vibrational wavenumber on the plot of $C^{\mathrm{V}}_{V,\mathrm{m}}$ against T.

(d)$^{\mathrm{LG}}$ Explore how the parameter $\gamma = C_{p,\mathrm{m}}/C_{V,\mathrm{m}}$ affects the dependence of the pressure on the relative volume. Does the pressure–volume dependence become stronger or weaker with increasing volume?

Mathematical background 8 Multivariate calculus

A thermodynamic property of a system typically depends on a number of variables, such as the internal energy depending on the amount, volume, and temperature. To understand how these properties vary with the conditions we need to understand how to manipulate their derivatives. This is the field of **multivariate calculus**, the calculus of several variables.

MB8.1 Partial derivatives

A **partial derivative** of a function of more than one variable, such as $f(x,y)$, is the slope of the function with respect to one of the variables, all the other variables being held constant (Fig. MB8.1). Although a partial derivative shows how a function changes when one variable changes, it may be used to determine how the function changes when more than one variable changes by an infinitesimal amount. Thus, if f is a function of x and y, then when x and y change by $\mathrm{d}x$ and $\mathrm{d}y$, respectively, f changes by

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y \qquad \text{(MB8.1)}$$

where the symbol ∂ ('curly d') is used (instead of d) to denote a partial derivative and the subscript on the parentheses indicates which variable is being held constant. The quantity $\mathrm{d}f$ is also called the **differential** of f. Successive partial derivatives may be taken in any order:

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y \qquad \text{(MB8.2)}$$

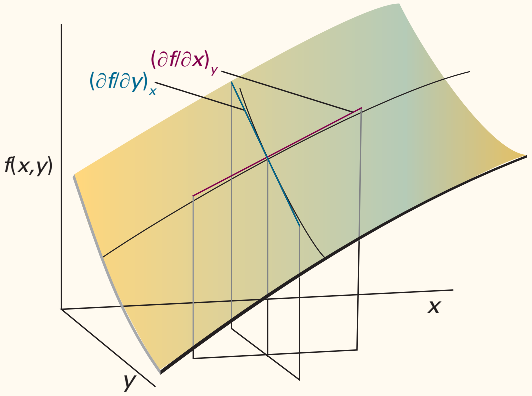

Figure MB8.1 A function of two variables, $f(x,y)$, as depicted by the coloured surface, and the two partial derivatives, $(\partial f/\partial x)_y$ and $(\partial f/\partial y)_x$, the slope of the function parallel to the x- and y-axes, respectively. The function plotted here is $f(x,y)=ax^3y+by^2$ with $a=1$ and $b=-2$.

Brief illustration MB8.1 Partial derivatives

Suppose that $f(x,y)=ax^3y+by^2$ (the function plotted in Fig. MB8.1). Then

$$\left(\frac{\partial f}{\partial x}\right)_y = 3ax^2y \qquad \left(\frac{\partial f}{\partial y}\right)_x = ax^3+2by$$

Then, when x and y undergo infinitesimal changes, f changes by

$$\mathrm{d}f = 3ax^2y\,\mathrm{d}x + (ax^3+2by)\,\mathrm{d}y$$

To verify that the order of taking the second partial derivative is irrelevant, we form

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial(3ax^2y)}{\partial y}\right)_x = 3ax^2$$

$$\left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y = \left(\frac{\partial(ax^3+2by)}{\partial x}\right)_y = 3ax^2$$

In the following, z is a variable on which x and y depend (for example, x, y, and z might correspond to p, V, and T).

Relation 1. When x is changed at constant z:

$$\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \qquad \text{(MB8.3a)}$$

Relation 2

$$\left(\frac{\partial y}{\partial x}\right)_z = \frac{1}{(\partial x/\partial y)_z} \qquad \text{(MB8.3b)}$$

Relation 3

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \qquad \text{(MB8.3c)}$$

By combining Relations 2 and 3 we obtain the **Euler chain relation**:

Euler chain relation

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1 \qquad \text{(MB8.4)}$$

MB8.2 Exact differentials

The relation in eqn MB8.2 is the basis of a test for an **exact differential**; that is, the test of whether

$$\mathrm{d}f = g(x,y)\mathrm{d}x + h(x,y)\mathrm{d}y \qquad \text{(MB8.3)}$$

has the form in eqn MB8.1. If it has that form, then g can be identified with $(\partial f/\partial x)_y$ and h can be identified with $(\partial f/\partial y)_x$. Then eqn MB8.2 becomes

$$\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y \qquad \text{(MB8.6)}$$

Test for exact differential

Brief illustration MB8.2 Exact differentials

Suppose, instead of the form $\mathrm{d}f = 3ax^2y\mathrm{d}x + (ax^3+2by)\mathrm{d}y$ in the previous *Brief illustration*, we were presented with the expression

$$\mathrm{d}f = \overbrace{3ax^2y}^{g(x,y)}\,\mathrm{d}x + \overbrace{(ax^2+2by)}^{h(x,y)}\,\mathrm{d}y$$

with ax^2 in place of ax^3 inside the second parentheses. To test whether this is an exact differential, we form

$$\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial(3ax^2y)}{\partial y}\right)_x = 3ax^2$$
$$\left(\frac{\partial h}{\partial x}\right)_y = \left(\frac{\partial(ax^2+2by)}{\partial x}\right)_y = 2ax$$

These two expressions are not equal, so this form of df is not an exact differential and there is not a corresponding integrated function of the form $f(x,y)$.

If df is exact, then we can do two things:

- From knowledge of the functions g and h we can reconstruct the function f.
- We can be confident that the integral of df between specified limits is independent of the path between those limits.

The first conclusion is best demonstrated with a specific example.

Brief illustration MB8.3 The reconstruction of an equation

We consider the differential $\mathrm{d}f = 3ax^2y\mathrm{d}x + (ax^3+2by)\mathrm{d}y$, which we know to be exact. Because $(\partial f/\partial x)_y = 3ax^2y$, we can integrate with respect to x with y held constant, to obtain

$$f = \int \mathrm{d}f = \int 3ax^2y\mathrm{d}x = 3ay\int x^2\,\mathrm{d}x = ax^3y + k$$

where the 'constant' of integration k may depend on y (which has been treated as a constant in the integration), but not on x. To find $k(y)$, we note that $(\partial f/\partial y)_x = ax^3+2by$, and therefore

$$\left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial(ax^3y+k)}{\partial y}\right)_x = ax^3 + \frac{dk}{dy} = ax^3+2by$$

Therefore

$$\frac{\mathrm{d}k}{\mathrm{d}y} = 2by$$

from which it follows that $k = by^2 + \text{constant}$. We have found, therefore, that

$$f(x,y) = ax^3y + by^2 + \text{constant}$$

which, apart from the constant, is the original function in *Brief illustration* MB8.1. The value of the constant is pinned down by stating the boundary conditions; thus, if it is known that $f(0,0)=0$, then the constant is zero.

To demonstrate that the integral of df is independent of the path is now straightforward. Because df is a differential, its integral between the limits a and b is

$$\int_a^b \mathrm{d}f = f(b) - f(a)$$

The value of the integral depends only on the values at the endpoints and is independent of the path between them. If df is not an exact differential, the function f does not exist, and this argument no longer holds. In such cases, the integral of df does depend on the path.

Brief illustration MB8.4 Path-dependent integration

Consider the inexact differential (the expression with ax^2 in place of ax^3 inside the second parentheses):

$$\mathrm{d}f = 3ax^2y\mathrm{d}x + (ax^2 + 2by)\mathrm{d}y$$

Suppose we integrate df from (0,0) to (2,2) along the two paths shown in Fig. MB8.2. Along Path 1,

$$\int_{\text{Path 1}} \mathrm{d}f = \int_{0,0}^{2,0} 3ax^2y\,\mathrm{d}x + \int_{2,0}^{2,2} (ax^2+2by)\,\mathrm{d}y$$
$$= 0 + 4a\int_0^2 \mathrm{d}y + 2b\int_0^2 y\,\mathrm{d}y = 8a + 4b$$

whereas along Path 2,

$$\int_{\text{Path 2}} \mathrm{d}f = \int_{0,2}^{2,2} 3ax^2y\ \mathrm{d}x + \int_{0,0}^{0,2} (ax^2+2by)\ \mathrm{d}y$$

$$= 6a\int_0^2 x^2\mathrm{d}x + 0 + 2b\int_0^2 y\,\mathrm{d}y = 16a + 4b$$

The two integrals are not the same.

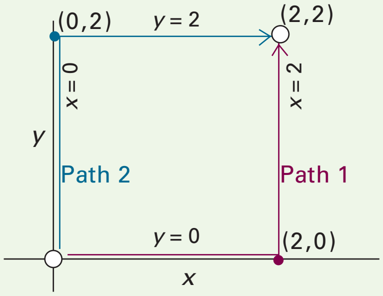

Figure MB8.2 The two integration paths referred to in *Brief illustration* MB8.4.

An inexact differential may sometimes be converted into an exact differential by multiplication by a factor known as an *integrating factor*. A physical example is the integrating factor $1/T$ that converts the inexact differential $\mathrm{d}q_{\text{rev}}$ into the exact differential $\mathrm{d}S$ in thermodynamics (Topic 61).

Brief illustration MB8.5 An integrating factor

We have seen that the differential $\mathrm{d}f = 3ax^2y\mathrm{d}x + (ax^2+2by)\mathrm{d}y$ is inexact; the same is true when we set $b=0$ and consider $\mathrm{d}f = 3ax^2y\mathrm{d}x + ax^2\mathrm{d}y$ instead. Suppose we multiply this $\mathrm{d}f$ by x^my^n and write $x^my^n\mathrm{d}f = \mathrm{d}f'$, then we obtain

$$\mathrm{d}f' = \overbrace{3ax^{m+2}y^{n+1}}^{g(x,y)}\mathrm{d}x + \overbrace{ax^{m+2}y^n}^{h(x,y)}\ \mathrm{d}y$$

We evaluate the following two partial derivatives:

$$\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial(3ax^{m+2}y^{n+1})}{\partial y}\right)_x = 3a(n+1)x^{m+2}y^n$$

$$\left(\frac{\partial h}{\partial x}\right)_y = \left(\frac{\partial(ax^{m+2}y^n)}{\partial x}\right)_y = a(m+2)x^{m+1}y^n$$

For the new differential to be exact, these two partial derivatives must be equal, so we write

$$3a(n+1)x^{m+2}y^n = a(m+2)x^{m+1}y^n$$

which simplifies to

$$3(n+1)x = m+2$$

The only solution that is independent of x is $n=-1$ and $m=-2$. It follows that

$$\mathrm{d}f' = 3a\mathrm{d}x + (a/y)\mathrm{d}y$$

is an exact differential. By the procedure already illustrated, its integrated form is $f'(x,y) = 3ax + a\ln y + \text{constant}$.

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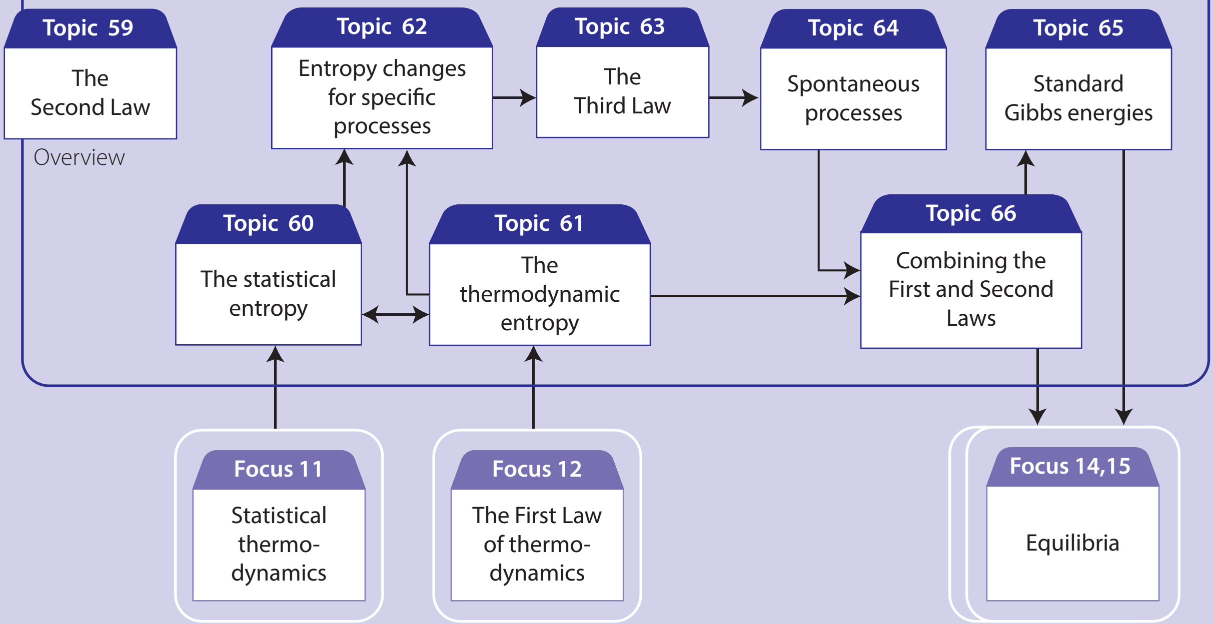
FOCUS 13 ON The Second and Third Laws of thermodynamics



The Second Law (**Topic 59**) identifies the criterion for a change being ‘spontaneous’, that is, having a tendency to occur without needing to do work to bring it about. It recognizes the tendency of matter and energy to disperse in disorder. *The First Law of thermodynamics* uses the internal energy to identify permissible changes; the Second Law uses the entropy to identify the spontaneous changes among those permissible changes and states that the entropy of an isolated system increases in the course of a spontaneous change. For our present purposes it is sufficient to think of entropy as a measure of disorder, with high entropy corresponding to great disorder.

The formal definition of entropy is set out from a statistical viewpoint in **Topic 60** and from a thermodynamic viewpoint in **Topic 61**. The statistical definition enables entropies of collections of individual molecules to be calculated from structural and spectroscopic data by using the partition function of *Statistical thermodynamics*. The thermodynamic definition is the basis of much of practical thermodynamics and enables changes in entropy to be determined from calorimetric and other observations (**Topic 62**). These measurements are brought into line with the statistical calculations by the Third Law of thermodynamics (**Topic 63**).

To assess spontaneity it is essential to take into account the change of entropy in the surroundings as well as the system of interest. However, provided we are content to work under certain constraints (such as constant pressure and temperature), the criterion of spontaneity can be expressed solely in terms of properties relating to the system by introducing the ‘Gibbs and Helmholtz energies’ (**Topic 64**) and expressing the former in terms of Gibbs energies of formation (**Topic 65**). These state functions, particularly the former, are then used in a wide variety of applications in many other Topics including *Physical equilibria* and *Chemical equilibria* and are the principal functions found in chemical thermodynamics.

The fact that the internal energy, the entropy, and the Gibbs and Helmholtz energies are state functions endows them with considerable power, especially when the First and Second Laws are combined to provide criteria for spontaneity under a variety of conditions (**Topic 66**).

What is the impact of this material?

Topics relating to the Second and Third Laws pervade the whole of chemistry and related disciplines, and here we highlight two issues, one from technology and the other from materials science. In the first (Impact 13.1), we show how the same arguments used to assess the efficiencies of heat engines can be applied to refrigerators and heat pumps. In the second (Impact 13.2), we explore how thermodynamics is used to assess the presence of defects in materials and the important consequences for their properties.

To read more about the impact of this material, scan the QR code or go to http://bcs.whfreeman.com/webpub/chemistry/qmc2e/impact/qchem_impact13.html.

TOPIC 59

The Second Law

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➤ Why do you need to know this material?

The Second Law of thermodynamics is central to an understanding of a wide variety of physical and chemical processes, including freezing, vaporization, dissolving, and chemical reaction. You need to be familiar with the law if you are to understand chemical equilibrium, bioenergetics, and the efficiency of engines.

➤ What is the key idea?

Matter and energy tend to disperse in disorder.

➤ What do you need to know already?

This Topic introduces a new group of ideas, and does not draw on other Topics except, by implication, the conservation of energy.

This is a short Topic. However, the Second Law is of immense importance in chemistry, and this Topic sets the scene for what is dealt with in the remaining Topics of this Focus group.

59.1 The recognition of spontaneous change

The Second Law is the recognition that some things happen naturally, but some things don't. A gas expands to fill the available volume, a hot body cools to the temperature of its surroundings, and a chemical reaction runs in one direction rather than another. Some aspect of the world determines the **spontaneous** direction of change, the direction of change that does not require work to be done to bring it about.

Brief illustration 59.1 Spontaneous changes

A gas can be confined to a smaller volume, an object can be cooled by using a refrigerator, and some reactions can be driven in reverse (as in the electrolysis of water). However, none of these processes is spontaneous; each one must be brought about by doing work. To compress a gas we need to do the work of driving in a piston. To cool an object in a refrigerator we need to do work on the compressor that drives the cooling system. To electrolyse water, we need to force an electric current though a sample using an external supply.

Self-test 59.1 Identify other spontaneous physical and chemical processes.

Answer: Two examples: dissipation of energy by friction; combustion

An important point is that throughout this text 'spontaneous' must be interpreted as a natural *tendency* that may or may not be realized in practice. Thermodynamics is silent on the rate at which a spontaneous change in fact occurs, and some spontaneous processes (such as the conversion of diamond to graphite) may be so slow that the tendency is never realized in practice whereas others (such as the expansion of a gas into a vacuum) are almost instantaneous.

The recognition of two classes of process, spontaneous and non-spontaneous, is summarized by the **Second Law of thermodynamics**. This law may be expressed in a variety of equivalent ways. One statement was formulated by Kelvin:

> No process is possible in which the *sole* result is the absorption of heat from a reservoir and its complete conversion into work.

Brief illustration 59.2 The Kelvin statement

It has proved impossible to construct an engine, like that shown in Fig. 59.1, in which heat is drawn from a hot reservoir and completely converted into work. All real heat engines have both a hot source and a cold sink; some energy is always discarded into the cold sink as heat and not converted into work. The Kelvin statement is a generalization of another everyday observation, that a ball at rest on a surface has never been observed to leap spontaneously upwards. An upward leap of the ball would be equivalent to the conversion of heat from the surface into work.

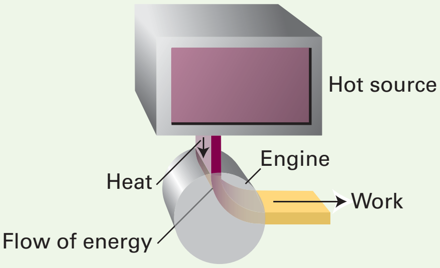

Figure 59.1 The Kelvin statement of the Second Law denies the possibility of the process illustrated here, in which heat is changed completely into work, there being no other change. The process is not in conflict with the First Law because energy is conserved.

Self-test 59.2 Why doesn't a spring wind itself spontaneously?

Answer: Atoms must move in an organized way, which would involve heat being converted into work

59.2 The direction of spontaneous change

What determines the direction of spontaneous change? It is not the total energy of the isolated system. The First Law of thermodynamics states that energy is conserved in any process, and we cannot disregard that law now and say that everything tends towards a state of lower energy: the total energy of an isolated system is constant.

Is it perhaps the energy of the system of interest, a region within the overall isolated system, that tends towards a minimum? Two arguments show that this cannot be so. First, a perfect gas expands spontaneously into a vacuum, yet its internal energy remains constant as it does so. Secondly, if the energy of a system does happen to decrease during a spontaneous change, the energy of its surroundings must increase by the same amount (by the First Law). The increase in energy of the surroundings is just as spontaneous a process as the decrease in energy of the system.

When a change occurs, the total energy of an isolated system remains constant but it is parcelled out in different ways. Can it be, therefore, that the direction of change is related to the *distribution* of energy? We shall see that this idea is the key, and that spontaneous changes are always accompanied by the random dispersal of energy.

We can begin to understand the role of the distribution of energy by thinking about a ball (the system) bouncing on a floor (the surroundings). The ball does not rise as high after each bounce because there are inelastic losses in the materials of the ball and floor. The kinetic energy of the ball's overall motion is spread out into the energy of thermal motion of its particles and those of the floor that it hits. The direction of spontaneous change is towards a state in which the ball is at rest with all its energy dispersed as the disorderly thermal motion of molecules in the air and spread over the atoms of the virtually infinite floor (Fig. 59.2).

A ball resting on a warm floor has never been observed to start bouncing. For bouncing to begin, something rather special would need to happen. In the first place, some of the thermal motion of the atoms in the floor would have to accumulate in a single small object, the ball. This accumulation requires a spontaneous localization of energy from the myriad vibrations of the atoms of the floor into the much smaller number of atoms that constitute the ball (Fig. 59.3). Furthermore, whereas the thermal motion is random, for the ball to move upwards

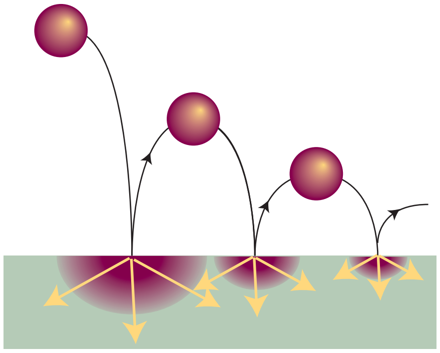

Figure 59.2 The direction of spontaneous change for a ball bouncing on a floor. On each bounce some of its energy is degraded into the thermal motion of the atoms of the floor, and that energy disperses. The reverse has never been observed to take place on a macroscopic scale.

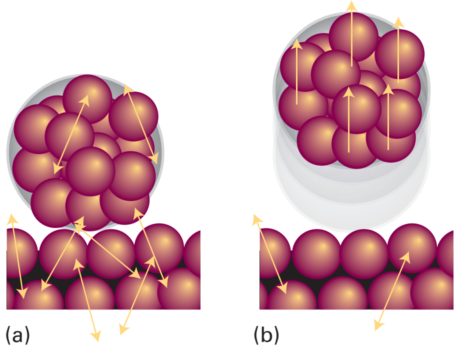

Figure 59.3 The molecular interpretation of the irreversibility expressed by the Second Law. (a) A ball resting on a warm surface; the atoms are undergoing thermal motion (vibration, in this instance), as indicated by the arrows. (b) For the ball to fly upwards, some of the random vibrational motion would have to change into coordinated, directed motion. Such a conversion is highly improbable.

its atoms must all move in the same direction. The localization of random, disorderly motion as concerted, ordered motion is so unlikely that we can dismiss it as virtually impossible except on the very small scale characteristic of 'Brownian motion', the jittering motion of small particles suspended in water.

We appear to have found the signpost of spontaneous change: *we look for the direction of change that leads to the random dispersal of the total energy of the isolated system.* This principle accounts for the direction of change of the bouncing ball, because its energy is spread out as thermal motion of the atoms of the floor. The reverse process is not spontaneous because it is highly improbable that energy will become not only localized but also localized as uniform motion of the ball's atoms.

Brief illustration 59.3 The molecular basis of spontaneous change

A gas does not contract spontaneously because to do so the random motion of its molecules, which distributes their kinetic energy throughout the container, would have to take them all into the same region of the container, thereby localizing the energy. The opposite change, spontaneous expansion, is a natural consequence of energy becoming more widely dispersed as the gas molecules occupy a larger volume. An object does not spontaneously become warmer than its surroundings because it is highly improbable that the jostling of randomly vibrating atoms in the surroundings will lead to the localization of thermal motion in the object. The opposite change, the spreading of the object's energy into the surroundings as thermal motion, is natural.

Self-test 59.3 Account for the Kelvin statement of the Second Law in molecular terms.

Answer: Work involves the uniform motion of atoms and cannot arise spontaneously from the same quantity of heat, the random motion of atoms (see Topic 55)

It may seem very puzzling that the spreading out of energy and matter, the collapse into disorder, can lead to the formation of such ordered structures as crystals or proteins. Nevertheless, in due course, we shall see that the tendency of energy and matter to disperse in disorder accounts for change in all its forms.

59.3 Entropy

The First Law of thermodynamics led to the introduction of the internal energy, U. The internal energy is a state function that lets us assess whether a change is permissible: only those changes may occur for which the internal energy of an isolated system remains constant. The law that is used to identify the signpost of spontaneous change, the Second Law of thermodynamics, may also be expressed in terms of another state function, the **entropy**, S. The entropy lets us assess whether one state is accessible from another by a spontaneous change. The First Law uses the internal energy to identify *permissible* changes; the Second Law uses the entropy to identify the *spontaneous changes* among those permissible changes. The formal definition of entropy is set out in Topics 60 and 61. For our present purposes it is sufficient to think of entropy as a measure of disorder, with high entropy corresponding to great disorder.

With the intuitive notion of entropy as a measure of disorder, we can re-express the tendency of matter and energy to disperse in disorder in its terms. Thus, in terms of entropy, the Second Law of thermodynamics states:

> The entropy of an isolated system increases in the course of a spontaneous change: $\Delta S_{\text{tot}} > 0$

where S_{tot} is the total entropy of the isolated system, which itself may consist of a smaller system (for example a beaker of hot water) and its surroundings. Thermodynamically irreversible processes (like cooling to the temperature of the surroundings and the free expansion of gases) are spontaneous processes, and hence must be accompanied by an increase in total entropy. There are many subtleties associated with this statement, and we introduce them and unfold the consequences of the Second Law in the following Topics.

Brief illustration 59.4 The increase in entropy

Consider the spontaneous processes mentioned earlier. When a perfect gas expands, the greater dispersal of its atoms corresponds to a greater entropy of the system. When an object cools, the greater dispersal of its energy corresponds to a greater entropy of the surroundings. When a fuel burns, the compact hydrocarbon liquid is dispersed as small water and carbon dioxide molecules and the energy released in the combustion spreads into the surroundings: both processes contribute to an increase in entropy.

Self-test 59.4 In what sense is there an increase in entropy when a solute forms a crystal?

Answer: The process is exothermic, and energy spreads into the surroundings

Checklist of concepts

☐ **1.** A **spontaneous change** is a change that does not require work to be done to bring it about.

☐ **2.** A spontaneous change is one that has a natural *tendency* to occur but might not be realized in practice.

☐ **3.** The **Kelvin statement of the Second Law** is that no process is possible in which the *sole* result is the absorption of heat from a reservoir and its complete conversion into work.

☐ **4.** The direction of spontaneous change is the one that leads to the random dispersal of the total energy of the isolated system.

☐ **5.** **Entropy** is a measure of the disorder of energy and matter.

☐ **6.** The entropy of an isolated system increases in the course of a spontaneous change: $\Delta S_{\text{tot}} > 0$.

TOPIC 60

The statistical entropy

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➤ Why do you need to know this material?

Entropy lies at the heart of the chemical applications of thermodynamics, but in some cases the only way to evaluate it is to use statistical thermodynamics and calculate it from spectroscopic and structural data. Moreover, the statistical approach described here gives you insight into the molecular features that are responsible for the entropy of a substance.

➤ What is the key idea?

The entropy of a substance can be calculated from the molecular partition function and is greatest when many molecular states are occupied.

➤ What do you need to know already?

You need to be familiar with the molecular partition function and its calculation from structural data, and its relation on the one hand to the weight of a configuration (Topic 51 and, for the canonical ensemble, Topic 54) and on the other to the calculation of molecular energies (Topic 53). There is an interplay between this Topic and that on the thermodynamic definition of entropy (Topic 61), and it will help if you have at least a passing familiarity with that approach.

If it is true, as claimed in Topic 52, that a partition function contains all the thermodynamic information about a system, then it must be possible to use it to calculate the entropy as well as the internal energy. Because, as argued in Topic 59, entropy is related to the dispersal of energy and, as described in Topic 52, a partition function is a measure of the number of thermally accessible states, we can be confident that the two are indeed related.

60.1 The statistical definition of entropy

All the calculations of entropy from structural and spectroscopic data spring from a single equation proposed originally by Ludwig Boltzmann. Here we present that equation and then evaluate various contributions to the entropy of isolated molecules.

(a) The Boltzmann formula

Boltzmann looked for a definition of entropy that was a measure of the dispersal of energy and was a state function, was extensive, and increased in the course of a spontaneous change. He suggested that an appropriate definition is what we now call the **Boltzmann formula** for the entropy:

$$S=k\ln\mathcal{W} \qquad \textit{Definition} \qquad \text{Boltzmann formula for the entropy} \tag{60.1}$$

where k is Boltzmann's constant and $\mathcal{W}$ is the weight of the most probable configuration of the system (Topic 51).

Brief illustration 60.1 The Boltzmann formula

Suppose that each diatomic molecule in a solid sample can be arranged in either of two orientations and that there are $N=6.022\times10^{23}$ molecules in the sample (that is, 1 mol of molecules). Then $\mathcal{W}=2^N$ and the entropy of the sample is

$$\begin{aligned}S&=k\ln 2^N=Nk\ln 2=(6.022\times10^{23})\times(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\ln 2\\&=5.76\,\mathrm{J\,K^{-1}}\end{aligned}$$

We see that the units of entropy are joules per kelvin ($\mathrm{J\,K^{-1}}$), the same as those of Boltzmann's constant. The molar entropy, $S_\mathrm{m}=S/n$, therefore has the units joules per kelvin per mole ($\mathrm{J\,K^{-1}\,mol^{-1}}$), the same as the gas constant. The standard molar entropy, $S_\mathrm{m}^\ominus$, is the molar entropy under standard conditions (pure, 1 bar).

Self-test 60.1 What is the molar entropy of a similar system in which each molecule can be arranged in four different orientations?

Answer: $11.5\,\mathrm{J\,K^{-1}\,mol^{-1}}$

(b) The connection with the thermodynamic entropy

The entropy defined in eqn 60.1 has properties that confirm that it can be identified with the thermodynamic entropy defined in Topic 61. It is clearly a state function, as the weight of the most probable configuration is independent of how the system was prepared. That S is extensive can be seen by considering a system as being composed of two parts with entropies $S_1=k\ln\mathcal{W}_1$ and $S_2=k\ln\mathcal{W}_2$, respectively. The total weight of the entire system (the total number of ways of achieving a configuration) is the product of the weights of the two component parts, $\mathcal{W}=\mathcal{W}_1\mathcal{W}_2$, and so the total entropy of the system is

$$S=k\ln\mathcal{W}_1\mathcal{W}_2=k\ln\mathcal{W}_1+k\ln\mathcal{W}_2=S_1+S_2$$

Because the total entropy is the sum of the entropies of its component parts, the entropy is extensive.

That S is the signpost of spontaneous change is plausible because an isolated system in an arbitrary initial configuration tends to collapse into the distribution with the greatest weight, so the entropy as defined in eqn 60.1 increases in a spontaneous change. Informally, we can imagine the system as exploring all the distributions available to it, with certain distributions achieved far more often than others. To an external observer, the system migrates into a configuration corresponding to the overwhelmingly dominant distribution.

To express this conclusion more formally, we first suppose that the two parts of an entire system are not in equilibrium with each other. Each part of the system is in internal equilibrium, and so $\mathcal{W}_1$ and $\mathcal{W}_2$ have their respective maximum values, the combined weight is $\mathcal{W}_\mathrm{i}=\mathcal{W}_1\mathcal{W}_2$, and the initial entropy is

$$S_\mathrm{i}=k\ln\mathcal{W}_\mathrm{i}=k\ln\mathcal{W}_1\mathcal{W}_2=k\ln\mathcal{W}_1+k\ln\mathcal{W}_2=S_1+S_2$$

When the two parts are allowed to interact, the weight becomes $\mathcal{W}_\mathrm{f}$, which—if any change occurs at all—will become larger than $\mathcal{W}_\mathrm{i}$ as the total system explores all the available configurations and settles into a configuration of greatest weight. The entropy becomes

$$S_\mathrm{f}=k\ln\mathcal{W}_\mathrm{f}>k\ln\mathcal{W}_\mathrm{i}=S_\mathrm{i}$$

That is, because $\ln\mathcal{W}_\mathrm{f}$ is greater than $\ln\mathcal{W}_\mathrm{i}$, the entropy of the final state is greater than that of the initial state, as we sought to demonstrate.

More specifically, we now show that the definition in eqn 60.1 implies the thermodynamic definition of entropy in Topic 61 (that $\mathrm{d}S=\mathrm{d}q_\mathrm{rev}/T$). From eqn 60.1 a change in entropy arises from a change in populations of the available states:

$$\mathrm{d}S=k\,\mathrm{d}\ln\mathcal{W}=k\sum_i\left(\frac{\partial\ln\mathcal{W}}{\partial N_i}\right)\mathrm{d}N_i$$

We established in eqn 51.10 that for the most probable distribution

$$\left(\frac{\partial\ln\mathcal{W}}{\partial N_i}\right)=\beta\varepsilon_i-\alpha$$

and therefore it follows that

$$\mathrm{d}S=k\beta\sum_i\varepsilon_i\mathrm{d}N_i-k\alpha\sum_i\mathrm{d}N_i$$

The second sum, over changes in populations, is zero for a system with a fixed number of particles, and so

$$\mathrm{d}S = k\beta\sum_i \varepsilon_i \mathrm{d}N_i = \frac{1}{T}\sum_i \varepsilon_i \mathrm{d}N_i$$

However, for a system that is heated, there is no change in the energy levels themselves and the change in energy of the system is due only to the change in populations of those unchanging energy levels. Moreover, if the heating is reversible, the populations retain their most probable values at all stages. It follows that the sum on the right in this expression can be identified with the energy transferred reversibly as heat. That is,

$$\mathrm{d}S = \frac{1}{T}\overbrace{\sum_i \varepsilon_i \mathrm{d}N_i}^{\mathrm{d}q_{\mathrm{rev}}} = \frac{\mathrm{d}q_{\mathrm{rev}}}{T} \qquad (60.2)$$

in accord with the classical definition, developed in Topic 61.

Brief illustration 60.2 The change in entropy

Equation 60.2 is developed fully in Topics 61 and 62, but there are two points worth illustrating here. First, suppose that 10 J is transferred reversibly as heat to a sample of water at 298 K, then (making the approximation that infinitesimal quantities (dX) can be replaced by small finite quantities (δX) in this case), the change in entropy of the water is

$$\delta S = \frac{10\,\mathrm{J}}{298\,\mathrm{K}} = +0.034\,\mathrm{J\,K^{-1}}$$

We see that the units are the same as in the Boltzmann definition, joules per kelvin. The second point is that calculations of entropy changes by using eqn 60.2 are typically very much easier than by using the Boltzmann formula, which relies on detailed structural information (as we see below).

Self-test 60.2 Calculate the change in entropy when 10 J of energy is removed as heat from water at −5.0 °C.

Answer: $-0.037\,\mathrm{J\,K^{-1}}$

60.2 The entropy in terms of the partition function

Here we establish the basic expression relating the entropy to the partition function, and then evaluate the contributions of each mode of motion.

(a) The basic equations

For eqn 60.1 to be a useful route to the calculation of the entropy, we need to express it in terms of the partition function. To do so, we substitute the expression for ln W given in Topic 51 into eqn 60.1 and, as shown in the following *Justification*, for independent, distinguishable particles obtain

$$S = \frac{U - U(0)}{T} + Nk\ln q \qquad \textit{Independent, distinguishable particles} \quad \text{Entropy} \qquad (60.3a)$$

and for independent, indistinguishable particles

$$S = \frac{U - U(0)}{T} + Nk\ln\frac{q\mathrm{e}}{N} \qquad \textit{Independent, indistinguishable particles} \quad \text{Entropy} \qquad (60.3b)$$

(The presence of the exponential e in the logarithm is explained in the *Justification*.) Apart from changes of detail, we see that the entropy increases as the number of thermally accessible states (as measured by q) increases, just as we should expect. The following sections give many examples of the application of these equations.

Brief illustration 60.3 Distinguishable and indistinguishable particles

The molecules of a perfect gas are indistinguishable and cannot be tracked, so we use eqn 60.3b to calculate the entropy. Once that gas has condensed and frozen to a solid, the molecules, although still identical and assumed to be independent of each other, can be labelled with their coordinates in the solid, and so can be tracked unambiguously. As a result, we now use eqn 60.3a to calculate the entropy.

Self-test 60.3 Do you need to consider indistinguishability when calculating the additional vibrational contribution to the entropy of a gaseous sample?

Answer: No; use once, only for the translational contribution

Justification 60.1 The statistical entropy

For a system composed of N distinguishable molecules, eqn 51.3 for ln W is

$$\ln W = N\ln N - \sum_i N_i \ln N_i = \sum_i N_i \ln N - \sum_i N_i \ln N_i$$
$$= \sum_i N_i(\ln N - \ln N_i) = -\sum_i N_i \ln\frac{N_i}{N}$$

because $N = \Sigma_i N_i$. Equation 60.1 ($S = k\ln W$) becomes

$$S = -k\sum_i N_i \ln\frac{N_i}{N}$$

The value of N_i/N for the most probable distribution is given by the Boltzmann distribution:

$$\frac{N_i}{N}=\frac{\mathrm{e}^{-\beta\varepsilon_i}}{q}$$

and so

$$\ln\frac{N_i}{N}=\ln \mathrm{e}^{-\beta\varepsilon_i}-\ln q=-\beta\varepsilon_i-\ln q$$

Therefore,

$$\begin{aligned}S&=k\beta\sum_i N_i\varepsilon_i+k\sum_i N_i\ln q\\&=Nk\beta\langle\varepsilon\rangle+Nk\ln q\end{aligned}$$

Finally, because $N\langle\varepsilon\rangle=U-U(0)$ and $\beta=1/kT$, we obtain eqn 60.3a.

To treat a system composed of N *in*distinguishable molecules, we need to reduce the weight $\mathcal{W}$ by a factor of $1/N!$, because the $N!$ permutations of the molecules among the states result in the same state of the system. Then, because $\ln(\mathcal{W}/N!)=\ln\mathcal{W}-\ln N!$, the equation in the first line of this *Justification* becomes

$$\begin{aligned}\ln\mathcal{W}&=N\ln N-\sum_i N_i\ln N_i-\overbrace{\ln N!}^{N\ln N-N}\\&=\sum_i N_i\ln N-\sum_i N_i\ln N_i-\overbrace{N}^{\sum_i N_i}\ln N+N\\&=-\sum_i N_i\ln N_i+N\end{aligned}$$

where we have used Stirling's approximation to write $\ln N!=N\ln N-N$. As before, we replace N_i by the Boltzmann value, $N_i=N\mathrm{e}^{-\beta\varepsilon_i}/q$:

$$\begin{aligned}\sum_i N_i\ln N_i&=\sum_i N_i(\ln N-\beta\varepsilon_i-\ln q)\\&=N\ln N-N\beta\langle\varepsilon\rangle-N\ln q\\&=-N\beta\langle\varepsilon\rangle-N\ln\frac{q}{N}\end{aligned}$$

The entropy in this case is therefore

$$S=Nk\beta\langle\varepsilon\rangle+Nk\ln\frac{q}{N}+Nk$$

Now note that Nk can be written $Nk\ln\mathrm{e}$ and $Nk\ln q/N+Nk\ln\mathrm{e}=Nk\ln q\mathrm{e}/N$, which gives eqn 60.3b.

Equation 60.3 expresses the entropy of a collection of independent molecules in terms of the internal energy and the molecular partition function. However, it is shown in Topic 52 that, to a good approximation, the energy of a molecule is a sum of independent contributions, such as translational (T), rotational (R), vibrational (V), and electronic (E), and therefore the partition function factorizes into a product of contributions (see eqn 52.6, $q=q^{\mathrm{T}}q^{\mathrm{R}}q^{\mathrm{V}}q^{\mathrm{E}}$). As a result, the entropy is the sum of the individual contributions. For independent, distinguishable particles, each contribution is of the form of eqn 60.3, and for a mode M we write

$$S^{\mathrm{M}}=\frac{\{U-U(0)\}^{\mathrm{M}}}{T}+Nk\ln q^{\mathrm{M}}\qquad(60.3\mathrm{c})$$

Independent, distinguishable particles, M ≠ T

Entropy due to mode M

This expression applies to M = R, V, and E (as in Self-test 60.3); the analogous version of eqn 60.3b should be used for M = T, for the molecules are then indistinguishable.

Equation 60.3 is in terms of the *molecular* partition function and is too restrictive to accommodate interactions between molecules. As in Topic 54, to accommodate interacting particles we have to use the canonical partition function Q and the weight $\mathcal{W}$ of the most probable configuration of the canonical ensemble, $\tilde{\mathcal{W}}$. However, because $\tilde{\mathcal{W}}=\mathcal{W}^{\tilde{N}}$ (each member of the ensemble is independent of the others, so we can multiply together their weights to get the overall weight of the ensemble) we can use $\mathcal{W}=\tilde{\mathcal{W}}^{1/\tilde{N}}$ in the Boltzmann formula and obtain

$$S=k\ln\tilde{\mathcal{W}}^{1/\tilde{N}}=\frac{k}{\tilde{N}}\ln\tilde{\mathcal{W}}\qquad(60.4)$$

The number of members of the ensemble, $\tilde{N}$, goes to infinity (to achieve the thermodynamic limit). The entropy can expressed in terms of Q by the same argument as in *Justification* 60.1, and we obtain

$$S=\frac{U-U(0)}{T}+k\ln Q\qquad(60.5)$$

General interacting system

Entropy

This expression reduces to eqn 60.3 when we write $Q=q^N$ for distinguishable, non-interacting particles and $Q=q^N/N!$ for indistinguishable, non-interacting particles.

(b) The translational contribution

The expressions we have derived for the entropy accord with what we should expect for entropy if it is a measure of the spread of the populations of molecules over the available states. For instance, we show in the following *Justification* that the **Sackur–Tetrode equation** for the molar entropy of a monatomic perfect gas, where the only motion is translation in three dimensions, is

$$S_{\mathrm{m}}=R\ln\left(\frac{V_{\mathrm{m}}\mathrm{e}^{5/2}}{N_{\mathrm{A}}\Lambda^3}\right)\qquad(60.6\mathrm{a})$$

Monatomic perfect gas

Sackur–Tetrode equation

where Λ is the thermal wavelength introduced in Topic 52 (eqn 52.7b, $\Lambda=h/(2\pi mkT)^{1/2}$). To calculate the standard molar entropy, we note that $V_m=RT/p$, and set $p=p^{\ominus}$:

$$S_m^{\ominus}=R\ln\left(\frac{RT\mathrm{e}^{5/2}}{p^{\ominus}N_A\Lambda^3}\right)=R\ln\left(\frac{kT\mathrm{e}^{5/2}}{p^{\ominus}\Lambda^3}\right) \qquad (60.6b)$$

We have used $R/N_A=k$. These expressions are based on the high-temperature approximation of the partition functions, which assumes that many levels are occupied; therefore, they do not apply when T is equal to or very close to zero.

Brief illustration 60.4 Molar entropy of a gas

To calculate the standard molar entropy of gaseous argon at 25 °C, we use eqn 60.6b with $\Lambda=h/(2\pi mkT)^{1/2}$. The mass of an Ar atom is $m=39.95m_u$. At 25 °C, its thermal wavelength is 16.0 pm (by the same kind of calculation as in *Brief illustration* 52.2) and $kT=4.12\times10^{-21}$ J. Therefore,

$$\begin{aligned}S_m^{\ominus}&=R\ln\left\{\frac{(4.12\times10^{-21}\,\mathrm{J})\times\mathrm{e}^{5/2}}{(10^5\,\mathrm{N\,m^{-2}})\times(1.60\times10^{-11}\,\mathrm{m})^3}\right\}\\&=18.6R=155\,\mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

We can anticipate, on the basis of the number of accessible states for a lighter molecule, that the standard molar entropy of Ne is likely to be smaller than for Ar; its actual value is $17.60R$ at 298 K.

Self-test 60.4 Calculate the translational contribution to the standard molar entropy of H_2 at 25 °C.

Answer: $14.2R$

The implications of eqn 60.6 are as follows:

- Because the molecular mass appears in the numerator (because it appears in the denominator of Λ), the molar entropy of a perfect gas of heavy molecules is greater than that of a perfect gas of light molecules under the same conditions.
- Because the molar volume appears in the numerator, the molar entropy increases with the molar volume of the gas.
- Because the temperature appears in the numerator (because, like m, it appears in the denominator of Λ), the molar entropy increases with increasing temperature.

Physical interpretation

We can understand the first feature in terms of the energy levels of a particle in a box being closer together for heavy particles than for light particles, so more states are thermally accessible. The reason for the second feature is similar: large containers have more closely spaced energy levels than small containers, so once again more states are thermally accessible. The reason for the third feature is that more energy levels become accessible as the temperature is raised.

Justification 60.2 The Sackur–Tetrode equation

We start with eqn 60.3b for a collection of independent, indistinguishable particles and write $N=nN_A$, where N_A is Avogadro's constant. The only mode of motion for a gas of atoms is translation, and, as shown in *Brief illustration* 55.2, $U-U(0)=\frac{3}{2}nRT$. The partition function is $q=V/\Lambda^3$ (eqn 52.10b), where Λ is the thermal wavelength. Therefore,

$$\begin{aligned}S&=\frac{\overbrace{U-U(0)}^{\frac{3}{2}nRT}}{T}+Nk\ln\frac{q\mathrm{e}}{N}=\tfrac{3}{2}nR+\overbrace{Nk}^{nR}\ln\frac{V\mathrm{e}}{nN_A\Lambda^3}\\&=nR\left\{\overset{\ln \mathrm{e}^{3/2}}{\overbrace{\tfrac{3}{2}}}+\ln\frac{V_m\mathrm{e}}{N_A\Lambda^3}\right\}=nR\ln\frac{V_m\mathrm{e}^{5/2}}{N_A\Lambda^3}\end{aligned}$$

where $V_m=V/n$ is the molar volume of the gas and we have used $\frac{3}{2}=\ln\mathrm{e}^{3/2}$. Division of both sides by n then results in eqn 60.6a.

The Sackur–Tetrode equation written in the form

$$S=nR\ln\frac{V\mathrm{e}^{5/2}}{nN_A\Lambda^3}=nR\ln aV,\quad a=\frac{\mathrm{e}^{5/2}}{nN_A\Lambda^3}$$

implies that when a monatomic perfect gas expands isothermally from V_i to V_f, its entropy changes by

$$\begin{aligned}\Delta S&=nR\ln aV_f-nR\ln aV_i\\&=nR\ln\frac{V_f}{V_i}\end{aligned} \qquad (60.7)$$

Perfect gas, isothermal Change of entropy on expansion

This expression, which is plotted in Fig. 60.1, shows that the entropy of a perfect gas increases logarithmically with volume (because more energy levels become accessible as they become less widely spaced), and that the increase is independent of the identity of the gas (because the factor a has cancelled). As shown in Topic 62, the same expression is obtained starting from the thermodynamic definition of entropy and is illustrated there.

(c) The rotational contribution

The rotational contribution to the molar entropy, S_m^R, can be calculated once we know the molecular partition function. For a linear molecule, the high-temperature limit of q is $kT/\sigma hc\tilde{B}$ (eqn 52.13) and the equipartition theorem gives the rotational

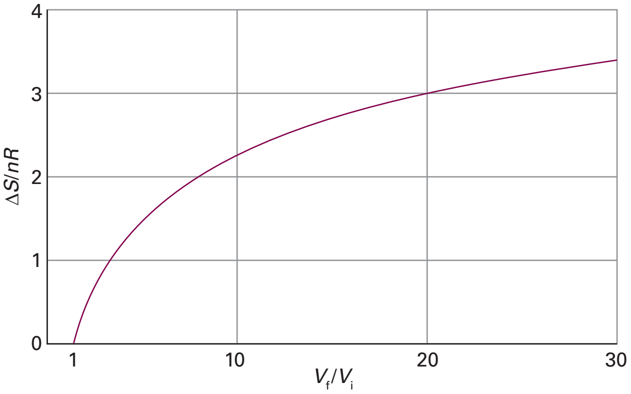

Figure 60.1 The logarithmic increase in entropy of a perfect gas as it expands isothermally.

contribution to the molar internal energy as RT; therefore, from eqn 60.3c,

$$S_m^R = \frac{\overbrace{U_m - U_m(0)}^{RT}}{T} + R\ln \overbrace{q^R}^{kT/\sigma hc\tilde{B}}$$

and the contribution at high temperatures is

$$S_m^R = R\left\{1 + \ln\frac{kT}{\sigma hc\tilde{B}}\right\} \qquad (60.8a)$$

Linear molecule, high temperature ($T \gg \theta^R$) Rotational contribution

Recall (Topic 52) that $\theta^R = hc\tilde{B}/k$. In terms of this rotational temperature,

$$S_m^R = R\left\{1 + \ln\frac{T}{\sigma\theta^R}\right\} \qquad (60.8b)$$

Linear molecule, high temperature ($T \gg \theta^R$) Rotational contribution

This function is plotted in Fig. 60.2. We see that:

- The rotational contribution to the entropy increases with temperature because more rotational states become accessible.
- The rotational contribution is large when $\tilde{B}$ is small, because then the rotational energy levels are close together.

Physical interpretation

Thus, large, heavy molecules have a large rotational contribution to their entropy. As we show in the following *Brief illustration*, the rotational contribution to the molar entropy of $^{35}Cl_2$ is 58.6 J K^{-1} mol^{-1}, whereas that for H_2 is only 12.7 J K^{-1} mol^{-1}. We can regard Cl_2 as a more rotationally disordered gas than H_2, in the sense that at a given temperature Cl_2 occupies a greater number of rotational states than H_2 does.

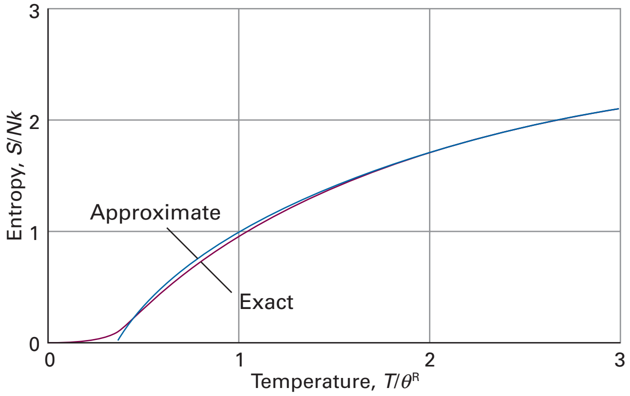

Figure 60.2 The variation of the rotational contribution to the entropy of a linear molecule ($\sigma = 1$) using the high-temperature approximation and the exact expression (the latter evaluated up to $J = 20$).

Brief illustration 60.5 The rotational contribution to the entropy

The rotational contribution for $^{35}Cl_2$ at 25 °C, for instance, is calculated by noting that $\sigma = 2$ for this homonuclear diatomic molecule and taking $\tilde{B} = 0.2441$ cm^{-1} (corresponding to 24.42 m^{-1}). The rotational temperature of the molecule is

$$\theta^R = \frac{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{8}\,\mathrm{m\,s^{-1}})\times(24.42\,\mathrm{m^{-1}})}{1.381\times10^{-23}\,\mathrm{J\,K^{-1}}}$$
$$= 0.351\,\mathrm{K}$$

Therefore,

$$S_m^R = R\left\{1 + \ln\frac{298\,\mathrm{K}}{2\times(0.351\,\mathrm{K})}\right\} = 7.05R = 58.6\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

Self-test 60.5 Calculate the rotational contribution to the molar entropy of H_2 at 25 °C.

Answer: 12.7 J K^{-1} mol^{-1}

Equation 60.8 is valid at high temperatures ($T \gg \theta^R$); to track the rotational contribution down to low temperatures it would be necessary to use the full form of the rotational partition function (Topic 52; see Problem 60.1); the resulting curve has the form shown in Fig. 60.2. We see, in fact, that the approximate curve matches the exact curve very well for T/θ^R greater than about 1.

(d) The vibrational contribution

The vibrational contribution to the molar entropy, S_m^V, is obtained by combining the expression for the molecular partition function (eqn 52.15, $q^{\mathrm{V}}=1/(1-\mathrm{e}^{-\beta\varepsilon})$) with the expression for the mean energy (eqn 53.8, $\langle\varepsilon^{\mathrm{V}}\rangle=\varepsilon/(\mathrm{e}^{\beta\varepsilon}-1)$), to obtain

$$\begin{aligned} S_{\mathrm{m}}^{\mathrm{V}} &= \frac{\overbrace{U_{\mathrm{m}}-U_{\mathrm{m}}(0)}^{N_{\mathrm{A}}\langle\varepsilon^{\mathrm{V}}\rangle}}{\underbrace{T}_{1/k\beta}}+R\ln q^{\mathrm{V}} \\ &= \frac{\overbrace{N_{\mathrm{A}}k}^{R}\,\beta\varepsilon}{\mathrm{e}^{\beta\varepsilon}-1}+R\ln\frac{1}{1-\mathrm{e}^{-\beta\varepsilon}} \\ &= R\left\{\frac{\beta\varepsilon}{\mathrm{e}^{\beta\varepsilon}-1}-\ln(1-\mathrm{e}^{-\beta\varepsilon})\right\} \end{aligned}$$

Now we recognize that $\varepsilon=hc\tilde{\nu}$ and obtain

$$S_{\mathrm{m}}^{\mathrm{V}}=R\left\{\frac{\beta hc\tilde{\nu}}{\mathrm{e}^{\beta hc\tilde{\nu}}-1}-\ln(1-\mathrm{e}^{-\beta hc\tilde{\nu}})\right\} \tag{60.9a}$$

Vibrational contribution to the entropy

Once again it is convenient to express this formula in terms of a characteristic temperature, in this case the vibrational temperature $\theta^{\mathrm{V}}=hc\tilde{\nu}/k$:

$$S_{\mathrm{m}}^{\mathrm{V}}=R\left\{\frac{\theta^{\mathrm{V}}/T}{\mathrm{e}^{\theta^{\mathrm{V}}/T}-1}-\ln(1-\mathrm{e}^{-\theta^{\mathrm{V}}/T})\right\} \tag{60.9b}$$

Vibrational contribution to the entropy

This function is plotted in Fig. 60.3. As usual, it is helpful to interpret it, with the graph in mind:

- Both terms multiplying R become zero as $T\rightarrow 0$, so the entropy is zero at $T=0$.
- The molar entropy rises as the temperature is increased as more vibrational states become accessible.
- The molar entropy is higher at a given temperature for molecules with heavy atoms or low force constant than one with light atoms or high force constant. The vibrational energy levels are closer together in the former case than in the latter, so more are thermally accessible.

Physical interpretation

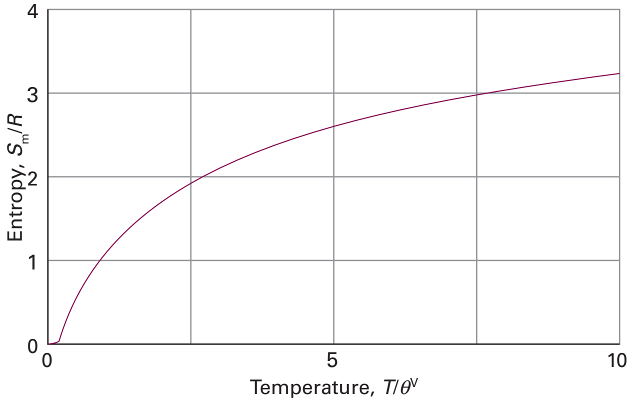

Figure 60.3 The temperature variation of the molar entropy of a collection of harmonic oscillators (expressed here as a multiple of R). The entropy approaches zero as $T\rightarrow 0$, and increases without limit as $T\rightarrow\infty$.

Brief illustration 60.6 The vibrational contribution to the entropy

The vibrational wavenumber of I_2 is $214.5\,\mathrm{cm}^{-1}$, corresponding to $2.145\times10^{4}\,\mathrm{m}^{-1}$, so its vibrational temperature is

$$\begin{aligned}\theta^{\mathrm{V}} &= \frac{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{8}\,\mathrm{m\,s^{-1}})\times(2.145\times10^{4}\,\mathrm{m^{-1}})}{1.381\times10^{-23}\,\mathrm{J\,K^{-1}}} \\ &= 309\,\mathrm{K}\end{aligned}$$

Therefore, at 25 °C, for instance, $\beta\varepsilon=1.036$ (Example 53.4), so $S_{\mathrm{m}}^{\mathrm{V}}=8.38\ \mathrm{J\ K^{-1}\ mol^{-1}}$.

$$S_{\mathrm{m}}^{\mathrm{V}}=R\left\{\frac{309/298}{\mathrm{e}^{309/298}-1}-\ln(1-\mathrm{e}^{-309/298})\right\}=1.01R=8.38\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

Self-test 60.6 Calculate the vibrational contribution to the molar entropy of $^{1}\mathrm{H}_2$ at 25 °C ($\theta^{\mathrm{V}}=6332\,\mathrm{K}$).

Answer: $0.11\,\mu\mathrm{J\,K^{-1}}$

(e) The electronic contribution

As in the calculation of the electronic contribution to the internal energy, in most cases molecules are in their electronic ground state at normal temperatures and excited states are thermally inaccessible. However, in some cases a limited number of excited states are accessible, and we need to take their contribution into account, just as we did for the internal energy.

If the ground electronic state is g^{E}-fold degenerate and there are no other thermally accessible states, then we know at once that $q^{\mathrm{E}}=g^{\mathrm{E}}$, and so the contribution to the molar entropy is

$$S_{\mathrm{m}}^{\mathrm{E}}=\frac{\overbrace{U_{\mathrm{m}}-U_{\mathrm{m}}(0)}^{0}}{T}+R\ln\overbrace{q^{\mathrm{E}}}^{g^{\mathrm{E}}}$$

That is,

$$S_{\mathrm{m}}^{\mathrm{E}}=R\ln g^{\mathrm{E}} \tag{60.10}$$

Degenerate ground state

Electronic contribution to the entropy

If some excited states are thermally accessible, then we proceed as in the case of the calculation of molecular energy, and write the partition function for the species specifically, taking into account the degeneracies of the levels.

Example 60.1 Calculating the electronic contribution to the entropy

This example is a continuation of Example 53.1, where we consider an atom that has a doubly degenerate electronic ground state and a fourfold degenerate excited state at 600 cm^{-1} above the ground state. What is the electronic contribution to the molar entropy at 25 °C?

Method The partition function and mean energy are calculated in Example 53.1, so all we need do is import them into the expression for the molar entropy, eqn 60.3c. As in that example, use $kT/hc = 207.226\,\text{cm}^{-1}$ at 25 °C.

Answer The partition function is

$$\begin{aligned} q^{\text{E}} &= 2+4\text{e}^{-\beta\varepsilon} = 2+4\text{e}^{-hc\tilde{\nu}/kT} \\ &= 2+4\text{e}^{-600/207.226} = 2.221 \end{aligned}$$

and the mean molar energy is

$$N_{\text{A}}hc\langle\tilde{\nu}^{\text{E}}\rangle = \frac{N_{\text{A}}hc\tilde{\nu}}{\frac{1}{2}\text{e}^{hc\tilde{\nu}/kT}+1} = N_{\text{A}}hc\times(59.7\,\text{cm}^{-1})$$

The contribution to the entropy is therefore

$$\begin{aligned} S_{\text{m}}^{\text{E}} &= \frac{\overbrace{U_{\text{m}}-U_{\text{m}}(0)}^{N_{\text{A}}hc\times(59.7\,\text{cm}^{-1})}}{T} + R\ln q^{\text{E}} \\ &= \frac{\overbrace{N_{\text{A}}k}^{R}hc(59.7\,\text{cm}^{-1})}{kT} + R\ln q^{\text{E}} \\ &= R\left\{\frac{59.7\,\text{cm}^{-1}}{207.226\,\text{cm}^{-1}} + \ln 2.221\right\} = 1.09R = 9.03\,\text{J K}^{-1}\,\text{mol}^{-1} \end{aligned}$$

Self-test 60.7 Repeat the problem for an atom that has a threefold degenerate ground state and a sevenfold degenerate excited state 400 cm^{-1} above.

Answer: 1.88R, 15.6 J K^{-1} mol^{-1}

As in the calculation of the electronic contribution to molecular energies, the explicit expression for a two-level system is instructive, for instance, if considering the spin state of a doublet species. The partition function and mean energy (with the superscript S denoting spin) are

$$q^{\text{S}} = 1+\text{e}^{-\beta\varepsilon} \qquad \langle\varepsilon^{\text{S}}\rangle = \frac{\varepsilon}{\text{e}^{\beta\varepsilon}+1}$$

The contribution to the molar entropy is therefore, with $1/T = k\beta$, simply

$$S_{\text{m}}^{\text{S}} = R\left\{\frac{\beta\varepsilon}{\text{e}^{\beta\varepsilon}+1} + \ln(1+\text{e}^{-\beta\varepsilon})\right\} \qquad \text{Two-level system} \qquad (60.11)$$

This awkward function is plotted in Fig. 60.4. It should be noted that as $T\to\infty$ (corresponding to $\beta\to 0$), the molar entropy approaches R ln 2. For an application of this expression, see Problem 60.6.

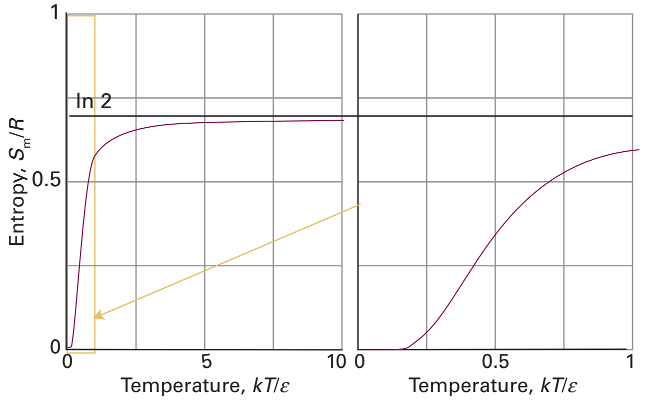

Figure 60.4 The temperature variation of the molar entropy of a two-level system (expressed as a multiple of R). As $T\to\infty$, the two states become equally populated and the molar entropy approaches R ln 2.

Checklist of concepts

- ☐ 1. The **statistical definition of the entropy** is given by the Boltzmann formula.
- ☐ 2. The statistical entropy has properties that coincide with those of the thermodynamic entropy.
- ☐ 3. The statistical entropy is a measure of the number of states that are occupied at a given temperature.
- ☐ 4. The **Boltzmann formula** for the entropy can be converted into an expression for the entropy in terms of the molecular partition function.
- ☐ 5. **Standard molar entropies** can be calculated by substituting calculated or spectroscopically determined structural parameters into the partition function.
- ☐ 6. The statistical entropy is the sum of contributions from individual modes of motion (provided they are independent).
- ☐ 7. The **Sackur–Tetrode equation** gives the standard molar entropy of a perfect gas.

Checklist of equations

Property	Equation	Comment	Equation number
Boltzmann formula	$S=k\ln \mathcal{W}$	Definition	60.1
Entropy	$S=\{U(T)-U(0)\}/T+Nk\ln q$	Independent, distinguishable particles	60.3a
	$S=\{U(T)-U(0)\}/T+Nk\ln (q\mathrm{e}/N)$	Independent, indistinguishable particles	60.3b
	$S=\{U(T)-U(0)\}/T+k\ln Q$	General case	60.5
Sackur–Tetrode equation	$S=nR\ln aV,\ a=\mathrm{e}^{5/2}/nN_\mathrm{A}\Lambda^3$	Monatomic perfect gas	60.6
Rotational contribution	$S_\mathrm{m}^\mathrm{R}=R\{1+\ln(T/\sigma\theta^\mathrm{R})\}$	Linear molecule, $T \gg \theta^\mathrm{R}$	60.8
Vibrational contribution	$S_\mathrm{m}^\mathrm{V}=\left\{R(\theta^\mathrm{V}/T)/(\mathrm{e}^{\theta^\mathrm{V}/T}-1)-\ln(1-\mathrm{e}^{-\theta^\mathrm{V}/T})\right\}$	Harmonic approximation	60.9
Electronic contribution	$S_\mathrm{m}^\mathrm{E}=R\ln g^\mathrm{E}$	Degenerate ground state (the only thermally accessible states)	60.10
Two-level system	$S_\mathrm{m}=R\{\beta\varepsilon/(\mathrm{e}^{\beta\varepsilon}+1)+\ln(1+\mathrm{e}^{-\beta\varepsilon})\}$		60.11

TOPIC 61

The thermodynamic entropy

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➤ Why do you need to know this material?

Because calculations of the entropy from its statistical definition are difficult, you also need to know how to apply calorimetric data to the study of entropy changes associated with chemical reactions.

➤ What is the key idea?

The thermodynamic entropy, a state function, is defined in terms of the heat supplied reversibly to a system.

➤ What do you need to know already?

This Topic makes use of the concepts of heat, reversibility, and state function (Topic 55). It refers to the work done during reversible isothermal and adiabatic expansion of a perfect gas (Topics 55 and 58).

The thermodynamic definition of entropy can be motivated in a variety of ways. One is developed in Topic 60, where it is shown that the Boltzmann formula for the entropy ($S = k \ln \mathcal{W}$) implies that

$$dS = \frac{dq_{rev}}{T} \qquad \textit{Definition} \quad \text{Entropy change} \qquad (61.1)$$

Whereas in Topic 60 this equation is derived from statistical considerations, in this Topic we take it as a definition.

The definition in eqn 61.1 has a straightforward physical interpretation. The change in entropy is proportional to the energy transferred as heat, for that stimulates greater thermal disorder in the system. However, the change in entropy brought about by a given transfer of energy as heat is greater at low temperatures than at high. The temperature at which the transfer occurs is a measure of the thermal disorder already present, and a given transfer of energy has a greater impact at low temperature (when the disorder initially present is small) than at high (when the disorder initially present is great).

For a measurable change between two states i and f, eqn 61.1 integrates to

$$\Delta S = \int_i^f \frac{dq_{rev}}{T} \qquad \text{Measurable entropy change} \qquad (61.2)$$

That is, to calculate the difference in entropy between any two states of a system from thermodynamic data, we identify a reversible path between them, and integrate the energy supplied as heat at each stage of the path divided by the temperature at which the heating occurs. Several examples of this procedure are given in the following sections and in Topic 62.

61.1 The entropy as a state function

Entropy is a state function. That is evident from the statistical definition in Topic 60, but is it true of the thermodynamic definition? To prove that it is, we need to show that the integral of dS between two specified states is independent of path. To do so, it is sufficient to prove that the integral of eqn 61.2 around an arbitrary cycle i → f → i is zero, for that guarantees that the entropy is the same at the initial and final states of the system regardless of the path taken between them (Fig. 61.1). That is, we need to show that

$$\oint \frac{\mathrm{d}q_{\mathrm{rev}}}{T}=0 \qquad (61.3)$$

where the symbol $\oint\ldots$ denotes integration around a closed path. The mathematical interpretation of eqn 61.3 is that whereas $\mathrm{d}q_{\mathrm{rev}}$ is an incomplete differential, in the sense that its integral depends on the path of integration (as explained in Topic 55), multiplication by $1/T$, which in calculus is called an 'integrating factor', converts it into a complete (exact) differential (see *Mathematical background* 8). This mathematical viewpoint can be regarded as another motivation of the definition in eqn 61.1, with the presence of $1/T$ ensuring that $\mathrm{d}S$ is an exact differential with a path-independent integral.

There are three steps in the argument that shows that $\mathrm{d}S$ is an exact differential (a consequence of $1/T$ being an integrating factor of $\mathrm{d}q_{\mathrm{rev}}$) and therefore that S is a state function:

- First, show that eqn 61.3 is true for a special cycle (a 'Carnot cycle') involving a perfect gas.
- Then show that the result is true whatever the working substance, not just a perfect gas.
- Finally, show that the result is true for any reversible cycle.

(a) The Carnot cycle

A **Carnot cycle**, which is named after the French engineer Sadi Carnot, consists of four reversible stages (Fig. 61.2):

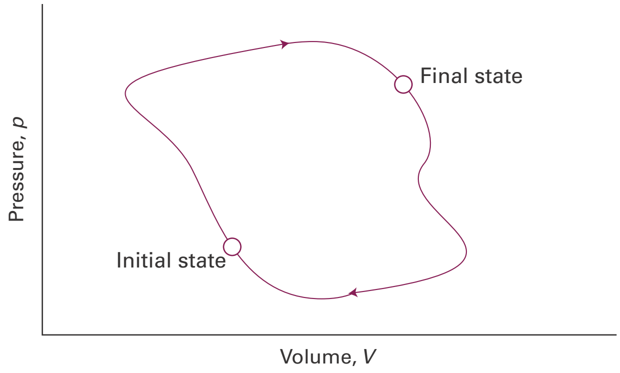


Figure 61.1 In a thermodynamic cycle, the overall change in a state function (from the initial state to the final state and then back to the initial state again) is zero.

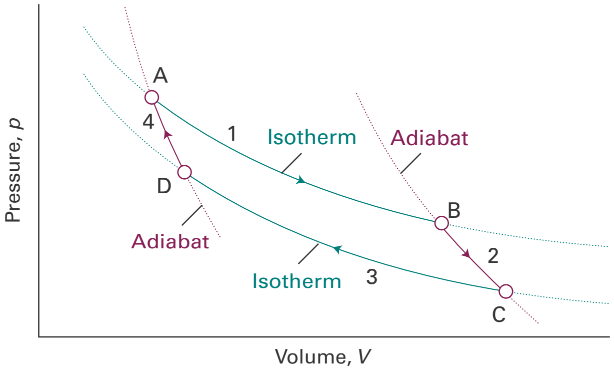


Figure 61.2 The basic structure of a Carnot cycle. In Step 1, there is isothermal reversible expansion at the temperature T_h. Step 2 is a reversible adiabatic expansion in which the temperature falls from T_h to T_c. In Step 3 there is an isothermal reversible compression at T_c, and that isothermal step is followed by an adiabatic reversible compression (Step 4), which restores the system to its initial state.

1. Reversible isothermal expansion from A to B at T_h; the entropy change is q_h/T_h, where q_h is the heat supplied from the hot source.
2. Reversible adiabatic expansion from B to C. No energy leaves the system as heat, so the change in entropy is zero. In the course of this expansion, the temperature falls from T_h to T_c, the temperature of the cold sink.
3. Reversible isothermal compression from C to D at T_c. Energy is released as heat to the cold sink; the corresponding change in entropy is q_c/T_c; in this expression q_c is negative.
4. Reversible adiabatic compression from D to A. No energy enters the system as heat, so the change in entropy is zero. The temperature rises from T_c to T_h.

The total change in entropy around the cycle is

$$\oint \mathrm{d}S=\overbrace{\frac{q_h}{T_h}}^{1}+\overbrace{0}^{2}+\overbrace{\frac{q_c}{T_c}}^{3}+\overbrace{0}^{4}=\frac{q_h}{T_h}+\frac{q_c}{T_c}$$

However, we show in the *Justification* below that for a perfect gas

$$\frac{q_h}{q_c}=-\frac{T_h}{T_c}, \quad \text{or} \quad \frac{q_h}{T_h}=-\frac{q_c}{T_c} \qquad \text{Perfect gas, reversible change} \qquad (61.4)$$

Substitution of this relation into the preceding equation gives zero on the right, which is what we wanted to prove.

Justification 61.1 Heating accompanying reversible adiabatic expansion

As explained in Topic 55, for a perfect gas,

$$q_{\rm h}=nRT_{\rm h}\ln\frac{V_{\rm B}}{V_{\rm A}}\qquad q_{\rm c}=nRT_{\rm c}\ln\frac{V_{\rm D}}{V_{\rm C}}$$

The temperatures $T_{\rm h}$ and $T_{\rm c}$ lie on the same adiabat in Fig. 61.2. From the relations between temperature and volume for reversible adiabatic processes (eqn 58.17, summarized as $VT^c=\text{constant}$ with $c=C_{V,\rm m}/R$):

$$V_{\rm A}T_{\rm h}^c=V_{\rm D}T_{\rm c}^c\qquad V_{\rm C}T_{\rm c}^c=V_{\rm B}T_{\rm h}^c$$

Multiplication of the first of these expressions by the second gives

$$V_{\rm A}V_{\rm C}T_{\rm h}^cT_{\rm c}^c=V_{\rm D}V_{\rm B}T_{\rm h}^cT_{\rm c}^c$$

which simplifies to

$$\frac{V_{\rm A}}{V_{\rm B}}=\frac{V_{\rm D}}{V_{\rm C}}$$

Consequently,

$$q_{\rm c}=nRT_{\rm c}\ln\frac{V_{\rm D}}{V_{\rm C}}=nRT_{\rm c}\ln\frac{V_{\rm A}}{V_{\rm B}}=-nRT_{\rm c}\ln\frac{V_{\rm B}}{V_{\rm A}}$$

and therefore

$$\frac{q_{\rm h}}{q_{\rm c}}=\frac{nRT_{\rm h}\ln(V_{\rm B}/V_{\rm A})}{-nRT_{\rm c}\ln(V_{\rm B}/V_{\rm A})}=-\frac{T_{\rm h}}{T_{\rm c}}$$

as in eqn 61.4.

Brief illustration 61.1 The Carnot cycle

The Carnot cycle can be regarded as a representation of the changes taking place in an actual idealized engine, where heat is converted into work. (However, other cycles are closer approximations to real engines.) In an engine running in accord with the Carnot cycle, 100 J of energy is withdrawn from the hot source ($q_{\rm h}=+100$ J) at 500 K and some is used to do work, with the remainder deposited in the cold sink at 300 K. According to eqn 61.4, the amount of heat deposited is

$$q_{\rm c}=-q_{\rm h}\times\frac{T_{\rm c}}{T_{\rm h}}=-100\,{\rm J}\times\frac{300\,{\rm K}}{500\,{\rm K}}=-60\,{\rm J}$$

That means that 40 J was used to do work.

Self-test 61.1 How much work can be extracted when the temperature of the hot source is increased to 800 K?

Answer: 62 J

(b) The independence of working substance

In the second step we need to show that eqn 61.4 applies to any material, not just a perfect gas. We begin this step of the argument by introducing the **efficiency**, η (eta), of a 'heat engine', a device (like that treated in *Brief illustration* 61.1) in which heat is converted into work:

$$\eta=\frac{\text{work performed}}{\text{heat absorbed}}=\frac{|w|}{|q_{\rm h}|}\qquad\textit{Definition}\quad\text{Efficiency}\qquad(61.5)$$

The modulus signs (|…|) are included to ensure that the efficiency is a positive number. The definition implies that the greater the work output for a given supply of heat from the hot reservoir, the greater is the efficiency of the engine.

The efficiency can be expressed in terms of the heat transactions alone, because (as shown in Fig. 61.3) the energy supplied as work by the engine is the difference between the energy supplied as heat by the hot reservoir and returned to the cold reservoir:

$$|w|=|q_{\rm h}|-|q_{\rm c}|$$

We have used absolute values because keeping track of signs can be tricky. Then the efficiency is

$$\eta=\frac{|q_{\rm h}|-|q_{\rm c}|}{|q_{\rm h}|}=1-\frac{|q_{\rm c}|}{|q_{\rm h}|}\qquad(61.6)$$

It then follows from eqn 61.4 in the form $|q_{\rm c}|/|q_{\rm h}|=|T_{\rm c}|/|T_{\rm h}|$ that

$$\eta=1-\frac{T_{\rm c}}{T_{\rm h}}\qquad\textit{Reversible change}\quad\text{Carnot efficiency}\qquad(61.7)$$

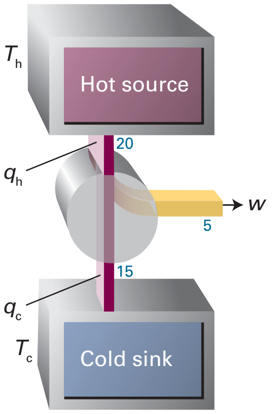


Figure 61.3 Suppose an energy $q_{\rm h}$ (for example, 20 kJ) is supplied to the engine and $q_{\rm c}$ is lost from the engine (for example, $q_{\rm c}=-15$ kJ) and discarded into the cold reservoir. The work done by the engine is equal to $q_{\rm h}+q_{\rm c}$ (for example, 20 kJ + (−15 kJ) = 5 kJ). The efficiency is the work done divided by the energy supplied as heat from the hot source (in this case, 5 kJ/20 kJ = 0.25).

Brief illustration 61.2 Thermal efficiency

A certain power station operates with superheated steam at 300 °C ($T_h = 573\,\text{K}$) and discharges the waste heat into the environment at 20 °C ($T_c = 293\,\text{K}$). The theoretical efficiency is therefore

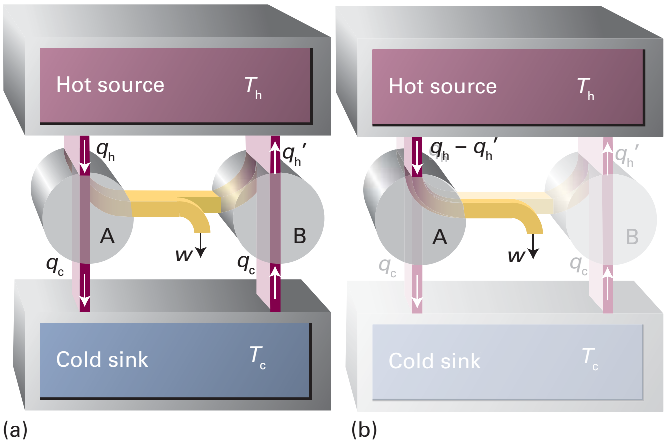
$$\eta = 1 - \frac{293\,\text{K}}{573\,\text{K}} = 0.489, \text{ or } 48.9 \text{ per cent}$$

In practice, there are other losses due to mechanical friction and the fact that the turbines do not operate reversibly.

Self-test 61.2 At what temperature of the hot source would the theoretical efficiency reach 80 per cent?

Answer: 1465 K

Now we are ready to generalize to any working substance. The Second Law of thermodynamics implies that *all reversible engines working between two reservoirs with fixed temperatures have the same efficiency regardless of their construction*. To see the truth of this statement, suppose two reversible engines are coupled together and run between the same two reservoirs (Fig. 61.4). The working substances and details of construction of the two engines are entirely arbitrary. Initially, suppose that engine A is more efficient than engine B, and that we choose a setting of the controls that causes engine B to take energy as heat from the cold reservoir and to release a certain quantity of energy as heat into the hot reservoir. However, because engine A is more efficient than engine B, not all the work that A produces is needed for this process, and the difference can be used to do work. The net result is that the cold reservoir is unchanged, work has been done, and the hot reservoir has lost a certain amount of energy. This outcome is contrary to the Kelvin statement of the Second Law (Topic 59), because some heat has been converted directly into work, and so the initial assumption that engines A and B can have different efficiencies must be false. It follows that the relation between the heat transfers and the temperatures must also be independent of the working material, and therefore that eqn 61.7 is true for any substance involved in a Carnot cycle.



(a) (b)

Figure 61.4 (a) The demonstration of the equivalence of the efficiencies of all reversible engines working between the same thermal reservoirs is based on the flow of energy represented in this diagram. (b) The net effect of the processes is the conversion of heat into work without there being a need for a cold sink: this is contrary to the Kelvin statement of the Second Law.

(c) Generalization to any cycle

For the final step in the argument, we note that any reversible cycle can be approximated as a collection of Carnot cycles and the cyclic integral around an arbitrary path is the sum of the integrals around each of the Carnot cycles (Fig. 61.5). This approximation becomes exact as the individual cycles are allowed to become infinitesimal. The entropy change around each individual cycle is zero, so the sum of entropy changes for all the cycles is zero. However, in the sum, the entropy change along any individual path is cancelled by the entropy change along the path it shares with the neighbouring cycle. Therefore, all the entropy changes cancel except for those along the perimeter of the overall cycle. That is,

$$\sum_{\text{all}} \frac{q_{\text{rev}}}{T} = \sum_{\text{perimeter}} \frac{q_{\text{rev}}}{T} = 0$$

In the limit of infinitesimal cycles, the non-cancelling edges of the Carnot cycles match the overall cycle exactly, and the sum

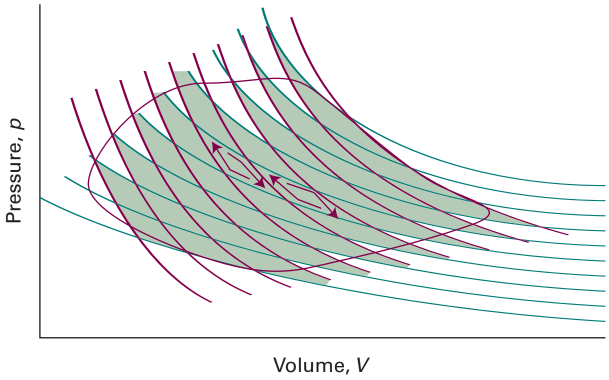


Figure 61.5 A general cycle can be divided into small Carnot cycles. The match is exact in the limit of infinitesimally small cycles. Paths cancel in the interior of the collection, and only the perimeter, an increasingly good approximation to the true cycle as the number of cycles increases, survives. Because the entropy change around every individual cycle is zero, the integral of the entropy around the perimeter is zero too.

becomes an integral. Equation 61.3 then follows immediately. This result implies that $\mathrm{d}S$ is an exact differential and therefore that S is a state function.

61.2 The thermodynamic temperature

The discussion of the efficiency of heat engines opens up the opportunity to establish a temperature scale that is independent of any working substance. Suppose we have an engine that is working reversibly between a hot source at a temperature T_h and a cold sink at a temperature T. Then we know from eqn 61.7 that

$$T = (1-\eta)T_h \qquad \text{Thermodynamic temperature} \qquad (61.8)$$

This expression enabled Kelvin to define the **thermodynamic temperature scale** in terms of the efficiency of a heat engine, which in principle can be measured by observing the rise and fall of weights in a gravitational field. That is, it can be put on a purely mechanical basis.

The zero of the scale, $T=0$, occurs for a Carnot efficiency of 1. The size of the unit to report other temperatures is entirely arbitrary, but until recently (2011) the Kelvin scale was defined by setting the temperature of the triple point of water as 273.16 K exactly (Topic 67). It is now (in 2014) intended to define the kelvin in a more abstract manner by setting Boltzmann's constant at an exact, defined value.

Brief illustration 61.3 The thermodynamic temperature

A heat engine was constructed that used a hot source at the triple-point temperature of water and used as a cold source a cooled liquid. The efficiency of the engine was measured as 0.400. The temperature of the liquid is therefore

$$T = (1-0.400)\times(273.16\ \text{K}) = 164\ \text{K}$$

Self-test 61.3 What temperature would be reported for the hot source if a thermodynamic efficiency of 0.500 was measured when the cold sink was at 273.16 K?

Answer: 546 K

61.3 The Clausius inequality

We now show that the thermodynamic definition of entropy, like the statistical definition (Topic 60), is consistent with the Second Law (Topic 59). To begin, we recall that more energy flows as work under reversible conditions than under irreversible conditions. That is,

$$-\mathrm{d}w_{\text{rev}} \geq -\mathrm{d}w, \quad \text{or} \quad \mathrm{d}w - \mathrm{d}w_{\text{rev}} \geq 0$$

where the equal sign applies when the process is reversible. Because the internal energy is a state function, its change is the same for irreversible and reversible paths between the same two states, so we can also write

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w = \mathrm{d}q_{\text{rev}} + \mathrm{d}w_{\text{rev}}$$

It follows that

$$\mathrm{d}q_{\text{rev}} - \mathrm{d}q = \mathrm{d}w - \mathrm{d}w_{\text{rev}} \geq 0, \quad \text{or} \quad \mathrm{d}q_{\text{rev}} \geq \mathrm{d}q$$

and therefore, on dividing by T, that

$$\frac{\mathrm{d}q_{\text{rev}}}{T} \geq \frac{\mathrm{d}q}{T}$$

Now we use the thermodynamic definition of the entropy (eqn 61.1, $\mathrm{d}S = \mathrm{d}q_{\text{rev}}/T$) to write

$$\mathrm{d}S \geq \frac{\mathrm{d}q}{T} \qquad \text{Clausius inequality} \qquad (61.9)$$

This expression is the **Clausius inequality**. The equality refers to a reversible change and the greater-than sign to an irreversible change. It proves to be of great importance for the discussion of the spontaneity of chemical reactions (Topic 73).

Example 61.1 Using the Clausius inequality

Use the Clausius inequality to show that the transfer of heat from hot to cold is spontaneous.

Method Consider the transfer of energy as heat from one system—the hot source—at a temperature T_h to another system—the cold sink—at a temperature T_c (Fig. 61.6) and show that the Clausius inequality implies that $\mathrm{d}S > 0$.

Answer When heat leaves the hot source, the Clausius inequality implies that the entropy of the hot source changes by $\mathrm{d}S_h \geq \mathrm{d}q_h/T_h$. In this case, because heat leaves the source, $\mathrm{d}q_h < 0$, so $\mathrm{d}q_h = -|\mathrm{d}q_h|$. When heat enters the cold sink the Clausius inequality implies that the entropy of the cold sink changes by $\mathrm{d}S_c \geq \mathrm{d}q_c/T_c$. In this case, because heat enters the sink $\mathrm{d}q_c > 0$, so $\mathrm{d}q_c = |\mathrm{d}q_c|$. Overall, therefore, the entropy change $\mathrm{d}S = \mathrm{d}S_h + \mathrm{d}S_c$ is

$$\mathrm{d}S \geq \frac{\mathrm{d}q_h}{T_h} + \frac{\mathrm{d}q_c}{T_c} = -\frac{|\mathrm{d}q_h|}{T_h} + \frac{|\mathrm{d}q_c|}{T_c}$$

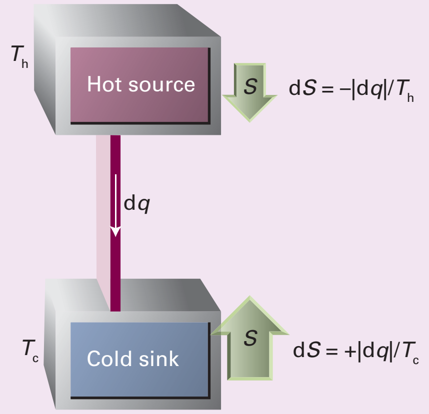


Figure 61.6 When energy leaves a hot reservoir as heat, the entropy of the reservoir decreases. When the same quantity of energy enters a cooler reservoir, the entropy increases by a larger amount. Hence, overall there is an increase in entropy and the process is spontaneous. Relative changes in entropy are indicated by the sizes of the arrows.

However, because the same quantity of heat enters the sink as left the source, $|dq_h| = |dq_c|$, so

$$dS \geq -\frac{|dq_c|}{T_h} + \frac{|dq_c|}{T_c} = |dq_c|\left(\frac{1}{T_c} - \frac{1}{T_h}\right)$$

which is positive (because $T_h \geq T_c$). Hence, cooling (the transfer of heat from hot to cold) is spontaneous, as we know from experience.

Self-test 61.4 What is the change in entropy when 1.0 J of energy as heat transfers from a large block of iron at 30 °C to another large block at 20 °C?

Answer: +0.1 mJ K^{-1}

We now suppose that the system is isolated from its surroundings, so that $dq = 0$. The Clausius inequality implies that

$$dS \geq 0 \tag{61.10}$$

and we conclude that *in an isolated system the entropy cannot decrease when a spontaneous change occurs*. This statement captures the content of the Second Law (Topic 59).

61.4 Entropy changes in the surroundings

The definition in eqn 61.1 can be used to formulate an expression for the change in entropy of the surroundings, ΔS_{sur}, which would be very difficult to evaluate statistically.

Consider an infinitesimal transfer of heat dq_{sur} to the surroundings. The surroundings consist of a reservoir of constant pressure and temperature, so the energy supplied to them as heat can be identified with the change in their enthalpy, dH_{sur}. The enthalpy is a state function and dH_{sur} is an exact differential. As we have seen, these properties imply that dH_{sur} is independent of how the change is brought about and in particular is independent of whether the process is reversible or irreversible. The same remarks therefore apply to dq_{sur}, to which dH_{sur} is equal. Therefore, we can adapt the definition in eqn 61.1 to write

$$dS_{sur} = \frac{dq_{sur,rev}}{T_{sur}} = \frac{dq_{sur}}{T_{sur}} \tag{61.11a}$$

Entropy change of surroundings

Furthermore, because the temperature of the surroundings is constant however much heat enters them (they have infinite heat capacity), for a measurable change

$$\Delta S_{sur} = \frac{q_{sur}}{T_{sur}} \tag{61.11b}$$

Entropy change of surroundings

That is, regardless of how the change is brought about in the system, reversibly or irreversibly, we can calculate the change of entropy of the surroundings by dividing the heat transferred by the temperature at which the transfer takes place.

Brief illustration 61.4 Entropy change in the surroundings

To calculate the entropy change in the surroundings when 1.00 mol $H_2O(l)$ is formed from its elements under standard conditions at 298 K, we use $\Delta H^{\ominus} = -286$ kJ from Table 57.4. The energy released as heat is supplied to the surroundings, so $q_{sur} = +286$ kJ. Therefore,

$$\Delta S_{sur} = \frac{2.86 \times 10^5\,\mathrm{J}}{298\,\mathrm{K}} = +960\,\mathrm{J\,K^{-1}}$$

This strongly exothermic reaction results in an increase in the entropy of the surroundings as energy is released into them as heat.

Self-test 61.5 Calculate the entropy change in the surroundings when 1.00 mol $N_2O_4(g)$ is formed from 2.00 mol $NO_2(g)$ under standard conditions at 298 K.

Answer: −192 J K^{-1}

Equation 61.11 makes it very simple to calculate the changes in entropy of the surroundings that accompany any process. For instance, for any adiabatic change, $q_{sur} = 0$, so

$$\Delta S_{sur} = 0 \tag{61.12}$$

Adiabatic change

This expression is true however the change takes place, reversibly or irreversibly.

Checklist of concepts

☐ 1. The definition of **thermodynamic entropy** conforms to it being a state function, with $1/T$ an integrating factor.

☐ 2. A **change in entropy** may be calculated by finding a reversible route between the specified initial and final states of a system.

☐ 3. The **change of entropy in the surroundings** is calculated by assessing the heat transferred to the surroundings.

Checklist of equations

Property	Equation	Comment	Equation number
Entropy change	$\mathrm{d}S = \mathrm{d}q_{\mathrm{rev}}/T$	Definition	61.1
Carnot efficiency	$\eta = 1 - T_{\mathrm{c}}/T_{\mathrm{h}}$	Reversible operation of heat engine	61.7
Thermodynamic temperature	$T = (1-\eta)T_{\mathrm{h}}$	Definition	61.8
Clausius inequality	$\mathrm{d}S \geq \mathrm{d}q/T$	Any change; equality for a reversible change	61.9
Entropy change of surroundings	$\Delta S_{\mathrm{sur}} = q_{\mathrm{sur}}/T_{\mathrm{sur}}$	Any change	61.11

TOPIC 62

Entropy changes for specific processes

Contents

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➤ **Why do you need to know this material?**

This section shows how to put the equations developed in Topic 61 into practice. You will see how to calculate the entropy changes accompanying a variety of common processes. The expressions are used extensively in the discussion of the thermodynamics of chemical reactions.

➤ **What is the key idea?**

The entropy changes associated with physical and chemical processes may be calculated from data on enthalpy changes and heat capacities.

➤ **What do you need to know already?**

This Topic makes use of the equations developed in Topic 61 for entropy changes for the system and surroundings. It also draws on the expression for the work done during reversible isothermal expansion of a perfect gas (Topic 55).

Here we see how to calculate the entropy changes that accompany a variety of basic processes. In each case we develop the argument using classical thermodynamics (Topic 61, based on $\mathrm{d}S=\mathrm{d}q_{\mathrm{rev}}/T$), but relate each result to the statistical definition (Topic 60, based on $S=k\ln \mathcal{W}$). You should always keep in mind that the entropy of a system increases as more states become accessible, either through a rise in temperature (which extends the tail of the Boltzmann distribution) or because there is a change in the energy levels that brings more of them within reach.

62.1 Isothermal expansion of a perfect gas

Equation 61.2 of Topic 61,

$$\Delta S=\int_{\mathrm{i}}^{\mathrm{f}}\frac{\mathrm{d}q_{\mathrm{rev}}}{T} \qquad (62.1)$$

instructs us to find the energy supplied as heat for a reversible path between the stated initial and final states regardless of the actual manner in which the process in fact takes place. When the expansion is isothermal the temperature is a constant and may be taken outside the integral. The energy absorbed as heat during a reversible isothermal expansion of a perfect gas can be calculated from $\mathrm{d}U=\mathrm{d}q+\mathrm{d}w$ and, because the internal energy is independent of volume for an isothermal change (Topic 58), we know that $\mathrm{d}U=0$. Therefore $\mathrm{d}q=-\mathrm{d}w$ in general and therefore $\mathrm{d}q_{\mathrm{rev}}=-\mathrm{d}w_{\mathrm{rev}}$ for a reversible change. The change in entropy of the gas is therefore

$$\Delta S=\int_{V_{\mathrm{i}}}^{V_{\mathrm{f}}}\frac{\mathrm{d}q_{\mathrm{rev}}}{T}=-\frac{1}{T}\int_{V_{\mathrm{i}}}^{V_{\mathrm{f}}}\mathrm{d}w_{\mathrm{rev}}=-\frac{w_{\mathrm{rev}}}{T}$$

The work of reversible isothermal expansion (or compression) is calculated in Topic 55 as

$$w_{\rm rev} = -nRT\ln\frac{V_{\rm f}}{V_{\rm i}}$$

It follows that

$$\Delta S = nR\ln\frac{V_{\rm f}}{V_{\rm i}} \qquad (62.2)$$

Perfect gas, isothermal Entropy change on expansion

exactly as obtained by statistical arguments (Topic 60). In that case the increase in entropy on expansion is ascribed to the fact that the energy levels available to the molecules become closer as the container expands, so more can be populated at a given temperature.

Brief illustration 62.1 The entropy change accompanying expansion

When the volume occupied by 1.00 mol of any perfect gas molecules is doubled at any constant temperature, $V_{\rm f}/V_{\rm i}=2$ and

$$\Delta S = (1.00\,{\rm mol})\times(8.3145\ {\rm J\ K^{-1}\ mol^{-1}})\times\ln 2 = +5.76\,{\rm J\,K^{-1}}$$

Self-test 62.1 Develop an expression for the change in entropy when the pressure of a perfect gas is changed isothermally from $p_{\rm i}$ to $p_{\rm f}$.

Answer: $\Delta S = nR\ln(p_{\rm i}/p_{\rm f})$

An important point is that because S is a state function, the value of ΔS *of the system* is independent of the path between the initial and final states, and eqn 62.2 applies whether the change of state occurs reversibly or irreversibly. The logarithmic dependence of entropy on volume is illustrated in Fig. 62.1.

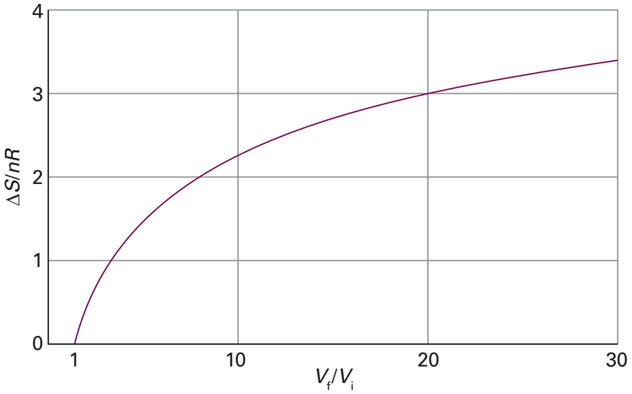

Figure 62.1 The logarithmic increase in entropy of a perfect gas as it expands isothermally.

The *total* change in entropy, the sum of the changes in the system and the surroundings, however, does depend on how the expansion takes place. For any process $dq_{\rm sur}=-dq$, and for a reversible isothermal change, we use $q=nRT\ln(V_{\rm f}/V_{\rm i})$ (see *Justification* 61.1 of Topic 61), with the surroundings at the same temperature T as the system, to write

$$\Delta S_{\rm sur} = \frac{q_{\rm sur}}{T} = -\frac{q}{T} = -nR\ln\frac{V_{\rm f}}{V_{\rm i}} \qquad (62.3)$$

Perfect gas, reversible, isothermal Entropy change of surroundings

This change is the negative of the change in the system, so we can conclude that $\Delta S_{\rm tot}=0$, which is what we should expect for a reversible process.

If the isothermal expansion occurs freely ($w=0$) and irreversibly, then $q=0$ (because $\Delta U=0$). Consequently, $\Delta S_{\rm sur}=0$, and the total entropy change is

$$\Delta S_{\rm tot} = nR\ln\frac{V_{\rm f}}{V_{\rm i}} \qquad (62.4)$$

Perfect gas, free expansion, isothermal Total entropy change

In this case, $\Delta S_{\rm tot}>0$, as we expect for an irreversible process.

62.2 Phase transitions

The entropy of a substance changes when a substance freezes or boils as a result of changes in the orderliness with which the molecules pack together and the extent to which the energy is localized or dispersed. For example, when a substance vaporizes, a compact condensed phase changes into a widely dispersed gas and we can expect the entropy of the substance to increase considerably. The entropy of a solid also increases when it melts to a liquid and when that liquid turns into a gas. Although we can *understand* the changes of entropy in these statistical, molecular terms, it is far easier to use classical thermodynamics to calculate numerical values, and we shall do that here.

Consider a system and its surroundings at the **normal transition temperature**, $T_{\rm trs}$, the temperature at which two phases are in equilibrium at 1 atm. This temperature is 0 °C (273 K) for ice in equilibrium with liquid water at 1 atm, and 100 °C (373 K) for water in equilibrium with its vapour at 1 atm. At the transition temperature, any transfer of energy as heat between the system and its surroundings is reversible because the two phases in the system are in equilibrium. Because at constant pressure $q=\Delta_{\rm trs}H$, the change in molar entropy of the system is

$$\Delta_{\rm trs}S = \frac{\Delta_{\rm trs}H}{T_{\rm trs}} \qquad (62.5)$$

Constant pressure, at the transition temperature Entropy of transition

Recall from Topic 57 that $\Delta_{\rm trs}H$ is an enthalpy change per mole of substance; so $\Delta_{\rm trs}S$ is also a molar quantity with units joules per kelvin per mole (J K^{-1} mol^{-1}). If the phase transition is exothermic ($\Delta_{\rm trs}H<0$, as in freezing or condensing), then the entropy change is negative. This decrease in entropy is consistent with localization of matter and energy that accompanies the formation of a solid from a liquid or a liquid from a gas. If the transition is endothermic ($\Delta_{\text{trs}}H>0$, as in melting and vaporization), then the entropy change is positive, which is consistent with dispersal of energy and matter in the system.

Table 62.1 lists some experimental entropies of transition. Table 62.2 lists in more detail the standard entropies of vaporization of several liquids at their normal boiling points. An interesting feature of the data is that a wide range of liquids give approximately the same standard entropy of vaporization (about 85 J K^{-1} mol^{-1}): this empirical observation is called **Trouton's rule**. The explanation of Trouton's rule is that a similar change in volume occurs (with an accompanying change in the number of accessible microstates) when any liquid evaporates and becomes a gas at 1 bar. Hence, all liquids can be expected to have similar standard entropies of vaporization.

Liquids that show significant deviations from Trouton's rule do so on account of strong molecular interactions that result in a partial ordering of their molecules. As a result, there is a greater change in disorder when the liquid turns into a vapour than for a fully disordered liquid. An example is water, where the large entropy of vaporization reflects the presence of structure arising from hydrogen-bonding in the liquid. Hydrogen bonds tend to organize the molecules in the liquid so that they are less random than, for example, the molecules in liquid hydrogen sulfide (in which there is little hydrogen bonding).

Methane has an unusually low entropy of vaporization. A part of the reason is that the entropy of the gas itself is slightly low (186 J K^{-1} mol^{-1} at 298 K); the entropy of N_2 under the same conditions is 192 J K^{-1} mol^{-1}. Small, light molecules have a low rotational contribution to their entropy because the rotational levels are far apart (Topic 41).

Table 62.1* Standard entropies (and temperatures) of phase transitions, $\Delta_{\text{trs}}S^{\ominus}/(\text{J K}^{-1}\,\text{mol}^{-1})$

	Fusion (at T_f)	Vaporization (at T_b)
Argon, Ar	14.17 (at 83.8 K)	74.53 (at 87.3 K)
Benzene, C_6H_6	38.00 (at 279 K)	87.19 (at 353 K)
Water, H_2O	22.00 (at 273.15 K)	109.1 (at 373.15 K)
Helium, He	4.8 (at 1.8 K and 30 bar)	19.9 (at 4.22K)

* More values are given in the *Resource section*.

Table 62.2* The standard entropies of vaporization of liquids

	$\Delta_{\text{vap}}H^{\ominus}$/(kJ mol^{-1})	θ_b/°C	T_b/K	$\Delta_{\text{vap}}S^{\ominus}$/(J K^{-1} mol^{-1})
Benzene	30.8	80.1	353.3	87.2
Carbon tetrachloride	30	76.7	349.9	85.8
Cyclohexane	30.1	80.7	353.9	85.1
Hydrogen sulfide	18.7	−60.4	212.8	87.9
Methane	8.18	−161.5	111.7	73.2
Water	40.7	100.0	373.2	109.1

* More values are given in the *Resource section*.

Brief illustration 62.2 Trouton's rule

There is no hydrogen bonding in liquid bromine and Br_2 is a heavy molecule that is unlikely to display unusual behaviour in the gas phase, so it is safe to use Trouton's rule. To predict the standard molar enthalpy of vaporization of bromine given that it boils at 59.2 °C, we use the rule in the form

$$\Delta_{\text{vap}}H^{\ominus}=T_b\times(85\,\text{J K}^{-1}\,\text{mol}^{-1})$$

Substitution of the data then gives

$$\begin{aligned}\Delta_{\text{vap}}H^{\ominus}&=(332.4\,\text{K})\times(85\,\text{J K}^{-1}\,\text{mol}^{-1})=+2.8\times10^{4}\,\text{J mol}^{-1}\\&=+28\,\text{kJ mol}^{-1}\end{aligned}$$

The experimental value is +29.45 kJ mol^{-1}.

Self-test 62.2 Predict the enthalpy of vaporization of ethane from its normal boiling point, −88.6 °C.

Answer: 16 kJ mol^{-1}

62.3 Entropy changes on heating

In Topic 60 it is explained that the translational, vibrational, and rotational contributions to the statistical entropy increase with temperature as more states become accessible. The thermodynamic definition can be used to draw the same conclusion. Thus, from eqn 62.1, the expression

$$S(T_f)=S(T_i)+\int_{T_i}^{T_f}\frac{\mathrm{d}q_{\text{rev}}}{T}\tag{62.6}$$

is used to calculate the entropy of a system at a temperature T_f from a knowledge of its entropy at a temperature T_i and the heat supplied to change its temperature from one value to the other. We shall be particularly interested in the entropy change when the system is subjected to constant pressure (such as from the atmosphere) during the heating. Then, from the definition of constant-pressure heat capacity (Topic 56), $\mathrm{d}q_{\text{rev}}=C_p\mathrm{d}T$ provided the system is doing no non-expansion work. Consequently, at constant pressure,

$$S(T_f)=S(T_i)+\int_{T_i}^{T_f}\frac{C_p}{T}\mathrm{d}T\tag{62.7}$$

Constant pressure Entropy change on heating

The same expression applies at constant volume, but with C_p replaced by C_V. When C_p is independent of temperature in the temperature range of interest, it can be taken outside the integral and we obtain

$$S(T_\mathrm{f})=S(T_\mathrm{i})+C_p\int_{T_\mathrm{i}}^{T_\mathrm{f}}\frac{1}{T}\,\mathrm{d}T$$

and therefore

$$S(T_\mathrm{f})=S(T_\mathrm{i})+C_p\ln\frac{T_\mathrm{f}}{T_\mathrm{i}} \qquad (62.8)$$

Constant pressure, C_p constant

Entropy change on heating

with a similar expression for heating at constant volume. The logarithmic dependence of entropy on temperature is illustrated in Fig. 62.2.

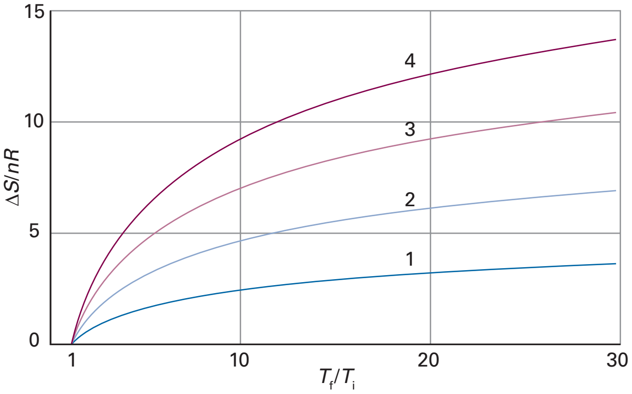

Figure 62.2 The logarithmic increase in entropy of a substance as it is heated at constant volume. Different curves correspond to different values of the constant-volume molar heat capacity (which is assumed constant over the temperature range) expressed as $C_{V,\mathrm{m}}/R$.

Example 62.1 Calculating an entropy change

Calculate the entropy change when argon at 25 °C and 1.00 bar in a container of volume 0.500 dm^3 is allowed to expand to 1.000 dm^3 and is simultaneously heated to 100 °C.

Method Because S is a state function we are free to choose the most convenient path from the initial state. One such path is reversible isothermal expansion to the final volume, followed by reversible heating at constant volume to the final temperature (Fig. 62.3). The entropy change in the first step is given by eqn 62.2 and that of the second step, provided C_V is independent of temperature, by eqn 62.8 (with C_V in place of C_p). In each case we need to know n, the amount of gas molecules, and can calculate it from the perfect gas equation and the data for the initial state from $n=p_\mathrm{i}V_\mathrm{i}/RT_\mathrm{i}$. The heat capacity at constant volume is given by the equipartition theorem as $\frac{3}{2}R$. (The equipartition theorem is reliable for monatomic gases: for others and in general use experimental data like that in Tables 57.3 and 57.4 of the *Resource section*.) If necessary, convert $C_{p,\mathrm{m}}$ to $C_{V,\mathrm{m}}$ by using the relation $C_{p,\mathrm{m}}-C_{V,\mathrm{m}}=R$.

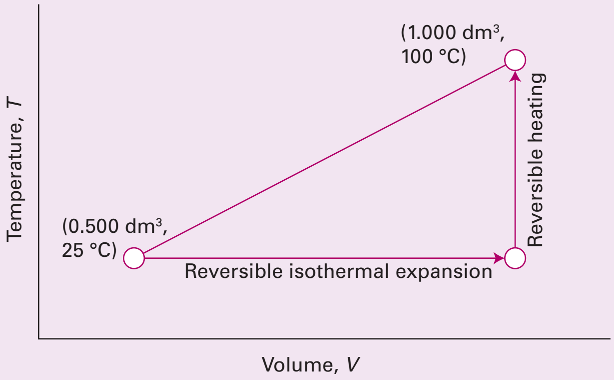

Figure 62.3 The overall path and the constituent paths used to reach the same destination in the system treated in Example 62.1.

Answer Because $n=p_\mathrm{i}V_\mathrm{i}/RT_\mathrm{i}$, from eqn 62.2

$$\Delta S(\text{Step 1})=\overbrace{\frac{p_\mathrm{i}V_\mathrm{i}}{RT_\mathrm{i}}}^{n}\times R\ln\frac{V_\mathrm{f}}{V_\mathrm{i}}=\frac{p_\mathrm{i}V_\mathrm{i}}{T_\mathrm{i}}\ln\frac{V_\mathrm{f}}{V_\mathrm{i}}$$

The entropy change in the second step, from 298 K to 373 K at constant volume, from eqn 62.8 with C_V replacing C_p, is

$$\Delta S(\text{Step 2})=\overbrace{\frac{p_\mathrm{i}V_\mathrm{i}}{RT_\mathrm{i}}}^{n}\times\overbrace{\frac{3}{2}R}^{C_{V,\mathrm{m}}}\times\ln\frac{T_\mathrm{f}}{T_\mathrm{i}}=\frac{p_\mathrm{i}V_\mathrm{i}}{T_\mathrm{i}}\ln\left(\frac{T_\mathrm{f}}{T_\mathrm{i}}\right)^{3/2}$$

where we have used $\frac{3}{2}\ln x=\ln x^{3/2}$. The overall entropy change, the sum of these two changes, is

$$\Delta S=\frac{p_\mathrm{i}V_\mathrm{i}}{T_\mathrm{i}}\ln\frac{V_\mathrm{f}}{V_\mathrm{i}}+\frac{p_\mathrm{i}V_\mathrm{i}}{T_\mathrm{i}}\ln\left(\frac{T_\mathrm{f}}{T_\mathrm{i}}\right)^{3/2}=\frac{p_\mathrm{i}V_\mathrm{i}}{T_\mathrm{i}}\ln\left\{\frac{V_\mathrm{f}}{V_\mathrm{i}}\left(\frac{T_\mathrm{f}}{T_\mathrm{i}}\right)^{3/2}\right\}$$

At this point we substitute the data and obtain (by using 1 Pa m^3 = 1 J)

$$\Delta S=\frac{(1.00\times10^5\,\mathrm{Pa})\times(0.500\times10^{-3}\,\mathrm{m}^3)}{298\,\mathrm{K}}\ln\left\{\frac{1.000}{0.500}\left(\frac{373}{298}\right)^{3/2}\right\}$$

$$=+0.173\,\mathrm{J\,K^{-1}}$$

A note on good practice It is sensible to proceed as generally as possible before inserting numerical data so that, if required, the formula can be used for other data; the procedure also minimizes rounding errors.

Self-test 62.3 Calculate the entropy change when the same initial sample is compressed to 50.0 cm^3 and cooled to −25 °C.

Answer: $-0.433\,\mathrm{J\,K^{-1}}$

The change of entropy with temperature is the basis of the calorimetric determination of entropies, which is described in Topic 63.

Checklist of concepts

☐ 1. The **entropy of a perfect gas** increases when it expands isothermally: the effect can be interpreted in terms of the separation of the translational energy levels becoming smaller.

☐ 2. The entropy of a substance changes when a substance freezes or boils and is proportional to the enthalpy of transition at the transition temperature.

☐ 3. **Trouton's rule** states that a wide range of liquids have approximately the same standard entropy of vaporization (about 85 J K^{-1} mol^{-1}).

☐ 4. The **dependence of the entropy on temperature** is logarithmic for substances with heat capacities that are independent of temperature.

Checklist of equations

Property	Equation	Comment	Equation number
Entropy change on expansion of gas	$\Delta S = nR\ln(V_f/V_i)$	Isothermal, perfect gas	62.2
Entropy of transition	$\Delta_{trs}S = \Delta_{trs}H/T_{trs}$	At the transition temperature	62.5
Entropy change on heating	$S(T_f) = S(T_i) + \int_{T_i}^{T_f} (C_p/T)\,dT$	Constant pressure	62.7
Entropy change on heating	$S(T_f) = S(T_i) + C_p\ln(T_f/T_i)$	Constant pressure, C_p a constant	62.8

TOPIC 63

The Third Law

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➤ Why do you need to know this material?

Much of chemical thermodynamics relies on knowing the entropies of substances. This Topic explains how entropies are measured. It also introduces the final law that completes the foundations of thermodynamics and allows thermodynamic properties to be determined and used.

➤ What is the key idea?

The entropies of all perfectly crystalline materials are zero at $T=0$; heat capacity data are used to determine values of the entropy at $T>0$.

➤ What do you need to know already?

This Topic is based on the thermodynamic definition of entropy (Topic 61) and the concept of heat capacity (Topics 55 and 56).

Topic 60 describes how to calculate the entropy of a substance from spectroscopic data. In this Topic we see how it may be measured calorimetrically. The procedure raises the question about matching the statistical and thermodynamic values, which is resolved by a series of experimental results summarized by the 'Third Law' of thermodynamics.

63.1 The calorimetric measurement of entropy

The entropy of a system at a temperature T is related to its entropy at $T=0$ by measuring its heat capacity C_p at different temperatures and evaluating the integral in Topic 62, which we repeat here for convenience:

$$S(T_2)=S(T_1)+\int_{T_1}^{T_2}\frac{C_p}{T}\,\mathrm{d}T \tag{63.1}$$

It is also necessary to add the entropy of transition ($\Delta_{\mathrm{trs}}H/T_{\mathrm{trs}}$) for each phase transition between $T=0$ and the temperature of interest. For example, if a substance melts at T_{f} and boils at T_{b}, then its entropy above its boiling temperature is given by

$$\begin{aligned}S(T)=S(0)&+\int_0^{T_{\mathrm{f}}}\frac{C_p(\mathrm{s})}{T}\,\mathrm{d}T+\frac{\Delta_{\mathrm{fus}}H}{T_{\mathrm{f}}}\\&+\int_{T_{\mathrm{f}}}^{T_{\mathrm{b}}}\frac{C_p(\mathrm{l})}{T}\,\mathrm{d}T+\frac{\Delta_{\mathrm{vap}}H}{T_{\mathrm{b}}}+\int_{T_{\mathrm{b}}}^{T}\frac{C_p(\mathrm{g})}{T}\,\mathrm{d}T\end{aligned} \tag{63.2}$$

where we have indicated the phases for the heat capacities. All the properties required, except $S(0)$, can be measured calorimetrically, and the integrals can be evaluated either graphically or, as is now more usual, by fitting a polynomial to the data and integrating the polynomial analytically or numerically. The former procedure is illustrated in Fig. 63.1: the area under the curve of C_p/T against T is the integral required. Because $\mathrm{d}T/T=\mathrm{d}\ln T$, an alternative procedure is to evaluate the area under a plot of C_p against $\ln T$.

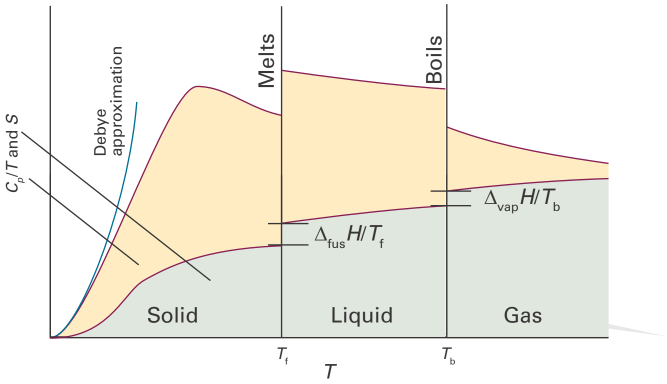

Figure 63.1 The calculation of a Third-Law entropy from heat capacity data. The variation of C_p/T with the temperature for a sample is shown by the line above the yellow region. The entropy, which is equal to the area beneath the upper curve up to the corresponding temperature, plus the entropy of each phase transition passed, is shown by the line above the green region. Note the use of the Debye approximation at low temperatures.

Example 63.1 Evaluating a change in entropy

Over a small range in temperature the molar constant-pressure heat capacity of carbon dioxide gas varies with temperature as $C_{p,\text{m}}=a+bT+c/T^2$ with the parameters $a=44.22\text{ J K}^{-1}\text{ mol}^{-1}$, $b=8.79\text{ mJ K}^{-2}\text{ mol}^{-1}$, and $c=-862\text{ kJ K mol}^{-1}$. What is the change in molar entropy when carbon dioxide is heated from 0 °C to 100 °C?

Method The general expression for the change in entropy with temperature is eqn 63.1, so we begin by substituting the polynomial expression for $C_{p,\text{m}}$ into that equation and simplifying the resulting expression as far as possible. Then there are two routes forward. One is to evaluate the resulting integrals analytically. The other is to feed the integral into mathematical software, and let it do the hard work. We demonstrate the former approach here. For the numerical evaluation, take $T_1=273\text{ K}$ (0 °C) and $T_2=373\text{ K}$ (100 °C).

Answer We substitute $C_{p,\text{m}}=a+bT+c/T^2$ into eqn 63.1 and obtain

$$\begin{aligned}S_{\text{m}}(T_2)&=S_{\text{m}}(T_1)+\int_{T_1}^{T_2}\frac{C_{p,\text{m}}}{T}\text{d}T\\&=S_{\text{m}}(T_1)+\int_{T_1}^{T_2}\left(\frac{a}{T}+b+\frac{c}{T^3}\right)\text{d}T\\&=S_{\text{m}}(T_1)+a\ln\frac{T_2}{T_1}+b(T_2-T_1)-\frac{1}{2}c\left(\frac{1}{T_2^2}-\frac{1}{T_1^2}\right)\end{aligned}$$

Insertion of the values of the coefficients and the initial and final temperatures gives $\Delta S_{\text{m}}=S_{\text{m}}(T_2)-S_{\text{m}}(T_1)=+11.99\text{ J K}^{-1}\text{ mol}^{-1}$.

Self-test 63.1 Find an expression for the temperature dependence of the molar entropy for a substance for which $C_{p,\text{m}}=a+b\ln T$.

Answer: $S_{\text{m}}(T_2)=S_{\text{m}}(T_1)+a\ln(T_2/T_1)+\tfrac{1}{2}b\ln(T_1T_2)\ln(T_2/T_1)$

One problem with the determination of entropy is the difficulty of measuring heat capacities near $T=0$. There are good theoretical grounds for assuming that the heat capacity of non-metallic solids is proportional to T^3 when T is low, and this dependence is the basis of an extrapolation based on the **Debye T^3 law**, which states that for non-metallic solids the heat capacity is proportional to T^3 as $T\rightarrow 0$. In this method, C_p is measured down to as low a temperature as possible and a curve of the form aT^3 is fitted to the data. That fit determines the value of a, and the expression $C_p(T)=aT^3$ is assumed valid down to $T=0$.

Example 63.2 Calculating the entropy at low temperatures

The molar constant-pressure heat capacity of a certain non-metallic solid at 4.2 K is $0.43\text{ J K}^{-1}\text{ mol}^{-1}$. What is its molar entropy at that temperature?

Method Because the temperature is so low, we can assume that the heat capacity varies with temperature as aT^3, in which case we can use eqn 63.1 to calculate the entropy at a temperature T in terms of the entropy at $T=0$ and the constant a. When the integration is carried out, it turns out that the result can be expressed in terms of the heat capacity at the temperature T, so the data can be used directly to calculate the entropy.

Answer The integration required is

$$\begin{aligned}S_{\text{m}}(T)&=S_{\text{m}}(0)+\int_0^T\frac{aT^3}{T}\text{d}T=S_{\text{m}}(0)+\int_0^T aT^2\text{d}T\\&=S_{\text{m}}(0)+\frac{1}{3}aT^3\end{aligned}$$

However, because aT^3 is the heat capacity at the temperature T,

$$S(T)=S(0)+\frac{1}{3}C_p(T)$$

from which it follows that

$$S_{\text{m}}(4.2\text{ K})=S_{\text{m}}(0)+0.14\text{ J K}^{-1}\text{ mol}^{-1}$$

Self-test 63.2 For metals, there is also a contribution to the heat capacity from the electrons which is linearly proportional to T when the temperature is low. Find its contribution to the entropy at low temperatures.

Answer: $S(T)=S(0)+C_p(T)$

63.2 The Nernst heat theorem and the Third Law

The question remains about the value of $S(0)$, the entropy at $T=0$. At $T=0$, all thermal motion has been quenched, and in a perfect crystal all the atoms or ions are in a regular, uniform array. The localization of matter and the absence of thermal motion suggest that such materials also have zero entropy. This conclusion is consistent with the statistical definition of entropy, because $S=k \ln \mathcal{W}=0$ if there is only one way of arranging the molecules and only one state is accessible (the ground state) and $\mathcal{W}=1$. However, because the argument used to relate the statistical definition to the thermodynamic definition in Topic 61 is in terms of *changes* of entropy, there remains the possibility that the definition in eqn 63.1 differs from the statistical entropy by a constant that might be different for each substance.

The experimental observation that turns out to be consistent with the view that the entropy of a regular array of molecules is zero at $T=0$ is summarized by the **Nernst heat theorem**:

> The entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero: $\Delta S \rightarrow 0$ as $T \rightarrow 0$ provided all the substances involved are perfectly ordered.

Brief illustration 63.1 The Nernst heat theorem

Consider the entropy of the transition between orthorhombic sulfur, S(α), and monoclinic sulfur, S(β), which can be calculated from the transition enthalpy (−402 J mol⁻¹) at the transition temperature (369 K):

$$\Delta_{\rm trs}S = S_{\rm m}(\alpha) - S_{\rm m}(\beta) = \frac{(-402\,{\rm J\,mol^{-1}})}{369\,{\rm K}} = -1.09\,{\rm J\,K^{-1}\,mol^{-1}}$$

The two individual entropies can also be determined by measuring the heat capacities from $T=0$ up to $T=369$ K. It is found that $S_{\rm m}(\alpha) = S_{\rm m}(\alpha,0) + 37\,{\rm J\,K^{-1}\,mol^{-1}}$ and $S_{\rm m}(\beta) = S_{\rm m}(\beta,0) + 38\,{\rm J\,K^{-1}\,mol^{-1}}$. These two values imply that at the transition temperature

$$\Delta_{\rm trs}S = S_{\rm m}(\alpha,0) - S_{\rm m}(\beta,0) - 1\,{\rm J\,K^{-1}\,mol^{-1}}$$

On comparing this value with the one above, we conclude that $S_{\rm m}(\alpha,0) - S_{\rm m}(\beta,0) \approx 0$, in accord with the theorem.

Self-test 63.3 Two forms of a metallic solid (see Self-test 63.2) undergo a phase transition at $T_{\rm trs}$, which is close to $T=0$. What is the enthalpy of transition at $T_{\rm trs}$ in terms of the heat capacities of the two polymorphs?

Answer: $\Delta_{\rm trs}H(T_{\rm trs}) = T_{\rm trs}\Delta C_p(T_{\rm trs})$

It follows from the Nernst theorem that, if we arbitrarily ascribe the value zero to the entropies of elements in their perfect crystalline form at $T=0$, then all perfect crystalline compounds also have zero entropy at $T=0$ (because the change in entropy that accompanies the formation of the compounds, like the entropy of all transformations at that temperature, is zero). This conclusion is summarized by the **Third Law of thermodynamics**:

> The entropy of all perfect crystalline substances is zero at $T=0$.

As far as thermodynamics is concerned, choosing this common value as zero is then a matter of convenience. The statistical formulation of entropy, however, justifies the value $S=0$ at $T=0$.

In most cases, $\mathcal{W}=1$ at $T=0$ because there is only one way of achieving the lowest total energy: put all the molecules into the same, lowest state. Therefore, $S=0$ at $T=0$, in accord with the Third Law of thermodynamics. In certain cases, though, $\mathcal{W}$ may differ from 1 at $T=0$. This is the case if there is no energy advantage in adopting a particular orientation even at absolute zero. For instance, for a diatomic molecule AB there may be almost no energy difference between the arrangements …AB AB AB… and …BA AB BA…, so $\mathcal{W}>1$ even at $T=0$. If $S>0$ at $T=0$ we say that the substance has a **residual entropy**.

Example 63.3 Estimating a residual entropy

Estimate the residual entropy of ice by taking into account the distribution of hydrogen bonds and chemical bonds about the oxygen atom of one H_2O molecule. The experimental value is 3.4 J K⁻¹ mol⁻¹.

Method Focus on the O atom, and consider the number of ways that that O atom can have two short (chemical) bonds and two long hydrogen bonds to its four neighbours. Refer to Fig. 63.2.

Answer Suppose each H atom can lie either close to or far from its 'parent' O atom, as depicted in Fig. 63.2. The total number of these conceivable arrangements in a sample that contains N H_2O molecules and therefore $2N$ H atoms is 2^{2N}. Now consider a single central O atom. The total number of possible arrangements of locations of H atoms around the central O atom of one H_2O molecule is $2^4 = 16$. Of these 16 possibilities, only 6 correspond to two short and two long bonds. That is, only $\frac{6}{16}=\frac{3}{8}$ of all possible arrangements are possible, and for N such molecules only $(\frac{3}{8})^N$ of all possible arrangements are possible. Therefore, the total number of allowed arrangements in the crystal is $2^{2N}(\frac{3}{8})^N = 4^N(\frac{3}{8})^N = (\frac{3}{2})^N$. If we suppose that all these arrangements are energetically identical, the residual entropy is

$$S(0) = k \ln\left(\frac{3}{2}\right)^N = Nk \ln\frac{3}{2} = nN_{\rm A}k \ln\frac{3}{2} = nR \ln\frac{3}{2}$$

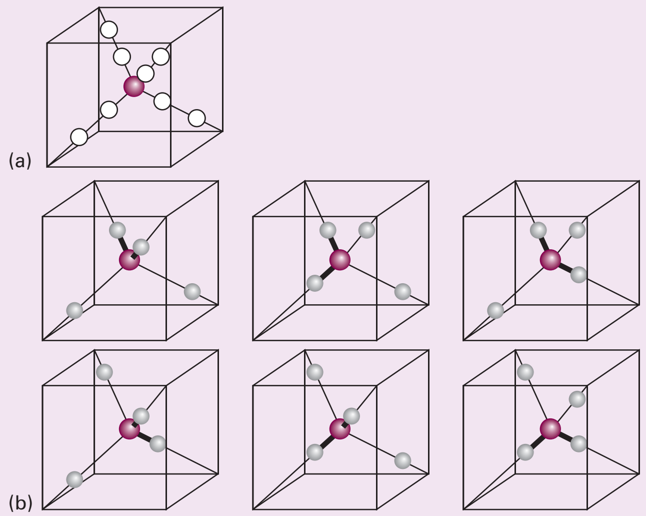

Figure 63.2 (a) The possible locations of H atoms around a central O atom in ice and (b) the permitted arrangements of short (chemical) and long (hydrogen) bonds in the local neighbourhood.

and the residual molar entropy would be

$$S_m(0)=R\ln\tfrac{3}{2}=3.4\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

in accord with the experimental value.

Self-test 63.4 What would be the residual molar entropy of HCF_3 on the assumption that each molecule could take up one of four tetrahedral orientations in a crystal?

Answer: 11.5 J K^{-1} mol^{-1}

63.3 Third-Law entropies

Entropies reported on the basis that $S(0)=0$ are called **Third-Law entropies** (and often just 'entropies'). They are measured calorimetrically by using eqn 63.2 and setting $S(0)=0$. When the substance is in its standard state at the temperature T, the **standard (Third-Law) entropy** is denoted $S^\ominus(T)$. A list of standard molar values at 298 K is given in Table 63.1.

Just as in the discussion of enthalpies in Topic 57, where it is acknowledged that solutions of cations cannot be prepared in the absence of anions, the standard molar entropies of ions in solution are reported on a scale in which the standard entropy of the H^+ ions in water is taken as zero at all temperatures:

$$S^\ominus(H^+,aq)=0 \qquad \textit{Definition} \quad \text{Standard reaction entropy} \qquad (63.3)$$

The values based on this choice are included in Tables 57.3 and 57.4 in the *Resource section*.

Table 63.1* Standard Third-Law entropies at 298 K

	$S_m^\ominus/(\mathrm{J\,K^{-1}\,mol^{-1}})$
Solids:	
Graphite, C(s)	5.7
Diamond, C(s)	2.4
Sucrose, $C_{12}H_{22}O_{11}(s)$	360.2
Iodine, $I_2(s)$	116.1
Liquids:	
Benzene, $C_6H_6(l)$	173.3
Water, $H_2O(l)$	69.9
Mercury, Hg(l)	76.0
Gases:	
Methane, $CH_4(g)$	186.3
Carbon dioxide, $CO_2(g)$	213.7
Hydrogen, $H_2(g)$	130.7
Helium, He	126.2
Ammonia, $NH_3(g)$	192.4

* More values are given in the *Resource section*.

Because the entropies of ions in water are values relative to the hydrogen ion in water, they may be either positive or negative. A positive entropy means that an ion has a higher molar entropy than H^+ in water and a negative entropy means that the ion has a lower molar entropy than H^+ in water. In terms of the language of 'partial molar' quantities introduced in Topic 69, the entropies of ions in solution are actually *partial molar entropies*, for their values include the consequences of their presence on the organization of the solvent molecules around them. As partial entropies, even their 'absolute' values may be negative. Thus, the entropies vary as expected on the basis that they are related to the degree to which the ions order the water molecules around them in the solution. Small, highly charged ions induce local structure in the surrounding water, and the disorder of the solution is decreased more than in the case of large, singly charged ions. The absolute, Third-Law standard partial molar entropy of the proton in water can be estimated by proposing a model of the structure it induces, and there is some agreement on the value −21 J K^{-1} mol^{-1}. The negative value indicates that the proton induces order in the solvent.

Brief illustration 63.2 Absolute and relative entropies

The standard molar entropy of $Cl^-(aq)$ is +57 J K^{-1} mol^{-1} and that of $Mg^{2+}(aq)$ is −128 J K^{-1} mol^{-1}. That is, the partial molar entropy of $Cl^-(aq)$ is 57 J K^{-1} mol^{-1} higher than that of the proton in water (presumably because it induces less local structure in the surrounding water), whereas that of $Mg^{2+}(aq)$ is 128 J K^{-1} mol^{-1} lower (presumably because its higher charge induces more local structure in the surrounding water).

Self-test 63.5 Estimate the absolute values of the partial molar entropies of these ions.

Answer: +36 J K^{-1} mol^{-1}, −149 J K^{-1} mol^{-1}

63.4 The standard reaction entropy

The **standard reaction entropy**, $\Delta_r S^{\ominus}$, is defined, like the standard reaction enthalpy, as the difference between the molar entropies of the pure, separated products and the pure, separated reactants, all substances being in their standard states at the specified temperature:

$$\Delta_r S^{\ominus} = \sum_J \nu_J S_m^{\ominus}(J) \qquad (63.4)$$

Definition Standard reaction entropy

where we have used the notation introduced in Topic 57. Standard reaction entropies are likely to be positive if there is a net formation of gas in a reaction, and are likely to be negative if there is a net consumption of gas.

Brief illustration 63.3 The standard reaction entropy

To calculate the standard reaction entropy of $H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(l)$ at 25 °C, we use the data in Table 57.4 of the *Resource section* to write

$$\begin{aligned}\Delta_r S^{\ominus} &= S_m^{\ominus}(H_2O,\ l)-S_m^{\ominus}(H_2,\ g)-\tfrac{1}{2}S_m^{\ominus}(O_2,\ g)\\ &= 69.9\,\mathrm{J\,K^{-1}\,mol^{-1}}-130.7\,\mathrm{J\,K^{-1}\,mol^{-1}}\\ &\quad -\tfrac{1}{2}(205.0)\,\mathrm{J\,K^{-1}\,mol^{-1}}\\ &=-163.3\,\mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

The negative value is consistent with the conversion of two gases to a compact liquid.

A note on good practice Do not make the mistake of setting the standard molar entropies of elements equal to zero: they have nonzero values (provided $T>0$), as we have already discussed.

Self-test 63.6 Calculate the standard reaction entropy for the combustion of methane to carbon dioxide and liquid water at 25 °C.

Answer: $-243\,\mathrm{J\,K^{-1}\,mol^{-1}}$

Checklist of concepts

☐ 1. Entropies are determined calorimetrically by measuring the heat capacity of a substance from low temperatures up to the temperature of interest.

☐ 2. The **Debye T^3 law** is used to estimate heat capacities of non-metallic solids close to $T=0$.

☐ 3. The **Nernst heat theorem** states that the entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero: $\Delta S\rightarrow 0$ as $T\rightarrow 0$ provided all the substances involved are perfectly ordered.

☐ 4. The **Third Law of thermodynamics** states that the entropy of all perfect crystalline substances is zero at $T=0$.

☐ 5. The **residual entropy** of a solid is the entropy arising from disorder that persists at $T=0$.

☐ 6. **Third-law entropies** are entropies based on $S(0)=0$.

☐ 7. The **standard entropies of ions in solution** are based on setting $S^{\ominus}(H^+,aq)=0$ at all temperatures.

☐ 8. The **standard reaction entropy**, $\Delta_r S^{\ominus}$, is the difference between the molar entropies of the pure, separated products and the pure, separated reactants, all substances being in their standard states at the specified temperature.

Checklist of equations

Property	Equation	Comment	Equation number
Entropy	$S(T_2)=S(T_1)+\int_{T_1}^{T_2}(C_p/T)\mathrm{d}T$	Constant pressure	63.1
Debye T^3 law	$C_p(T)=aT^3$	Non-metallic solid; low temperature	Text
Standard entropy of ions	$S^{\ominus}(H^+,aq)=0$	Convention, all temperatures	63.3
Standard reaction entropy	$\Delta_r S^{\ominus}=\sum_J \nu_J S_m^{\ominus}(J)$	Definition	63.4

TOPIC 64

Spontaneous processes

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➤ Why do you need to know this material?

Almost the whole of chemical thermodynamics—from predicting how much work a system can do to establishing criteria of equilibrium—is expressed in terms of the Gibbs energy, which is introduced in this Topic.

➤ What is the key idea?

At constant temperature and pressure, a system tends towards lower Gibbs energy.

➤ What do you need to know already?

You need to be aware of the concept of entropy (Topic 59) and its determination (Topic 63). The development of criteria for spontaneity of physical and chemical processes is based on the Clausius inequality (Topic 61).

Entropy is the basic concept for discussing the direction of natural change, but to use it we have to analyse changes in both the system and its surroundings. It is shown in Topic 61 that it is always very simple to calculate the entropy change in the surroundings; in this Topic we see that it is possible to devise a simple method for taking that contribution into account automatically. This approach focuses our attention on the system and simplifies discussions. Moreover, it is the foundation of all the applications of chemical thermodynamics described in other Topics.

64.1 Criteria of spontaneity

Consider a process taking place in a system in thermal equilibrium with its surroundings at a temperature T. The Clausius inequality derived in Topic 61 reads

$$\mathrm{d}S \geq \frac{\mathrm{d}q}{T}, \quad \text{or} \quad T\mathrm{d}S \geq \mathrm{d}q \tag{64.1}$$

We now develop this inequality in two ways according to the conditions (of constant volume or constant pressure) under which the process occurs.

(a) Changes at constant volume

First, consider the transfer of energy as heat at constant volume. Then, in the absence of non-expansion work (such as electrical work), we can write $\mathrm{d}q_V = \mathrm{d}U$; consequently the second form of eqn 64.1 becomes

$$T\mathrm{d}S \geq \mathrm{d}U \qquad (64.2)$$

Constant volume, no non-expansion work Spontaneous process

(The equality here and in the following applies to a system in which the process has reached equilibrium.) The importance of the inequality in this form is that it expresses the criterion for spontaneous change solely in terms of state functions. At either constant internal energy ($\mathrm{d}U=0$) or constant entropy ($\mathrm{d}S=0$), this expression becomes, respectively,

$$\text{(a) } \mathrm{d}S_{U,V} \geq 0 \quad \text{(b) } \mathrm{d}U_{S,V} \leq 0 \qquad (64.3)$$

Spontaneous process

The subscripts specify the constant properties.

The first inequality in eqn 64.3 states that at constant volume and constant internal energy (such as an isolated system), the entropy increases in a spontaneous change. That statement is essentially the content of the Second Law. In statistical terms, it corresponds to the tendency of an isolated system to collapse into its most probable distribution and never into a less probable one. The second inequality is less obvious, for it says that if the entropy and volume are constant, then the internal energy of the system must decrease in a spontaneous change. Do not interpret this criterion as a tendency of a system to sink to lower energy. It is a disguised statement about entropy, and should be interpreted as implying that if the entropy of the system is unchanged, then there must be an increase in entropy of the surroundings, which can be achieved only if the energy of the system decreases as energy flows out as heat.

Brief illustration 64.1 Spontaneous changes at constant volume

A concrete example of the criterion $\mathrm{d}S_{U,V} \geq 0$ is the diffusion of a solute B through a solvent A to form an ideal solution (in the sense of Topic 70, in which AA, BB, and AB interactions are identical). There is no change in internal energy or volume of the system or the surroundings as B spreads into A, but the process is spontaneous.

Self-test 64.1 Invent an example of the criterion $\mathrm{d}U_{S,V} \leq 0$.

Answer: A phase change in which one perfectly ordered phase changes into another of lower energy and equal density at $T=0$

(b) Changes at constant pressure

When energy is transferred as heat at constant pressure, and there is no work other than expansion work, we can write $\mathrm{d}q_p = \mathrm{d}H$, substitute this equality into the second form of eqn 64.2, and obtain

$$T\mathrm{d}S \geq \mathrm{d}H \qquad (64.4)$$

Constant pressure, no additional work Spontaneous process

At either constant enthalpy ($\mathrm{d}H=0$) or constant entropy ($\mathrm{d}S=0$) this inequality becomes, respectively,

$$\text{(a) } \mathrm{d}S_{H,p} \geq 0 \quad \text{(b) } \mathrm{d}H_{S,p} \leq 0 \qquad (64.5)$$

Spontaneous process

The interpretations of these two inequalities are similar to those of eqn 64.3. The entropy of the system at constant pressure must increase if its enthalpy remains constant (for there can then be no change in entropy of the surroundings if no heat flows into them). Alternatively, the enthalpy must decrease if the entropy of the system is constant, for then it is essential to have an increase in entropy of the surroundings, which requires heat to spread into them.

Brief illustration 64.2 Spontaneous changes at constant pressure

A concrete example of the criterion $\mathrm{d}S_{H,p} \geq 0$ is the mixing of two perfect gases. For instance, if gas A is in a container at a certain pressure and the same amount of B is in a container of the same volume and at the same pressure, then when the connection between the containers is opened, the gases mix spontaneously. The pressure remains the same and, in the absence of intermolecular interactions, the enthalpy is unchanged. Only the entropy increases.

Self-test 64.2 Invent an example of the criterion $\mathrm{d}H_{S,p} \leq 0$.

Answer: An exothermic phase change at $T=0$ and 1 bar in which one perfectly ordered phase changes into another of differing density

64.2 The Helmholtz and Gibbs energies

Because eqns 64.2 and 64.4 can be written in the form $\mathrm{d}U - T\mathrm{d}S \leq 0$ and $\mathrm{d}H - T\mathrm{d}S \leq 0$, respectively, they can be expressed more simply by introducing two more thermodynamic quantities. One is the **Helmholtz energy**, A, which is defined as

$$A = U - TS \qquad (64.6)$$

Definition Helmholtz energy

The other function we introduce is the **Gibbs energy**, G:

$$G = H - TS \qquad \textit{Definition} \quad \text{Gibbs energy} \qquad (64.7)$$

For reasons that will become clear, both functions are also often referred to as 'free energies' and distinguished as 'Helmholtz free energy' and 'Gibbs free energy'.

(a) Criteria of spontaneity and equilibrium

When the state of the system changes at constant temperature ($\mathrm{d}T = 0$), the two properties change as follows:

$$\begin{aligned} &\text{(a)}\ \mathrm{d}A = \mathrm{d}U - T\mathrm{d}S \\ &\text{(b)}\ \mathrm{d}G = \mathrm{d}H - T\mathrm{d}S \end{aligned} \qquad \textit{Constant temperature} \quad \text{Changes in } A \text{ and } G \qquad (64.8)$$

When we introduce eqns 64.2 ($T\mathrm{d}S \geq \mathrm{d}U$) and 64.4 ($T\mathrm{d}S \geq \mathrm{d}H$), respectively, we obtain the criteria of spontaneous change as

$$\text{(a)}\ \mathrm{d}A_{T,V} \leq 0 \quad \text{(b)}\ \mathrm{d}G_{T,p} \leq 0 \qquad \text{Spontaneous process} \qquad (64.9)$$

These inequalities are the most important conclusions from thermodynamics for chemistry.

The expressions $\mathrm{d}A = \mathrm{d}U - T\mathrm{d}S$ and $\mathrm{d}A < 0$ are sometimes interpreted as follows. A negative value of $\mathrm{d}A$ is favoured by a negative value of $\mathrm{d}U$ and a positive value of $T\mathrm{d}S$. This observation suggests that the tendency of a system to move to lower A is due to its tendency to move towards states of lower internal energy and higher entropy. However, this interpretation is false (even though it is a good rule of thumb for remembering the expression for $\mathrm{d}A$) because the tendency to lower A is solely a tendency towards states of greater overall entropy. Systems change spontaneously if in doing so the total entropy of the system and its surroundings increases, not because they tend to lower internal energy. The form of $\mathrm{d}A$ may give the impression that systems favour lower energy, but that is misleading: $\mathrm{d}S$ is the entropy change of the system, $-\mathrm{d}U/T$ is the entropy change of the surroundings (when the volume of the system is constant), and their total tends to a maximum.

The Gibbs energy is more common in chemistry than the Helmholtz energy because, at least in laboratory chemistry, we are usually more interested in changes occurring at constant pressure than at constant volume. The criterion $\mathrm{d}G_{T,p} < 0$ carries over into chemistry as the observation that, *at constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy*. Therefore, if we want to know whether a reaction is spontaneous, the pressure and temperature being constant, we assess the change in the Gibbs energy. If G decreases as the reaction proceeds, then the reaction has a spontaneous tendency to convert the reactants into products. If G increases, then the reverse reaction is spontaneous.

Brief illustration 64.3 The spontaneity of endothermic reactions

The existence of spontaneous endothermic reactions provides an illustration of the role of G. In such reactions, H increases, the system rises spontaneously to states of higher enthalpy, and $\mathrm{d}H > 0$. Because the reaction is spontaneous we know that $\mathrm{d}G < 0$ despite $\mathrm{d}H > 0$; it follows that the entropy of the system increases so much that $T\mathrm{d}S$ outweighs $\mathrm{d}H$ in $\mathrm{d}G = \mathrm{d}H - T\mathrm{d}S$. Endothermic reactions are therefore driven by the increase of entropy of the system, and this entropy change overcomes the reduction of entropy brought about in the surroundings by the inflow of heat into the system ($\mathrm{d}S_{\mathrm{sur}} = -\mathrm{d}H/T$ at constant pressure).

Self-test 64.3 Why are so many exothermic reactions spontaneous?

Answer: With $\mathrm{d}H < 0$, it is common for $\mathrm{d}G < 0$ unless $T\mathrm{d}S$ is strongly negative

According to the discussion so far, a change in a system at constant temperature and volume is spontaneous if $\mathrm{d}A_{T,V} < 0$ and, if instead temperature and pressure are constant, then if $\mathrm{d}G_{T,p} < 0$. That is, a change under these conditions is spontaneous if it corresponds to a decrease in the Helmholtz energy or Gibbs energy, respectively. Such systems move spontaneously towards states of lower A or G if a path is available. The criterion of equilibrium, when neither the forward nor reverse process has a tendency to occur, is

$$\text{(a)}\ \mathrm{d}A_{T,V} = 0 \quad \text{(b)}\ \mathrm{d}G_{T,p} = 0 \qquad \text{Equilibrium} \qquad (64.10)$$

We build on these criteria, and especially the second, in other Topics.

(b) The statistical basis of the Helmholtz and Gibbs energies

Both A and G can be expressed in terms of the partition functions developed in Topics 52 and 54, which give a route to their calculation and molecular interpretation. The Helmholtz energy has a very simple relation to the canonical partition function. First, note that $A(0) = U(0)$, and then use eqn 60.5 ($S = \{U - U(0)\}/T + k \ln Q$) to find

$$A - A(0) = -kT \ln Q \qquad \text{Helmholtz energy} \qquad (64.11a)$$

For a system composed of independent, indistinguishable molecules (as in a perfect gas), we may replace Q by $q^N/N!$ and obtain

$$A-A(0)=-kT\ln\frac{q^N}{N!}=-NkT\ln q+kT\ln N!$$

Then, by using Stirling's approximation (eqn 51.2b, that $\ln N!\approx N\ln N-N$) and expressing NkT as $NkT\ln \mathrm{e}$ (because $\ln \mathrm{e}=1$),

$$\begin{aligned}A-A(0)&=-NkT\ln q+kT(N\ln N-N)\\&=-NkT\ln q+NkT\ln N-NkT\ln \mathrm{e}\\&=-NkT(\ln q-\ln N+\ln \mathrm{e})\end{aligned}$$

That is,

$$A-A(0)=-NkT\ \ln\frac{q\mathrm{e}}{N} \qquad (64.11\mathrm{b})$$

Independent, indistinguishable molecules Helmholtz energy

We see that $A-A(0)$ is essentially proportional to the logarithm of the molecular partition function, and therefore that it is (negatively) large when many energy levels are thermally accessible.

Brief illustration 64.4 The molar Helmholtz energy

In Topic 52, *Brief illustration* 52.2, it is calculated that $q=2.77\times10^{26}$ for the translational partition function of H_2 in a 100 cm³ vessel at 25 °C. For a sample of the gas that contains 1 mol H_2, corresponding to 6.022×10^{23} molecules, the contribution to the Helmholtz energy due to translational motion is

$$\begin{aligned}A-A(0)=&-(6.022\times10^{23})\times(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\\&\times(298\,\mathrm{K})\times\ln\frac{(2.77\times10^{26})\times\mathrm{e}}{6.022\times10^{23}}\\=&-17.7\,\mathrm{kJ}\end{aligned}$$

Therefore, because this number of molecules corresponds to 1 mol H_2, the contribution to the molar Helmholtz energy is −17.7 kJ mol⁻¹.

Self-test 64.4 What is the total contribution of the translational and rotational motion of the molecules? The rotational partition function of H_2 at 25 °C is 1.14.

Answer: −18.0 kJ mol⁻¹

The Gibbs energy can now be expressed in terms of a partition function. Because $H=U+pV$ and $A=U-TS$, we can write $G=A+pV$ and from eqn 64.11a obtain the statistical thermodynamic expression for the Gibbs energy as

$$G-G(0)=-kT\ \ln Q+pV \qquad (64.12\mathrm{a})$$

Gibbs energy

For a gas of independent particles, pV can be replaced by nRT and Q by $q^N/N!$. It follows that

$$\begin{aligned}G-G(0)&=-kT\ln\frac{q^N}{N!}+\overbrace{nRT}^{nN_AkT=NkT}\\&=-NkT\ln q+kT\overbrace{\ln N!}^{\ln N!\approx N\ln N-N}+NkT\\&=-NkT\ln q+kT(N\ln N-N)+NkT\\&=-NkT\ln q+NkT\ln N\end{aligned}$$

In the second line we have once again used Stirling's approximation. We conclude that

$$G-G(0)=-NkT\ln\frac{q}{N} \qquad (64.12\mathrm{b})$$

Independent, indistinguishable molecules Gibbs energy

Brief illustration 64.5 The molar Gibbs energy

The only difference between eqns 64.11b and eqn 64.12b is the presence of e in the former, so it is easy to adapt the calculation in *Brief illustration* 64.4 to find the translational contribution to the molar Gibbs energy of $H_2(g)$. First we note that

$$\begin{aligned}G-G(0)=&-(6.022\times10^{23})\times(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\\&\times(298\,\mathrm{K})\times\ln\frac{2.77\times10^{26}}{6.022\times10^{23}}\\=&-15.2\,\mathrm{kJ}\end{aligned}$$

Therefore, because this number of molecules corresponds to 1 mol H_2, the contribution to the molar Gibbs energy is −15.2 kJ mol⁻¹.

Self-test 64.5 What is the total contribution of the translational and rotational motion of the molecules? The rotational partition function of H_2 at 25 °C is 1.14.

Answer: −15.5 kJ mol⁻¹

As we shall see, it is easier to give precise molecular interpretations of the Helmholtz energy than of the Gibbs energy, just as it is easier to give precise molecular interpretations of the internal energy than the enthalpy. However, it will also turn out that the Gibbs energy is more important than the Helmholtz energy in chemistry, just as enthalpy is more important than the internal energy. Fortunately, because (like H and U), G differs from A by the addition of the term pV, we may use—with caution in some cases—the molecular interpretation of A to interpret most of the properties of G.

64.3 Maximum work

It turns out that A and G carry a greater significance than being simply a signpost of spontaneous change. They each indicate the maximum work, of various kinds, that can be extracted from a process under certain conditions.

(a) Maximum total work

As we show in the following *Justification*: *the change in the Helmholtz energy is equal to the maximum work accompanying a process at constant temperature*:

$$\mathrm{d}w_{\max} = \mathrm{d}A \qquad (64.13)$$

Constant temperature Maximum work

As a result, A is sometimes called the 'maximum work function', or the 'work function'. (*Arbeit* is the German word for work; hence the symbol A.)

Justification 64.1 Maximum work

To demonstrate that maximum work can be expressed in terms of the changes in Helmholtz energy, we combine the Clausius inequality $\mathrm{d}S \geq \mathrm{d}q/T$ (Topic 61) in the form $T\mathrm{d}S \geq \mathrm{d}q$ with the First Law, $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$, and obtain

$$\mathrm{d}U \leq T\mathrm{d}S + \mathrm{d}w$$

($\mathrm{d}U$ can be smaller than the term on the right because we are replacing $\mathrm{d}q$ by $T\mathrm{d}S$, which in general is larger.) This expression rearranges to $\mathrm{d}U - T\mathrm{d}S \leq \mathrm{d}w$ and therefore to

$$\mathrm{d}w \geq \mathrm{d}U - T\mathrm{d}S$$

Now recall that a large negative w means that a lot of energy has been transferred *from* the system as work—the system has done a lot of work. It follows that the most negative value of $\mathrm{d}w$, and therefore the maximum energy that can be obtained from the system as work, must correspond to the equals sign in this expression because a higher (less negative) value of $\mathrm{d}w$ implies that less work has been done. Therefore,

$$\mathrm{d}w_{\max} = \mathrm{d}U - T\mathrm{d}S$$

This maximum work is done only when the path is traversed reversibly (because then the equality in $\mathrm{d}S \geq \mathrm{d}q/T$ applies). Because at constant temperature $\mathrm{d}A = \mathrm{d}U - T\mathrm{d}S$, we conclude that $\mathrm{d}w_{\max} = \mathrm{d}A$.

The relation between A and maximum work can be understood in molecular terms by noting that, in terms of the molecular partition function and eqn 64.11b ($A = A(0) - NkT\ln(q\mathrm{e}/N)$),

$$\Delta A = \overbrace{A(0) - NkT\ln\frac{q_\mathrm{f}\mathrm{e}}{N}}^{A_\mathrm{f}} - \left(\overbrace{A(0) - NkT\ln\frac{q_\mathrm{i}\mathrm{e}}{N}}^{A_\mathrm{i}}\right) = -NkT\ln\frac{q_\mathrm{f}}{q_\mathrm{i}} \qquad (64.14)$$

where q_f is the partition function for the final state and q_i that of the initial state. The rotational and vibrational partition functions are unchanged on expansion because they depend on only the internal variables of the molecules (Topic 52), so cancel in the expression $q_\mathrm{f}/q_\mathrm{i}$, leaving only the ratio of translational contributions. However, because q for translational motion is proportional to V (from Topic 52, $q^\mathrm{T} = V/\Lambda^3$) we immediately find that

$$w_{\max} = -NkT\ln\frac{V_\mathrm{f}}{V_\mathrm{i}} \qquad (64.15)$$

which is the same expression as we found for the reversible, isothermal expansion of a perfect gas. We can now see that reversible expansion produces maximum work because it corresponds to the progressive change of the distribution of molecules through a sequence of equilibrium states (those corresponding to the Boltzmann distribution, as expressed by the partition function).

When a measurable isothermal change takes place in the system, eqn 64.13 becomes

$$w_{\max} = \Delta A, \quad \Delta A = \Delta U - T\Delta S \qquad (64.16)$$

Constant temperature Maximum work

This expression shows that in some cases, depending on the sign of $T\Delta S$, not all the change in internal energy may be available for doing work. If the change occurs with a decrease in entropy (of the system), in which case $T\Delta S < 0$, then $\Delta A = \Delta U - T\Delta S$ is not as negative as ΔU itself, and consequently the maximum work is less than ΔU. For the change to be spontaneous, some of the energy must escape as heat in order to generate enough entropy in the surroundings to overcome the reduction in entropy in the system (Fig. 64.1). In this case, Nature is

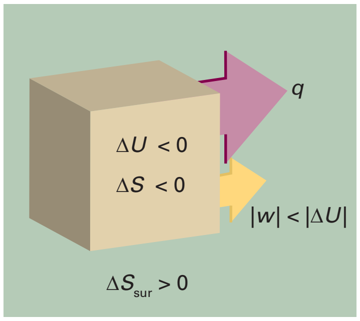

Figure 64.1 In a system not isolated from its surroundings, the work done may be different from the change in internal energy. Moreover, the process is spontaneous if overall the entropy of the system and its surroundings increases. In the process depicted here, the entropy of the system decreases, so that of the surroundings must increase in order for the process to be spontaneous, which means that energy must pass from the system to the surroundings as heat. Therefore, less work than ΔU can be obtained.

demanding a tax on the internal energy as it is converted into work. This is the origin of the alternative name ‘Helmholtz free energy’ for A, because ΔA is that part of the change in internal energy that we are free to use to do work.

Further insight into the relation between the work that a system can do and the Helmholtz energy is to recall that work is energy transferred to the surroundings as the uniform motion of atoms. We can interpret the expression $A = U - TS$ as showing that A is the total internal energy of the system, U, less a contribution that is stored as energy of thermal motion (the quantity TS). Because energy stored in random thermal motion cannot be used to achieve uniform motion in the surroundings, only the part of U that is not stored in that way, the quantity $U - TS$, is available for conversion into work.

If the change occurs with an increase of entropy of the system (in which case $T\Delta S > 0$), then $\Delta A = \Delta U - T\Delta S$ is more negative than ΔU. In this case, the maximum work that can be obtained from the system is greater than ΔU. The explanation of this apparent paradox is that the system is not isolated and energy may flow in as heat as work is done. Because the entropy of the system increases, we can afford a reduction of the entropy of the surroundings yet still have, overall, a spontaneous process. Therefore, some energy (no more than the value of $T\Delta S$) may leave the surroundings as heat and contribute to the work the change is generating (Fig. 64.2). Nature is now providing a tax refund.

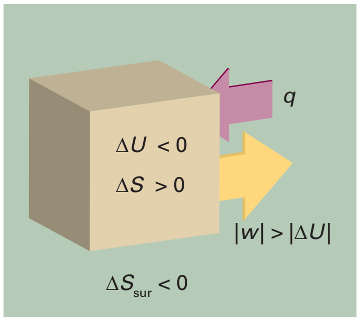

Figure 64.2 In this process, the entropy of the system increases, hence we can afford to lose some entropy of the surroundings. That is, some of their energy may be lost as heat to the system. This energy can be returned to them as work. Hence the work done can exceed ΔU.

Example 64.1 Calculating the maximum available work

When 1.000 mol $C_6H_{12}O_6$ (glucose) is oxidized to carbon dioxide and water at 25 °C according to the equation $C_6H_{12}O_6(s) + 6\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O(l)$, calorimetric measurements give $\Delta_r U^{\ominus} = -2808$ kJ mol^{-1} and $\Delta_r S^{\ominus} = +182.4$ J K^{-1} mol^{-1} at 25 °C. How much of this energy change can be extracted as (a) heat at constant pressure, (b) work?

Method We know that the heat released at constant pressure is equal to the value of ΔH, so we need to relate $\Delta_r H^{\ominus}$ to $\Delta_r U^{\ominus}$, which is given. To do so, we suppose that all the gases involved are perfect, and use eqn 57.3 of Topic 57 ($\Delta H = \Delta U + \Delta n_g RT$). For the maximum work available from the process we use eqn 64.16.

Answer (a) Because $\Delta n_g = 0$, we know that $\Delta_r H^{\ominus} = \Delta_r U^{\ominus} = -2808$ kJ mol^{-1}. Therefore, at constant pressure, the energy available as heat is 2808 kJ mol^{-1}. (b) Because $T = 298$ K, the value of $\Delta_r A^{\ominus}$ is

$$\Delta_r A^{\ominus} = \Delta_r U^{\ominus} - T\Delta_r S^{\ominus} = -2862\,\mathrm{kJ\,mol^{-1}}$$

Therefore, the combustion of 1.000 mol $C_6H_{12}O_6$ can be used to produce up to 2862 kJ of work. The maximum work available is greater than the change in internal energy on account of the positive entropy of reaction (which is partly due to the generation of a large number of small molecules from one big one). The system can therefore draw in energy from the surroundings (so reducing their entropy) and make it available for doing work.

Self-test 64.6 Repeat the calculation for the combustion of 1.000 mol $CH_4(g)$ under the same conditions, using data from Tables 57.3 and 57.4 of the *Resource section*.

Answer: $|q_p| = 890$ kJ, $|w_{\mathrm{max}}| = 813$ kJ

(b) Maximum non-expansion work

The analogue of the maximum work interpretation of ΔA, and the origin of the name ‘Gibbs free energy’, can be found for ΔG. In the following *Justification* we show that at constant temperature and pressure (note the two constraints), the maximum additional (non-expansion) work, $w_{\mathrm{add,max}}$, is given by the change in Gibbs energy:

$$\mathrm{d}w_{\mathrm{add,max}} = \mathrm{d}G \qquad (64.17a)$$

Constant temperature and pressure Maximum non-expansion work

The corresponding expression for a measurable change is

$$w_{\mathrm{add,max}} = \Delta G, \ \Delta G = \Delta H - T\Delta S \qquad (64.17b)$$

Constant temperature and pressure Maximum non-expansion work

This expression is particularly useful for assessing the electrical work that may be produced by fuel cells and electrochemical cells, and we shall see many applications of it.

Justification 64.2 Maximum non-expansion work

Because $H=U+pV$, for a general change in conditions, the change in enthalpy is

$$\mathrm{d}H=\mathrm{d}q+\mathrm{d}w+\mathrm{d}(pV)$$

The corresponding change in Gibbs energy ($G=H-TS$) is

$$\mathrm{d}G=\mathrm{d}H-T\mathrm{d}S-S\mathrm{d}T=\mathrm{d}q+\mathrm{d}w+\mathrm{d}(pV)-T\mathrm{d}S-S\mathrm{d}T$$

When the change is isothermal we can set $\mathrm{d}T=0$; then

$$\mathrm{d}G=\mathrm{d}q+\mathrm{d}w+\mathrm{d}(pV)-T\mathrm{d}S$$

When the change is reversible, $\mathrm{d}w=\mathrm{d}w_{\mathrm{rev}}$ and $\mathrm{d}q=\mathrm{d}q_{\mathrm{rev}}=T\mathrm{d}S$, so for a reversible, isothermal process

$$\mathrm{d}G=T\mathrm{d}S+\mathrm{d}w_{\mathrm{rev}}+\mathrm{d}(pV)-T\mathrm{d}S=\mathrm{d}w_{\mathrm{rev}}+\mathrm{d}(pV)$$

The work consists of expansion work, which for a reversible change is given by $-p\mathrm{d}V$, and possibly some other kind of work (for instance, the electrical work of pushing electrons through a circuit or of raising a column of liquid); this additional work we denote $\mathrm{d}w_{\mathrm{add}}$. Therefore, with $\mathrm{d}(pV)=p\mathrm{d}V+V\mathrm{d}p$,

$$\mathrm{d}G=(-p\mathrm{d}V+\mathrm{d}w_{\mathrm{add,rev}})+p\mathrm{d}V+V\mathrm{d}p=\mathrm{d}w_{\mathrm{add,rev}}+V\mathrm{d}p$$

If the change occurs at constant pressure (as well as constant temperature), we can set $\mathrm{d}p=0$ and obtain $\mathrm{d}G=\mathrm{d}w_{\mathrm{add,rev}}$. Therefore, at constant temperature and pressure, $\mathrm{d}w_{\mathrm{add,rev}}=\mathrm{d}G$. However, because the process is reversible, the work done must now have its maximum value, so eqn 64.17 follows.

Example 64.2 Calculating the maximum non-expansion work of a reaction

How much energy is available for sustaining muscular and nervous activity from the combustion of 1.00 mol of glucose molecules under standard conditions at 37 °C (blood temperature)? The standard entropy of reaction is $+182.4\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

Method The non-expansion work available from the reaction is equal to the change in standard Gibbs energy for the reaction ($\Delta_\mathrm{r}G^\ominus$, a quantity defined more fully in Topic 65). To calculate this quantity, it is legitimate to ignore the temperature dependence of the reaction enthalpy, to obtain $\Delta_\mathrm{r}H^\ominus$ from Tables 57.3 and 57.4, and to substitute the data into $\Delta_\mathrm{r}G^\ominus=\Delta_\mathrm{r}H^\ominus-T\Delta_\mathrm{r}S^\ominus$.

Answer Because the standard reaction enthalpy is $-2808\,\mathrm{kJ\,mol^{-1}}$ (see Example 64.1), it follows that the standard reaction Gibbs energy is

$$\begin{aligned}\Delta_\mathrm{r}G^\ominus&=-2808\ \mathrm{kJ\ mol^{-1}}-(310\,\mathrm{K})\times(182.4\,\mathrm{J\,K^{-1}mol^{-1}})\\&=-2865\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Therefore, $w_{\mathrm{add,max}}=-2865$ kJ for the combustion of 1 mol glucose molecules (180 g of glucose), and the reaction can be used to do up to 2865 kJ of non-expansion work. To place this result in perspective, consider that a person of mass 70 kg needs to do 2.1 kJ of work to climb vertically through 3.0 m; therefore, at least (2.1 kJ/2865 kJ) × 180 g = 0.13 g of glucose is needed to complete the task (and in practice significantly more).

Self-test 64.7 How much non-expansion work can be obtained from the combustion of 1.00 mol $CH_4(g)$ under standard conditions at 298 K? Use $\Delta_\mathrm{r}S^\ominus=-243\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

Answer: 818 kJ

Checklist of concepts

☐ 1. The **Gibbs and Helmholtz energies** provide criteria for spontaneity at constant pressure and constant volume, respectively.

☐ 2. The change in the Helmholtz energy is equal to the **maximum work** accompanying a process at constant temperature.

☐ 3. The change in the Gibbs energy is equal to the **maximum non-expansion work** accompanying a process at constant temperature and pressure.

Checklist of equations

Property	Equation	Comment	Equation number
Criteria of spontaneity	(a) $\mathrm{d}S_{U,V}\geq 0$, (b) $\mathrm{d}U_{S,V}\leq 0$	Constant volume (etc.)*	64.3
	(a) $\mathrm{d}S_{H,p}\geq 0$, (b) $\mathrm{d}H_{S,p}\leq 0$	Constant pressure (etc.)	64.5
Helmholtz energy	$A=U-TS$	Definition	64.6

Property	Equation	Comment	Equation number
Gibbs energy	$G = H - TS$	Definition	64.7
Criteria of spontaneity	(a) $\mathrm{d}A_{T,V} \le 0$, (b) $\mathrm{d}G_{T,p} \le 0$	Constant temperature (etc.)	64.9
Equilibrium	(a) $\mathrm{d}A_{T,V} = 0$, (b) $\mathrm{d}G_{T,p} = 0$	Constant temperature (etc.)	64.10
Statistical calculation	$A - A(0) = -kT \ln Q$	General case	64.11a
	$A - A(0) = -NkT \ln (qe/N)$	Independent and indistinguishable molecules	64.11b
	$G - G(0) = -kT \ln Q + pV$	General case	64.12a
	$G - G(0) = -NkT \ln(q/N)$	Independent and indistinguishable molecules	64.12b
Maximum work	$\mathrm{d}w_{\max} = \mathrm{d}A$, $w_{\max} = \Delta A$	Constant temperature	64.13, 64.16
Maximum non-expansion work	$\mathrm{d}w_{\mathrm{add,max}} = \mathrm{d}G$, $w_{\mathrm{add,max}} = \Delta G$	Constant temperature and pressure	64.17

* The other constant properties are specified as subscripts; the equality applies at equilibrium

TOPIC 65

Standard Gibbs energies

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➤ Why do you need to know this material?

The practical implementation of thermodynamics in a wide range of problems, including the discussion of equilibrium and electrochemistry, depends on being able to use the data described in this Topic to calculate the Gibbs energies of reactions.

➤ What is the key idea?

The standard Gibbs energy of reaction can be calculated from the standard Gibbs energies of formation of the reactants and products.

➤ What do you need to know already?

You need to be aware of the definition of the Gibbs energy (Topic 64) and of the concepts of standard and reference states (Topic 57). The standard enthalpy and entropy of reaction are defined in Topics 57 and 63. The statistical interpretation of values of thermodynamic properties draws on the material in Topics 53 and 60. The derivation of the Born equation uses information on electrostatics described in *Foundations*, Topic 2.

The definition of Gibbs energy (Topic 64) is $G=H-TS$. It follows that the standard value of the Gibbs energy, the value it has when the species are in their standard states (pure, at 1 bar) is $G^{\ominus}=H^{\ominus}-TS^{\ominus}$. The **standard Gibbs energy of reaction** (or 'standard reaction Gibbs energy'), $\Delta_r G^{\ominus}$, is the difference in standard molar Gibbs energies of the products and reactants in their standard states at the temperature specified for the reaction as written. In the notation introduced in Topic 57,

$$\Delta_r G^{\ominus}=\sum_J \nu_J G_m^{\ominus}(J) \qquad (65.1)$$

Definition Standard reaction Gibbs energy

where ν_J is positive for products and negative for reactants. (That is, eqn 65.1 gives the difference 'products − reactants', weighted by their respective stoichiometric coefficients.) One approach to the calculation of standard Gibbs energy of reaction $\Delta_r G^{\ominus}$ is simply to combine the corresponding standard enthalpy and entropy of reaction, and to write

$$\Delta_r G^{\ominus}=\Delta_r H^{\ominus}-T\Delta_r S^{\ominus} \qquad (65.2)$$

Standard reaction Gibbs energy

Values of $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$ may be obtained from calorimetric measurements, as described in Topics 57 and 63. Another route to the determination of $\Delta_r G^{\ominus}$ is electrochemistry, as described in Topics 76 and 77.

65.1 Gibbs energies of formation

As in the case of standard reaction enthalpies (Topic 57), it is convenient to define the **standard Gibbs energies of formation**, $\Delta_f G^{\ominus}$, the standard reaction Gibbs energy for the formation per mole of a compound from its elements in their reference states, their most stable states at the specified temperature and 1 bar. Standard Gibbs energies of formation of the elements in their reference states are zero, because their formation is a 'null' reaction. A selection of values for compounds is given in Table 65.1. From the values given there, it is a simple matter to obtain the

Table 65.1* Standard Gibbs energies of formation (at 298 K)

	$\Delta_f G^{\ominus}/(\text{kJ mol}^{-1})$
Diamond, C(s)	+2.9
Benzene, C_6H_6(l)	+124.3
Methane, CH_4(g)	−50.7
Carbon dioxide, CO_2(g)	−394.4
Water, H_2O(l)	−237.1
Ammonia, NH_3(g)	−16.5
Sodium chloride, NaCl(s)	−384.1

* More values are given in the *Resource section*.

standard Gibbs energy of reaction by taking the appropriate 'products – reactants' combination:

$$\Delta_r G^{\ominus} = \sum_J \nu_J \Delta_f G^{\ominus}(J) \qquad (65.3)$$

Practical implementation Standard reaction Gibbs energy

Brief illustration 65.1 The reaction Gibbs energy

To calculate the standard Gibbs energy of the reaction $CO(g)+\frac{1}{2}O_2(g)\rightarrow CO_2(g)$ at 298 K, we write

$$\begin{aligned}\Delta_r G^{\ominus} &= \Delta_f G^{\ominus}(CO_2,g)-\Delta_f G^{\ominus}(CO,g)-\tfrac{1}{2}\Delta_f G^{\ominus}(O_2,g)\\ &= -394.4\,\text{kJ mol}^{-1}-(-137.2)\,\text{kJ mol}^{-1}-\tfrac{1}{2}(0)\\ &= -257.2\,\text{kJ mol}^{-1}\end{aligned}$$

Self-test 65.1 Calculate the standard reaction Gibbs energy for the combustion of CH_4(g) at 298 K.

Answer: −818 kJ mol⁻¹

Calorimetry (for ΔH directly, and for S from heat capacities) is only one of the ways of determining standard Gibbs energies of formation by forming the combination $\Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$. They may also be calculated from spectroscopic data. Thus, it is established in Topic 64 that the Gibbs energy of a gaseous species can be calculated from the molecular partition function by using eqn 64.12 ($G - G(0) = -NkT\ln(q/N)$, with $Nk = nN_A k = nR$) by using data from spectroscopy. For such calculations, it is convenient to introduce the **molar partition function**, $q_m = q/n$, with $n = N/N_A$, and then to write the expression for the standard value of G_m as

$$G_m^{\ominus} = G_m^{\ominus}(0) - RT\ln\frac{q_m^{\ominus}}{N_A} \qquad (65.4)$$

Calculation of G

To use this equation, note that $G_m^{\ominus}(0) = U_m^{\ominus}(0)$ and that $U_m^{\ominus}(0)$ is simply the molar ground-state energy of the species, E_m, because no other states are occupied at $T = 0$. The E_m may then be identified with the dissociation energies of the species.

Example 65.1 Calculating a standard Gibbs energy of formation from partition functions

Calculate the standard Gibbs energy of formation of H_2O(g) at 25 °C.

Method Write the chemical equation for the formation reaction, and then the expression for the standard Gibbs energy of formation in terms of the Gibbs energy of each molecule; then express those Gibbs energies in terms of the molecular partition function of each species by using eqn 64.12. Ignore molecular vibration as it is unlikely to be excited at 25 °C. Take numerical values from the *Resource section* together with the following rotational constants of H_2O: 27.877, 14.512, and 9.285 cm⁻¹.

Answer The chemical reaction is $H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(g)$. Therefore,

$$\Delta_f G^{\ominus} = G_m^{\ominus}(H_2O,g) - G_m^{\ominus}(H_2,g) - \tfrac{1}{2}G_m^{\ominus}(O_2,g)$$

Now write the standard molar Gibbs energies in terms of the standard molar partition functions of each species J:

$$G_m^{\ominus}(J) = E_m(J) - RT\ln\frac{q_m^{\ominus}(J)}{N_A},$$

$$q_m^{\ominus}(J) = q_m^{T\ominus}(J)\,q^R(J) = \frac{V_m^{\ominus}}{\Lambda(J)^3}\,q^R(J)$$

Therefore

$$\begin{aligned}\Delta_f G^{\ominus} &= \left\{E_m(H_2O) - RT\ln\frac{q_m^{\ominus}(H_2O)}{N_A}\right\}\\ &\quad -\left\{E_m(H_2) - RT\ln\frac{q_m^{\ominus}(H_2)}{N_A}\right\}\\ &\quad -\frac{1}{2}\left\{E_m(O_2) - RT\ln\frac{q_m^{\ominus}(O_2)}{N_A}\right\}\\ &= \Delta E_m - RT\ln\frac{\overbrace{\{V_m^{\ominus}/N_A\Lambda(H_2O)^3\}q^R(H_2O)}^{q_m^{\ominus}(H_2O)/N_A}}{\left[\underbrace{\{V_m^{\ominus}/N_A\Lambda(H_2)^3\}q^R(H_2)}_{q_m^{\ominus}(H_2)/N_A}\right]\times\left[\underbrace{\{V_m^{\ominus}/N_A\Lambda(O_2)^3\}q^R(O_2)}_{q_m^{\ominus}(O_2)/N_A}\right]^{1/2}}\\ &= \Delta E_m - RT\ln\frac{N_A^{1/2}\{\Lambda(H_2)\Lambda(O_2)^{1/2}/\Lambda(H_2O)\}^3}{V_m^{\ominus 1/2}\{q^R(H_2)q^R(O_2)^{1/2}/q^R(H_2O)\}}\end{aligned}$$

where

$$\Delta E_m = E_m(H_2O) - E_m(H_2) - \frac{1}{2}E_m(O_2)$$

At this point we introduce the thermal wavelengths and the rotational partition functions (eqns 52.7b, 52.13, and 52.14 of Topic 52):

$$\Lambda(\mathrm{J})=\frac{h}{\{2\pi m(\mathrm{J})kT\}^{1/2}} \qquad q^{\mathrm{R}}=\overbrace{\frac{kT}{2hc\tilde{B}}}^{\text{Linear molecule, }\sigma=2}$$

$$\text{and} \quad q^{\mathrm{R}}=\overbrace{\frac{1}{2}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2}}^{\text{Nonlinear molecule, }\sigma=2}$$

and set $V_{\mathrm{m}}^{\ominus}=RT/p^{\ominus}$. Now substitute the data, and find

$$\Lambda(\mathrm{H_2})=71.21\,\mathrm{pm} \qquad \Lambda(\mathrm{O_2})=17.87\,\mathrm{pm} \qquad \Lambda(\mathrm{H_2O})=23.82\,\mathrm{pm}$$
$$q^{\mathrm{R}}(\mathrm{H_2})=1.702 \qquad q^{\mathrm{R}}(\mathrm{O_2})=71.60 \qquad q^{\mathrm{R}}(\mathrm{H_2O})=42.13$$

It then follows that

$$\Delta_{\mathrm{f}}G^{\ominus}=\Delta E_{\mathrm{m}}-RT\ln 0.0291=\Delta E_{\mathrm{m}}+8.77\,\mathrm{kJ\,mol^{-1}}$$

Now use

$$\begin{aligned}\Delta E_{\mathrm{m}}&=-D(\mathrm{H_2O})+D(\mathrm{H_2})+\tfrac{1}{2}D(\mathrm{O_2})\\&=-(498+428)+436+\tfrac{1}{2}\times 498\,\mathrm{kJ\,mol^{-1}}=-241\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

where the D are dissociation energies. Thus,

$$\Delta_{\mathrm{f}}G^{\ominus}=-241+8.77\,\mathrm{kJ\,mol^{-1}}=-232\,\mathrm{kJ\,mol^{-1}}$$

The value quoted in Table 65.1 is –228.57 kJ mol^{-1}; the discrepancy is probably due to the use of the high-temperature approximation for the rotational partition functions.

Self-test 65.2 Estimate the standard Gibbs energy of formation of $\mathrm{NH_3}$(g) at 25 °C.

Answer: Experimental value: –16.45 kJ mol^{-1}

65.2 Ions in solution

Ions in solution present a special problem for the definition of their standard Gibbs energy of formation, for cations are always accompanied by anions. Therefore, to discuss individual ions, we need to adopt a convention.

(a) The convention

Just as in Topic 57 for enthalpies of formation, we define one ion, conventionally the hydrogen ion, to have zero standard Gibbs energy of formation at all temperatures:

$$\Delta_{\mathrm{f}}G^{\ominus}(\mathrm{H^+,aq})=0 \qquad \textit{Convention} \qquad \text{Standard Gibbs energy of formation of H}^+\text{(aq)} \tag{65.5}$$

In essence, this definition adjusts the actual values of the Gibbs energies of formation of ions by a fixed amount, which is chosen so that the standard value for one of them, H$^+$(aq), has the value zero. Then for the reaction

$$\tfrac{1}{2}\mathrm{H_2(g)}+\tfrac{1}{2}\mathrm{Cl_2(g)}\rightarrow \mathrm{H^+(aq)}+\mathrm{Cl^-(aq)}$$
$$\Delta_{\mathrm{r}}G^{\ominus}=-131.23\ \mathrm{kJ\,mol^{-1}}$$

we can write

$$\Delta_{\mathrm{r}}G^{\ominus}=\Delta_{\mathrm{f}}G^{\ominus}(\mathrm{H^+,aq})+\Delta_{\mathrm{f}}G^{\ominus}(\mathrm{Cl^-,aq})=\Delta_{\mathrm{f}}G^{\ominus}(\mathrm{Cl^-,aq})$$

and hence identify $\Delta_{\mathrm{f}}G^{\ominus}$ (Cl$^-$,aq) as –131.23 kJ mol^{-1}. All the Gibbs energies of formation of ions tabulated in the *Resource section* were calculated in the same way.

Brief illustration 65.2 Standard Gibbs energies of ions

With the value of $\Delta_{\mathrm{f}}G^{\ominus}(\mathrm{Cl^-,aq})$ established, we can find the value of $\Delta_{\mathrm{f}}G^{\ominus}(\mathrm{Ag^+,aq})$ from

$$\mathrm{Ag(s)}+\tfrac{1}{2}\mathrm{Cl_2(g)}\rightarrow \mathrm{Ag^+(aq)}+\mathrm{Cl^-(aq)}$$
$$\Delta_{\mathrm{r}}G^{\ominus}=-54.12\,\mathrm{kJ\,mol^{-1}}.$$

It follows that $\Delta_{\mathrm{f}}G^{\ominus}(\mathrm{Ag^+,aq})=-54.12$ kJ mol^{-1} – (–131.23 kJ mol^{-1}) = +77.11 kJ mol^{-1}.

Self-test 65.3 Develop this point to calculate the value of $\Delta_{\mathrm{f}}G^{\ominus}(\mathrm{Ca^{2+},aq})$ given that

$$\mathrm{Ca(s)}+\mathrm{Cl_2(g)}\rightarrow \mathrm{Ca^{2+}(aq)}+2\ \mathrm{Cl^-(aq)}$$
$$\Delta_{\mathrm{r}}G^{\ominus}=-816.0\,\mathrm{kJ\,mol^{-1}}.$$

Answer: $\Delta_{\mathrm{f}}G^{\ominus}(\mathrm{Ca^{2+},aq})=-553.5$ kJ mol^{-1}

The factors responsible for the magnitude of the Gibbs energy of formation of an ion in solution can be identified by analysing it in terms of a thermodynamic cycle. An important point to note is that the value of $\Delta_{\mathrm{f}}G^{\ominus}$ of an ion X is not determined by the properties of X alone but includes contributions from the dissociation, ionization, and hydration of hydrogen.

Example 65.2 Setting up an expression for the Gibbs energy of formation of an ion

Set up an expression for the Gibbs energy of formation of Cl$^-$ in water at 298 K.

Method Treat the formation reaction of an ion X$^-$(aq), $\tfrac{1}{2}\mathrm{H_2(g)}+\tfrac{1}{2}\mathrm{X_2(g)}\rightarrow\mathrm{H^+(aq)}+\mathrm{X^-(aq)}$, as the outcome of the sequence of steps shown in Fig. 65.1a and take values from the *Resource section*. The standard Gibbs energies of formation of the gas-phase ions are unknown. Therefore, use ionization energies and electron affinities and neglect any errors arising from the conversion of enthalpies to Gibbs energies. The conclusions from the cycles are therefore only approximate.

Answer The cycle leading to the formation of Cl^-(aq) is shown in Fig. 65.1a. The sum of the Gibbs energies for all the steps around a closed cycle is zero, so

$$\begin{aligned}&-\{\Delta_f G^\ominus(Cl^-,aq)+\Delta_f G^\ominus(H^+,aq)\}\\ &\quad+(218+1312+106-349)\,kJ\,mol^{-1}\\ &\quad+\Delta_{solv}G^\ominus(Cl^-)+\Delta_{solv}G^\ominus(H^+)=0\end{aligned}$$

Therefore, with $\Delta_f G^\ominus(H^+,aq)=0$,

$$\Delta_f G^\ominus(Cl^-,aq)=1287\,kJ\,mol^{-1}+\Delta_{solv}G^\ominus(Cl^-)+\Delta_{solv}G^\ominus(H^+)$$

The Gibbs energies of solvation of the ions are unknown (but see the following section), and it would be dangerous to identify them with the enthalpies of solvation because the two types of ions are likely to have significantly different effects on the entropy of solvation. The experimental value of $\Delta_f G^\ominus(Cl^-,aq)$, from electrochemical measurements of the type described in Topic 77, is −131 kJ mol⁻¹, so we can conclude that

$$\Delta_{solv}G^\ominus(Cl^-)+\Delta_{solv}G^\ominus(H^+)=-1418\ kJ\ mol^{-1}$$

This conclusion is taken further in *Brief illustration* 65.3 and its Self-test.

Self-test 65.4 Estimate the value of $\Delta_{solv}G^\ominus(I^-)+\Delta_{solv}G^\ominus(H^+)$ in water at 298 K.

Answer: See Fig. 65.1b; −1357 kJ mol⁻¹

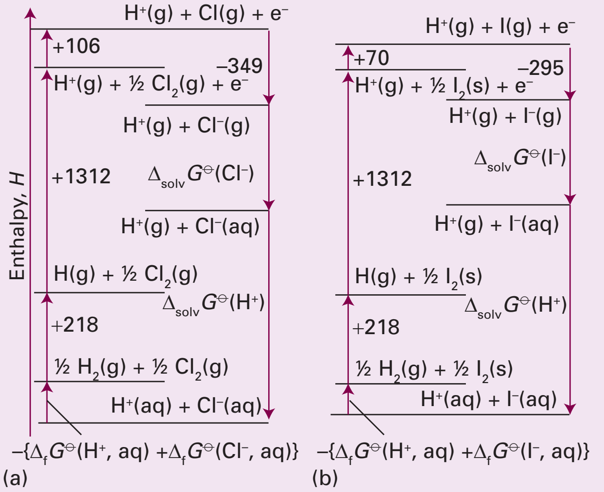

Figure 65.1 The thermodynamic cycles for the discussion of the Gibbs energies of solvation (hydration) and formation of (a) chloride ions, (b) iodide ions in aqueous solution. The sum of the changes in Gibbs energies around the cycle sum to zero because *G* is a state function.

(b) The Born equation

Gibbs energies of solvation of individual ions, which appear in the thermodynamic cycle used to estimate Gibbs energies of formation, may be estimated from an equation derived by Max Born. He identified $\Delta_{solv}G^\ominus$ with the electrical work of transferring an ion from a vacuum into the solvent treated as a continuous dielectric of relative permittivity ε_r. The resulting **Born equation**, which is derived in the following *Justification*, is

$$\Delta_{solv}G^\ominus=-\frac{z_i^2e^2N_A}{8\pi\varepsilon_0 r_i}\left(1-\frac{1}{\varepsilon_r}\right)\qquad \text{Born equation}\qquad(65.6a)$$

where z_i is the charge number of the ion and r_i its radius (N_A is Avogadro's constant). Note that $\Delta_{solv}G^\ominus<0$, and that $\Delta_{solv}G^\ominus$ is strongly negative for small, highly charged ions in media of high relative permittivity. For water, for which $\varepsilon_r=78.54$ at 25 °C,

$$\Delta_{solv}G^\ominus=-\frac{Az_i^2}{(r_i/pm)},\quad A=6.86\times10^4\,kJ\,mol^{-1}\qquad(65.6b)$$

Brief illustration 65.3 The Born equation

To see how closely the Born equation reproduces the experimental data, we calculate the difference in the values of $\Delta_f G^\ominus$ for Cl^- and I^- in water, at 25 °C, given their radii as 181 pm and 220 pm (Table 38.2), respectively; the difference is

$$\begin{aligned}\Delta_{solv}G^\ominus(Cl^-)-\Delta_{solv}G^\ominus(I^-)&=-A\left(\frac{1}{181}-\frac{1}{220}\right)\\&=-1.0\times10^3A=-67\,kJ\,mol^{-1}\end{aligned}$$

This estimated difference is in good agreement with the experimental difference, which is −61 kJ mol⁻¹.

Self-test 65.5 Estimate the value of $\Delta_{solv}G^\ominus(H^+)$ from the conclusion in Example 65.1 and the Born equation.

Answer: −1039 kJ mol⁻¹

Justification 65.1 The Born equation

We model an ion as a sphere of radius r_i immersed in a medium of permittivity ε. If the charge of the sphere is Q, the electric potential at its surface is the same as the potential due to a point charge at its centre, so (Topic 2)

$$\phi(r_i)=\frac{Q}{4\pi\varepsilon r_i}$$

The work of bringing up a charge dQ to the sphere is $\phi(r_i)$ dQ. Therefore, the total work of charging the sphere from 0 to z_ie is

$$w=\int_0^{z_ie}\phi(r_i)\mathrm{d}Q=\frac{1}{4\pi\varepsilon r_i}\int_0^{z_ie}Q\mathrm{d}Q=\frac{z_i^2e^2}{8\pi\varepsilon r_i}$$

This electrical work of charging, when multiplied by Avogadro's constant, is the molar Gibbs energy for charging the ions.

The work of charging an ion in a vacuum is obtained by setting $\varepsilon=\varepsilon_0$, the vacuum permittivity The corresponding value for charging the ion in a medium regarded as a continuum is obtained by setting $\varepsilon=\varepsilon_r\varepsilon_0$, where ε_r is the relative permittivity of the medium. It follows that the change in molar Gibbs energy that accompanies the transfer of ions from a vacuum to a solvent is the difference of these two quantities:

$$\begin{aligned}\Delta_{\text{solv}}G&=\frac{N_Az_i^2e^2}{8\pi\varepsilon r_i}-\frac{N_Az_i^2e^2}{8\pi\varepsilon_0 r_i}\\&=-\frac{N_Az_i^2e^2}{8\pi\varepsilon_0 r_i}\left(1-\frac{1}{\varepsilon_r}\right)\end{aligned}$$

which is eqn 65.6a.

Checklist of concepts

☐ 1. The **standard Gibbs energies of formation** is the standard reaction Gibbs energy for the formation of a compound from its elements in their reference states.

☐ 2. The Gibbs energies of formation of ions in solution are relative to the Gibbs energy of formation of H^+(aq).

☐ 3. The **Born equation** is used to estimate the Gibbs energies of formation of ions in solution.

Checklist of equations

Property	Equation	Comment	Equation number
Standard reaction Gibbs energy	$\Delta_rG^\ominus=\Delta_rH^\ominus-T\Delta_rS^\ominus$	Definition	65.2
	$\Delta_rG^\ominus=\sum_J \nu_J\Delta_fG^\ominus(J)$	Practical implementation	65.3
Ions in solution	$\Delta_fG^\ominus(H^+,aq)=0$	Convention, all temperatures	65.5
Born equation	$\Delta_{\text{solv}}G^\ominus=-(z_i^2e^2N_A/8\pi\varepsilon_0r_i)(1-1/\varepsilon_r)$	Solvent a continuous dielectric of relative permittivity ε_r	65.6a

TOPIC 66

Combining the First and Second Laws

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➤ Why do you need to know this material?

By combining the First and Second Laws we obtain a very powerful device for discussing the thermodynamic properties of matter. In this Topic you see how to derive expressions for the pressure and temperature dependence of the Gibbs energy, and thus provide the foundations for discussing the response of equilibria to changes in the conditions.

➤ What is the key idea?

The fact that thermodynamic functions are state functions implies important relations between them and their variation with changes in the conditions.

➤ What do you need to know already?

You need to be aware of the concept of 'state function' (Topic 55) and the mathematical concept of exact differential (*Mathematical background* 8). This Topic combines the discussion of internal energy in Topic 58 with the discussion of the Gibbs and Helmholtz energies in Topic 64.

The First and Second Laws of thermodynamics are both relevant to the behaviour of matter, and we can bring the whole force of thermodynamics to bear on a problem by setting up a formulation that combines them.

66.1 The fundamental equation

The First Law of thermodynamics (Topic 55) may be written $\mathrm{d}U=\mathrm{d}q+\mathrm{d}w$. For a reversible change in a closed system of constant composition, and in the absence of any additional (non-expansion) work, we may set $\mathrm{d}w_{\mathrm{rev}}=-p\mathrm{d}V$ and (from the thermodynamic definition of entropy, Topic 61) $\mathrm{d}q_{\mathrm{rev}}=T\mathrm{d}S$, where p is the pressure of the system and T its temperature. Therefore, for a reversible change in a closed system,

$$\mathrm{d}U=T\mathrm{d}S-p\mathrm{d}V \qquad \text{Fundamental equation of thermodynamics} \qquad (66.1)$$

However, because $\mathrm{d}U$ is an exact differential, its value is independent of path. Therefore, the same value of $\mathrm{d}U$ is obtained whether the change is brought about irreversibly or reversibly. Consequently, *eqn 66.1 applies to any change—reversible* *or irreversible—of a closed system that does no additional (non-expansion) work*. We shall call this combination of the First and Second Laws the **fundamental equation of thermodynamics.**

The fact that the fundamental equation applies to both reversible and irreversible changes may be puzzling at first sight. The reason is that only in the case of a reversible change may $T\mathrm{d}S$ be identified with $\mathrm{d}q$ and $-p\mathrm{d}V$ with $\mathrm{d}w$. When the change is irreversible, $T\mathrm{d}S>\mathrm{d}q$ (the Clausius inequality, Topic 61) and $-p\mathrm{d}V<\mathrm{d}w$ (work has its most negative value for the reversible process, Topic 55). The sum of $\mathrm{d}w$ and $\mathrm{d}q$ remains equal to the sum of $T\mathrm{d}S$ and $-p\mathrm{d}V$, provided the composition is constant.

66.2 Properties of the internal energy

Equation 66.1 shows that the internal energy of a closed system changes in a simple way when either S or V is changed ($\mathrm{d}U \propto \mathrm{d}S$ and $\mathrm{d}U \propto \mathrm{d}V$). These simple proportionalities suggest that U should be regarded as a function of S and V. We could regard U as a function of other variables, such as S and p or T and V, because they are all interrelated; but the simplicity of the fundamental equation suggests that $U(S,V)$ is the best choice. From that simple observation, powerful consequences flow.

(a) The Maxwell relations

It follows from the discussion in *Mathematical background* 8 that the *mathematical* consequence of U being a function of S and V is that we can express an infinitesimal change $\mathrm{d}U$ in terms of changes $\mathrm{d}S$ and $\mathrm{d}V$ by

$$\mathrm{d}U=\left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S+\left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V \tag{66.2}$$

The two partial derivatives are the slopes of the plots of U against S and V, respectively, with the other variable held constant. When this *mathematical* expression is compared to the *thermodynamic* relation, eqn 66.1, we see that, for systems of constant composition,

$$\left(\frac{\partial U}{\partial S}\right)_V=T \qquad \left(\frac{\partial U}{\partial V}\right)_S=-p \tag{66.3}$$

The first of these two equations is a purely thermodynamic definition of temperature (a Zeroth-Law concept)[1] as the ratio of the changes in the internal energy (a First-Law concept) and entropy (a Second-Law concept) of a constant-volume, closed, constant-composition system. We are beginning to generate relations between the properties of a system and to discover the power of thermodynamics for establishing unexpected relations.

Because the fundamental equation, eqn 66.1, is an expression for an exact differential, the functions multiplying $\mathrm{d}S$ and $\mathrm{d}V$ (namely T and $-p$) must pass the test for exact differentials set out in *Mathematical background* 8 (that $\mathrm{d}f=g\mathrm{d}x+h\mathrm{d}y$ is exact if $(\partial g/\partial y)_x=(\partial h/\partial x)_y$). That is,

for $\mathrm{d}U=\overbrace{T}^{g}\,\overbrace{\mathrm{d}S}^{\mathrm{d}x}\,\overbrace{-p}^{+h}\,\overbrace{\mathrm{d}V}^{\mathrm{d}y}$ to be exact, it must be the case that

$$\overbrace{\left(\frac{\partial T}{\partial V}\right)_S}^{(\partial g/\partial y)_x}=-\overbrace{\left(\frac{\partial p}{\partial S}\right)_V}^{(\partial h/\partial x)_y} \tag{66.4}$$

We have generated a relation between quantities which, at first sight, would not seem to be related and are certainly very difficult to justify on a molecular basis.

Equation 66.4 is an example of a **Maxwell relation**. However, apart from being unexpected, it does not look particularly interesting. Nevertheless, it does suggest that there may be other similar relations that are more useful. Indeed, we can use the fact that H, G, and A are all state functions to derive three more Maxwell relations. The argument to obtain them runs in the same way in each case: because H, G, and A are state functions, the expressions for $\mathrm{d}H$, $\mathrm{d}G$, and $\mathrm{d}A$ satisfy relations that yield expressions like eqn 66.4. All four relations are listed in Table 66.1.

Table 66.1 The Maxwell relations

State function	Exact differential	Maxwell relation
U	$\mathrm{d}U=T\mathrm{d}S-p\mathrm{d}V$	$\left(\frac{\partial T}{\partial V}\right)_S=-\left(\frac{\partial p}{\partial S}\right)_V$
H	$\mathrm{d}H=T\mathrm{d}S+V\mathrm{d}p$	$\left(\frac{\partial T}{\partial p}\right)_S=\left(\frac{\partial V}{\partial S}\right)_p$
A	$\mathrm{d}A=-p\mathrm{d}V-S\mathrm{d}T$	$\left(\frac{\partial p}{\partial T}\right)_V=\left(\frac{\partial S}{\partial V}\right)_T$
G	$\mathrm{d}G=V\mathrm{d}p-S\mathrm{d}T$	$\left(\frac{\partial V}{\partial T}\right)_p=-\left(\frac{\partial S}{\partial p}\right)_T$

Brief illustration 66.1 The Maxwell relations

Suppose that for a certain gas $(\partial p/\partial T)_V=+380\ \mathrm{Pa\,K^{-1}}$. Then we would know from the Maxwell relation $(\partial S/\partial V)_T=(\partial p/\partial T)_V$ that the variation of entropy with volume at constant temperature is also $+380\ \mathrm{Pa\,K^{-1}}$, which is equivalent to $+380\ \mathrm{J\,K^{-1}\,m^{-3}}$, and therefore that an increase in volume by $1.0\ \mathrm{dm^3}$ would result in an increase in entropy of about $0.38\ \mathrm{J\,K^{-1}}$.

---

[1] This point is elaborated in our other *Physical chemistry* (2014).

Self-test 66.1 Suppose we know that for a certain gas that $(\partial V_m/\partial T)_p = 8.3\times10^{-5}\,\mathrm{m^3\,mol^{-1}\,K^{-1}}$. What can be inferred about the variation of its molar entropy with pressure?

Answer: $(\partial S_m/\partial p)_T = -8.3\times10^{-5}\,\mathrm{J\,K^{-1}\,mol^{-1}\,Pa^{-1}}$

(b) The thermodynamic equation of state

As an example of the use of the Maxwell relations, we show in the following *Justification* that the internal pressure $\pi_T = (\partial U/\partial V)_T$ introduced in Topic 36 may be expressed as

Thermodynamic equation of state

$$\pi_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \qquad (66.5)$$

This relation is called a **thermodynamic equation of state** because it is an expression for pressure in terms of a variety of thermodynamic properties of the system.

Justification 66.1 The thermodynamic equation of state

We obtain an expression for the coefficient π_T by dividing both sides of eqn 66.2 by dV and imposing the constraint of constant temperature, which gives

$$\overbrace{\left(\frac{\partial U}{\partial V}\right)_T}^{\pi_T} = \overbrace{\left(\frac{\partial U}{\partial S}\right)_V}^{T}\left(\frac{\partial S}{\partial V}\right)_T + \overbrace{\left(\frac{\partial U}{\partial V}\right)_S}^{-p}$$

We have used eqn 66.3 to identify T and $-p$. Next, as shown by the annotations, this equation is the same as

$$\pi_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$$

The third Maxwell relation in Table 66.1 turns $(\partial S/\partial V)_T$ into $(\partial p/\partial T)_V$, which completes the proof of eqn 66.5.

Example 66.1 Deriving a thermodynamic relation

Show thermodynamically that $\pi_T = 0$ for a perfect gas, and derive its value for a van der Waals gas.

Method Proving a result 'thermodynamically' means basing it entirely on general thermodynamic relations and equations of state, without drawing on molecular arguments (such as the existence of intermolecular forces). We know that, for a perfect gas, $p = nRT/V$, so this relation should be used in eqn 66.5. Similarly, the van der Waals equation (Topic 36) should be used instead for the second part of the question.

Answer For a perfect gas we write

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial(nRT/V)}{\partial T}\right)_V = \frac{nR}{V}$$

Then, eqn 66.5 becomes

$$\pi_T = \frac{nRT}{V} - p = 0$$

The equation of state of a van der Waals gas (Topic 36) is

$$p = \frac{nRT}{V-nb} - a\frac{n^2}{V^2}$$

Because a and b are independent of temperature,

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V-nb}$$

Therefore, from eqn 66.5,

$$\pi_T = \overbrace{\frac{nRT}{V-nb}}^{T(\partial p/\partial T)_V} \overbrace{-\frac{nRT}{V-nb} + a\frac{n^2}{V^2}}^{-p} = a\frac{n^2}{V^2}$$

exactly as obtained in Topics 36 and 54 on the basis of molecular arguments and the formulation of a model intermolecular potential with an attractive region proportional to a.

Self-test 66.2 Calculate π_T for a gas that obeys the virial equation of state (Topic 36).

Answer: $\pi_T = RT^2(\partial B/\partial T)_V/V_m^2 + \ldots$

66.3 Properties of the Gibbs energy

The same arguments that we have used for U can be used for the Gibbs energy (Topic 64, $G = H - TS$). They lead to expressions showing how G varies with pressure and temperature that are important for discussing phase transitions (Topics 67–69) and chemical reactions (Topic 73).

(a) General considerations

When the system undergoes a change of state, G may change because H, T, and S all change:

$$\mathrm{d}G = \mathrm{d}H - \mathrm{d}(TS) = \mathrm{d}H - T\mathrm{d}S - S\mathrm{d}T$$

Because $H = U + pV$, we know that

$$\mathrm{d}H = \mathrm{d}U + \mathrm{d}(pV) = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

and therefore

$$dG = dU + pdV + Vdp - TdS - SdT$$

For a closed system doing no non-expansion work, we can replace dU by the fundamental equation $dU = TdS - pdV$ and obtain

$$dG = TdS - pdV + pdV + Vdp - TdS - SdT$$

Four terms now cancel on the right, and we conclude that for a closed system in the absence of non-expansion work and at constant composition

$$dG = Vdp - SdT \tag{66.6}$$

Variation of G with p and T

This expression, which shows that a change in G is proportional to a change in p or T, suggests that G may be best regarded as a function of p and T. It confirms that G is an important quantity in chemistry because the pressure and temperature are usually the variables under our control. In other words, G carries around the combined consequences of the First and Second Laws in a way that makes it particularly suitable for chemical applications.

The same argument that led to eqn 66.3, when applied to the exact differential $dG = Vdp - SdT$, now gives

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \left(\frac{\partial G}{\partial p}\right)_T = V \tag{66.7}$$

Variation of G with temperature and pressure

These relations show how the Gibbs energy varies with temperature and pressure (Fig. 66.1). The first implies that:

- Because $S > 0$ for all substances, G always *decreases* when the temperature is raised (at constant pressure and composition).

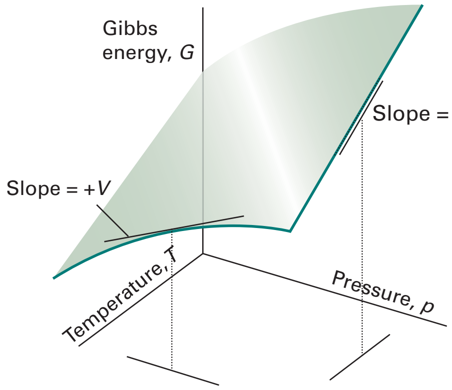

Figure 66.1 The variation of the Gibbs energy of a system with temperature and pressure. The slope of the former is equal to the negative of the entropy of the system and that of the latter is equal to the volume.

Insofar as G is the negative logarithm of the molecular partition function (Topic 64, $G - G(0) = -NkT\ln(q/N)$), we can understand this behaviour on the basis that q increases with temperature as more states become thermally accessible, and therefore $-\ln q$ becomes more negative.

- Because $(\partial G/\partial T)_p$ becomes more negative as S increases, G decreases most sharply when the entropy of the system is large.

A large entropy implies that many states are occupied, and therefore that many are thermally accessible. Such a system is more sensitive to changes in temperature than one in which only a small number of states are accessible. In macroscopic terms, the Gibbs energy of the gaseous phase of a substance, which has a high molar entropy, is more sensitive to temperature than its liquid and solid phases (Fig. 66.2).

Brief illustration 66.2 The variation of Gibbs energy with temperature

The standard molar entropy of liquid water at 25 °C is $69.91\ \mathrm{J\,K^{-1}\,mol^{-1}}$. Therefore, when the temperature is increased to 30 °C we can expect its standard molar Gibbs energy to change by

$$\Delta G_\mathrm{m}^\ominus \approx \left(\frac{\partial G_\mathrm{m}^\ominus}{\partial T}\right)_p \Delta T = -S_\mathrm{m}^\ominus \Delta T = -(69.91\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (5\ \mathrm{K})$$
$$= -350\ \mathrm{J\,mol^{-1}}$$

The same calculation for gaseous water (for which the standard molar entropy is $188.83\ \mathrm{J\,K^{-1}\,mol^{-1}}$) gives a decrease of $944\ \mathrm{J\,mol^{-1}}$.

Self-test 66.3 Estimate the change in the value of $G_\mathrm{m}^\ominus$ when the temperature of liquid mercury is changed from 25 °C to 0 °C.

Answer: $-1.9\ \mathrm{kJ\,mol^{-1}}$

Similarly, the second relation implies that:

- Because $V > 0$ for all substances, G always *increases* when the pressure of the system is increased (at constant temperature and composition).

We can understand this behaviour on the basis (once again, using Topic 64, $G - G(0) = -NkT\ln(q/N)$) that q decreases with decreasing volume as states move apart and become less thermally accessible, and therefore $-\ln q$ becomes less negative.

- Because $(\partial G/\partial p)_T$ increases with V, G is more sensitive to pressure when the volume of the system is large.

Once again, a large volume implies closely spaced translational energy levels, and therefore a responsiveness to change. Because the molar volume of the gaseous phase of a substance is greater than that of its condensed phases, the molar Gibbs

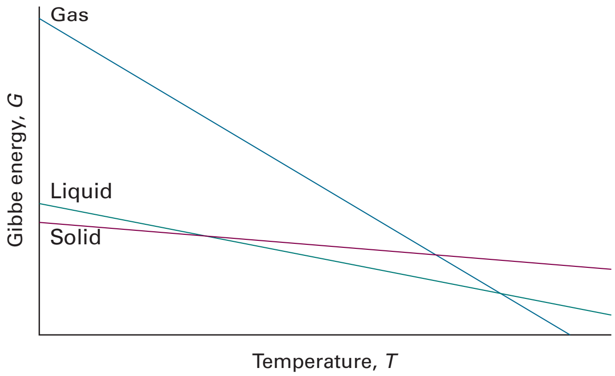

Figure 66.2 The variation of the Gibbs energy with the temperature is determined by the entropy. Because the entropy of the gaseous phase of a substance is greater than that of the liquid phase, and the entropy of the solid phase is smallest, the Gibbs energy changes most steeply for the gas phase, followed by the liquid phase, and then the solid phase of the substance.

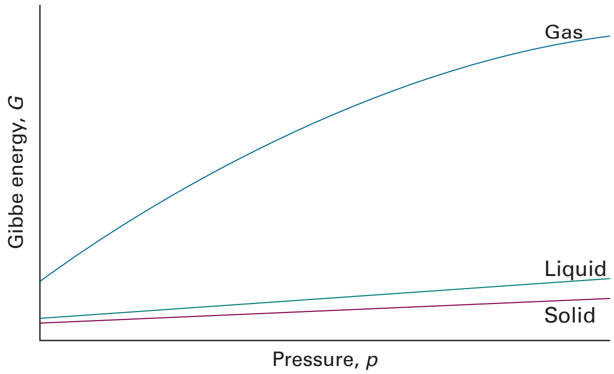

Figure 66.3 The variation of the Gibbs energy with the pressure is determined by the volume of the sample. Because the volume of the gaseous phase of a substance is greater than that of the same amount of liquid phase, and the entropy of the solid phase is smallest (for most substances), the Gibbs energy changes most steeply for the gas phase, followed by the liquid phase, and then the solid phase of the substance. Because the volumes of the solid and liquid phases of a substance are similar, their molar Gibbs energies vary by similar amounts as the pressure is changed.

energy of a gas is more sensitive to pressure than its liquid and solid phases (Fig. 66.3).

Brief illustration 66.3 The variation of Gibbs energy with pressure

The mass density of water at 25 °C is close to 1.0 g cm^{-3}, so its molar volume at that temperature is (18.02 g mol^{-1})/(1.0 g cm^{-3}) = 18 cm^3 mol^{-1} (corresponding to 1.8×10^{-5} m^3 mol^{-1}). Therefore, when the pressure is increased from 1.0 bar to 2.0 bar, so $\Delta p = +1.0\text{ bar} = +1.0\times10^5\text{ Pa}$, we can expect its standard molar Gibbs energy to change by

$$\Delta G_\text{m}^\ominus \approx \left(\frac{\partial G_\text{m}^\ominus}{\partial p}\right)_T \Delta p = V_\text{m}^\ominus \Delta p$$
$$= (1.8\times10^{-5}\text{ m}^3\text{ mol}^{-1})\times(1.0\times10^5\text{ Pa}) = +1.8\text{ J mol}^{-1}$$

(We have used 1 Pa m^3 = 1 J.) Provided we ignore at this stage the compression that occurs, the same calculation for gaseous water (for which the standard molar volume is 2.5×10^{-2} m^3 mol^{-1}) gives an increase of 2.5 kJ mol^{-1}. The effect of compression is taken into account in *Brief illustration* 66.5.

Self-test 66.4 Estimate the change in the value of $G_\text{m}^\ominus$ when the pressure of liquid mercury is changed from 1.0 bar to (a) 2.0 bar; (b) 1.0 kbar. (The mass density of mercury is 13.5 g cm^{-3}.)

Answer: (a) +1.5 J mol^{-1}; (b) +1.5 kJ mol^{-1}

(b) The variation of the Gibbs energy with temperature

Although eqn 66.7 expresses the variation of G in terms of the entropy, we can express it in terms of the enthalpy by using the definition of $G = H - TS$ to write $-S = (G-H)/T$. Then we obtain the **Gibbs–Helmholtz equation**:

$$\left(\frac{\partial G}{\partial T}\right)_p = \frac{G-H}{T} \qquad \text{Gibbs–Helmholtz equation} \qquad (66.8a)$$

As we show in the following *Justification*, an alternative (and more useful) form is

$$\left(\frac{\partial}{\partial T}\frac{G}{T}\right)_p = -\frac{H}{T^2} \qquad \text{Gibbs–Helmholtz equation} \qquad (66.8b)$$

This expression shows that if we know the enthalpy of the system, then we know how G/T varies with temperature.

Justification 66.2 The Gibbs–Helmholtz equation

First, we reorganize eqn 66.8a into

$$\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T} = -\frac{H}{T}$$

Then we combine the two terms on the left by noting that

$$\left(\frac{\partial}{\partial T}\frac{G}{T}\right)_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p + G\overbrace{\left(\frac{\partial}{\partial T}\frac{1}{T}\right)_p}^{-1/T^2}$$
$$= \frac{1}{T}\left\{\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T}\right\}$$

When we substitute eqn 66.7, that $(\partial G/\partial T)_p = -S$, into this expression, we obtain

$$\left(\frac{\partial}{\partial T}\frac{G}{T}\right)_p = \frac{1}{T}\left\{-S-\frac{\overbrace{G}^{H-TS}}{T}\right\} = -\frac{H}{T^2}$$

which is eqn 66.8b.

The Gibbs–Helmholtz equation is most useful when it is applied to changes, including changes of physical state and chemical reactions at constant pressure. Then, because $\Delta G = G_f - G_i$ for the change of Gibbs energy between the final and initial states and because the equation applies to both G_f and G_i, we can write

$$\left(\frac{\partial}{\partial T}\frac{\Delta G}{T}\right)_p = -\frac{\Delta H}{T^2} \qquad \text{Gibbs–Helmholtz equation for changes} \qquad (66.9)$$

This equation shows that if we know the change in enthalpy of a system that is undergoing some kind of transformation (such as vaporization or reaction), then we know how the corresponding change in Gibbs energy varies with temperature. As we see in Topics 73 and 75, this is a crucial piece of information in chemistry.

Brief illustration 66.4 The Gibbs–Helmholtz equation

In Topic 73 it is shown that $\Delta_r G^\ominus/T = -R \ln K$, where K is the equilibrium constant of the reaction for which $\Delta_r G^\ominus$ is the standard reaction Gibbs energy. Suppose we know that the standard enthalpy of the reaction is $-200\,\text{kJ mol}^{-1}$ at 298 K. Then from eqn 66.9 we can predict that

$$\left(\frac{\partial}{\partial T}\ln K\right)_p = \frac{\Delta_r H^\ominus}{RT^2} = \frac{-2.00\times10^5\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(298\,\text{K})^2}$$
$$= -0.27\,\text{K}^{-1}$$

That is, the logarithm of the equilibrium constant decreases by 0.27 for each 1 K rise in temperature.

Self-test 66.5 Estimate the change in ln K for a reaction for which $\Delta_r H^\ominus = +500\,\text{kJ mol}^{-1}$ at 298 K.

Answer: $+0.68\,\text{K}^{-1}$

(c) The variation of the Gibbs energy with pressure

To find the Gibbs energy at one pressure in terms of its value at another pressure, the temperature being constant, we set $\mathrm{d}T = 0$ in eqn 66.6, which gives $\mathrm{d}G = V\mathrm{d}p$, and integrate:

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V\mathrm{d}p \qquad \text{Pressure dependence of } G \qquad (66.10a)$$

For molar quantities,

$$G_m(p_f) = G_m(p_i) + \int_{p_i}^{p_f} V_m\mathrm{d}p \qquad \text{Pressure dependence of } G_m \qquad (66.10b)$$

This expression is applicable to any phase of matter, but to evaluate it we need to know how the molar volume, V_m, depends on the pressure.

The molar volume of a condensed phase changes only slightly as the pressure changes (Fig. 66.4), so we can treat V_m as a constant and take it outside the integral:

$$\int_{p_i}^{p_f} V_m\mathrm{d}p = V_m\int_{p_i}^{p_f}\mathrm{d}p = V_m\times\overbrace{(p_f-p_i)}^{\Delta p}$$

Therefore,

$$G_m(p_f) = G_m(p_i) + V_m\Delta p \qquad \textit{Incompressible substance} \qquad \text{Pressure dependence of } G_m \qquad (66.11)$$

(The molar volume of a substance of molar mass M is related to its mass density ρ by $V_m = M/\rho$.) Under normal laboratory conditions $V_m\Delta p$ is very small and may be neglected. Hence, we may usually suppose that the Gibbs energies of solids and liquids are independent of pressure. For the implication of this expression, see *Brief illustration* 66.3.

The molar volumes of gases are large, so the Gibbs energy of a gas depends strongly on the pressure: the closeness of its translational energy levels makes the partition function highly responsive to external influences. Furthermore, because the volume also varies markedly with the pressure, we cannot treat it as a constant in the integral in eqn 66.10b (Fig. 66.5). For a

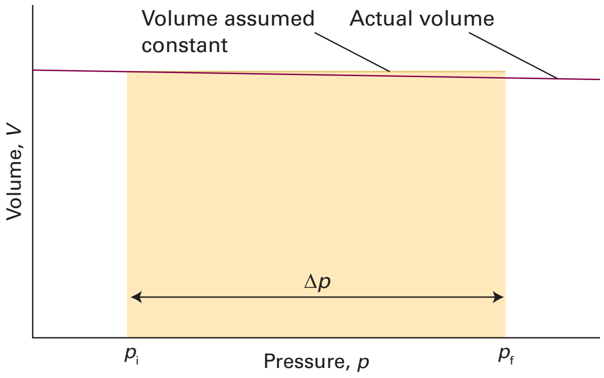

Figure 66.4 The difference in Gibbs energy of a solid or liquid at two pressures is equal to the rectangular area shown. We have assumed that the variation of volume with pressure is negligible.

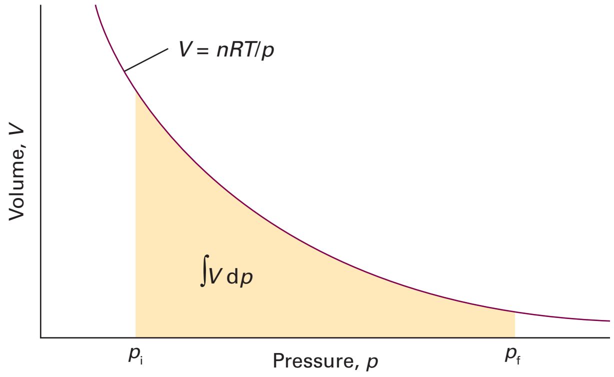

Figure 66.5 The difference in Gibbs energy for a perfect gas at two pressures is equal to the area shown below the perfect-gas isotherm.

perfect gas we substitute $V_m = RT/p$ into the integral, treat RT as a constant, use

$$\int_{p_i}^{p_f} V_m \mathrm{d}p = RT\int_{p_i}^{p_f} \frac{1}{p}\mathrm{d}p = RT\ln\frac{p_f}{p_i}$$

and conclude that

$$G_m(p_f) = G_m(p_i) + RT\ln\frac{p_f}{p_i} \qquad (66.12)$$

Perfect gas Pressure dependence of G_m

This expression shows that when the pressure is increased tenfold at room temperature, the molar Gibbs energy increases by $RT\ln 10 \approx 6\,\mathrm{kJ\,mol^{-1}}$. It also follows from this equation that if we set $p_i = p^{\ominus}$ (the standard pressure of 1 bar), then the molar Gibbs energy of a perfect gas at a pressure p (set $p_f = p$) is related to its standard value by

$$G_m(p) = G_m^{\ominus} + RT\ln\frac{p}{p^{\ominus}} \qquad (66.13)$$

Perfect gas Pressure dependence of G_m

The logarithmic dependence of the molar Gibbs energy on the pressure predicted by eqn 66.13 is illustrated in Fig. 66.6.

Brief illustration 66.5 The pressure dependence of the Gibbs energy of a gas

To calculate the change in the molar Gibbs energy of water vapour (treated as a perfect gas) when the pressure is increased isothermally from 1.0 bar to 2.0 bar (and, unlike in *Brief illustration* 66.3, now allowing for compression) at 298 K we write eqn 66.12 as

$$\Delta G_m = RT\ln\frac{p_f}{p_i} = (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})\times\ln\frac{2.0\,\mathrm{bar}}{1.0\,\mathrm{bar}}$$
$$= +1.7\,\mathrm{kJ\,mol^{-1}}$$

Note that whereas the change in molar Gibbs energy for a condensed phase (Self-test 66.4) is a few joules per mole, this change is of the order of kilojoules per mole. The value obtained here is smaller than in *Brief illustration* 66.3 (+2.5 kJ mol^{-1}) where compression was ignored because the compression that results from the application of pressure diminishes the volume progressively, so $\mathrm{d}G/\mathrm{d}p$ becomes smaller than its initial value as the pressure is increased.

Self-test 66.6 Repeat the calculation for iron vapour at 3000 °C treated as a perfect gas.

Answer: +19 kJ mol^{-1}

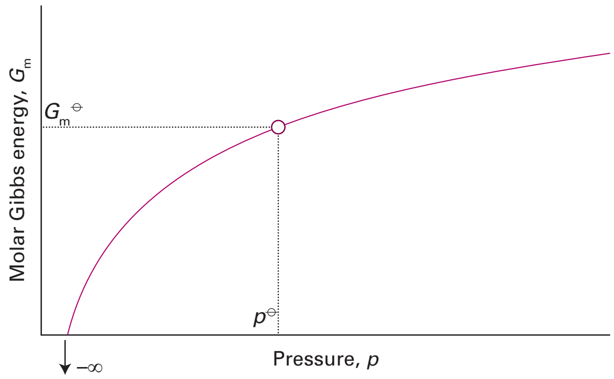

Figure 66.6 The molar Gibbs energy of a perfect gas is proportional to ln p, and the standard state is reached at $p^{\ominus}$. Note that as $p \to 0$, the molar Gibbs energy becomes negatively infinite.

66.4 Properties of the Helmholtz energy

By exactly the same kind of argument that led to eqn 66.7, we can compare the two equations for the variation of the Helmholtz energy A with temperature and volume. From the definition of A,

$$\mathrm{d}A = p\mathrm{d}V - S\mathrm{d}T \qquad (66.14)$$

and from the general mathematical form

$$\mathrm{d}A = \left(\frac{\partial A}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial A}{\partial T}\right)_V \mathrm{d}T$$

it follows that

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad \left(\frac{\partial A}{\partial V}\right)_T = -p \qquad (66.15)$$

Variation of A with temperature and volume

The second of these relations gives us a valuable route to the calculation of the pressure from the partition function, for we already know how to calculate A. Thus, from Topic 64 ($A=A(0)-kT\ln Q$) we obtain the simple relation

$$p=kT\left(\frac{\partial\ln Q}{\partial V}\right)_T \qquad (66.16)$$

Pressure in terms of the partition function

Example 66.2 Deriving the equation of state of a gas

Show that eqn 66.16 reduces to the perfect gas equation of state in the case of a gas of independent particles.

Method Substitute $Q=q^N/N!$ (Topic 54), and note that only the translational contribution depends on the volume.

Answer On substituting $Q=q^N/N!$ into eqn 66.16 we obtain

$$p=kT\left(\frac{\partial\ln(q^N/N!)}{\partial V}\right)_T=kT\overbrace{\left(\frac{\partial\ln q^N}{\partial V}\right)_T}^{N(\partial\ln q/\partial V)_T}-kT\overbrace{\left(\frac{\partial\ln N!}{\partial V}\right)_T}^{0}$$
$$=NkT\left(\frac{\partial\ln q}{\partial V}\right)_T$$

because only q (and not N) depends on V. Moreover, because $\ln q=\ln q^{\mathrm{T}}q^{\mathrm{R}}q^{\mathrm{V}}q^{\mathrm{E}}=\ln q^{\mathrm{T}}+\ln q^{\mathrm{R}}q^{\mathrm{V}}q^{\mathrm{E}}$, and q^{R}, q^{V}, and q^{E} are independent of volume, we need consider only the translational partition function. Thus we use $q=V/\Lambda^3$ (Topic 52) to obtain

$$\left(\frac{\partial\ln q}{\partial V}\right)_T=\left(\frac{\partial\ln q^{\mathrm{T}}}{\partial V}\right)_T=\frac{1}{q^{\mathrm{T}}}\left(\frac{\partial q^{\mathrm{T}}}{\partial V}\right)_T=\frac{\Lambda^3}{V}\left(\frac{\partial(V/\Lambda^3)}{\partial V}\right)_T=\frac{1}{V}$$

When this relation is substituted into the preceding one

$$p=\frac{NkT}{V}$$

and we use $N=nN_{\mathrm{A}}$ and $N_{\mathrm{A}}k=R$, we find $p=NkT/V=nRT/V$, the equation of state of a perfect gas.

Self-test 66.7 Obtain the corresponding expression for a real gas in terms of the configuration integral $\mathcal{Z}$ introduced in Topic 54.

Answer: $p=kT(\partial\ln\mathcal{Z}/\partial V)_T$

We are at the point where we can confirm that $\beta=1/kT$, as asserted in Topic 51. Thus, if we had not made the identification $\beta=1/kT$ in the derivation of eqn 66.16 we would have found

$$p=\frac{1}{\beta}\left(\frac{\partial\ln Q}{\partial V}\right)_T$$

The work in the preceding Example would have led to

$$p=\frac{N}{\beta V}$$

which requires us to identify β as $1/kT$ in order to recover the perfect gas law.

Checklist of concepts

1. The **fundamental equation of thermodynamics** (see below) combines the First and Second Laws of thermodynamics.
2. The **Maxwell relations** (Table 66.1) relate the derivatives of thermodynamic state functions.
3. A **thermodynamic equation of state** is an expression for pressure in terms of a variety of thermodynamic properties of the system.
4. The Gibbs energy of a pure substance decreases when the temperature is raised but increases when the pressure is raised.
5. The **Gibbs–Helmholtz equation** (see below) expresses the variation of G/T with temperature in terms of the enthalpy of the system.

Checklist of equations

Property	Equation	Comment	Equation number
Fundamental equation	$\mathrm{d}U=T\mathrm{d}S-p\mathrm{d}V$	Closed system of constant composition	66.1
Variation of U	$(\partial U/\partial S)_V=T$, $(\partial U/\partial V)_S=-p$		66.3
Maxwell relations	See Table 66.1		66.4
Thermodynamic equation of state	$\pi_T=T(\partial p/\partial T)_V-p$		66.5
Change in Gibbs energy	$\mathrm{d}G=V\mathrm{d}p-S\mathrm{d}T$		66.6
Variation of G	$(\partial G/\partial T)_p=-S$, $(\partial G/\partial p)_T=V$		66.7
Gibbs–Helmholtz equation	$(\partial(\Delta G/T)/\partial T)_p=-\Delta H/T^2$		66.9
Variation of Gibbs energy with pressure	$G_\mathrm{m}(p_\mathrm{f})=G_\mathrm{m}(p_\mathrm{i})+V_\mathrm{m}\Delta p$	Incompressible substance	66.11
	$G_\mathrm{m}(p)=G_\mathrm{m}^{\ominus}+RT\ln(p/p^{\ominus})$	Perfect gas	66.13
Change in Helmholtz energy	$\mathrm{d}A=-p\mathrm{d}V-S\mathrm{d}T$		66.14
Variation of A	$(\partial A/\partial T)_V=-S$, $(\partial A/\partial V)_T=-p$		66.15
Pressure in terms of the partition function	$p=kT(\partial\ln Q/\partial V)_T$		66.16

Focus 13 on The Second and Third Laws of thermodynamics

Assume that all gases are perfect and that data refer to 298.15 K unless otherwise stated.

Topic 59 The Second Law

Discussion questions

59.1 The evolution of life requires the organization of a very large number of molecules into biological cells. Does the formation of living organisms violate the Second Law of thermodynamics? State your conclusion clearly and present detailed arguments to support it.

59.2 Discuss the significance of the terms 'dispersal' and 'disorder' in the context of the Second Law.

Exercises

59.1(a) During a hypothetical process, the entropy of a system increases by 125 J K^{-1} while the entropy of the surroundings decreases by 125 J K^{-1}. Is the process spontaneous?

59.1(b) During a hypothetical process, the entropy of a system increases by 105 J K^{-1} while the entropy of the surroundings decreases by 95 J K^{-1}. Is the process spontaneous?

Topic 60 The statistical entropy

Discussion questions

60.1 Discuss the relationship between the thermodynamic and statistical definitions of entropy.

60.2 Justify the differences between the partition function expression for the entropy for distinguishable particles and the expression for indistinguishable particles.

60.3 Account for the temperature and volume dependence of the entropy of a perfect gas in terms of the Boltzmann distribution.

Exercises

60.1(a) Calculate the standard molar entropy at 298 K of (a) gaseous helium, (b) gaseous xenon.
60.1(b) Calculate the translational contribution to the standard molar entropy at 298 K of (a) $H_2O(g)$, (b) $CO_2(g)$.

60.2(a) At what temperature is the standard molar entropy of helium equal to that of xenon at 298 K?
60.2(b) At what temperature is the translational contribution to the standard molar entropy of $CO_2(g)$ equal to that of $H_2O(g)$ at 298 K?

60.3(a) Calculate the rotational partition function of H_2O at 298 K from its rotational constants 27.878 cm^{-1}, 14.509 cm^{-1}, and 9.287 cm^{-1} and use your result to calculate the rotational contribution to the molar entropy of gaseous water at 25 °C.
60.3(b) Calculate the rotational partition function of SO_2 at 298 K from its rotational constants 2.027 36 cm^{-1}, 0.34417 cm^{-1}, and 0.293 535 cm^{-1} and use your result to calculate the rotational contribution to the molar entropy of sulfur dioxide at 25 °C.

60.4(a) Calculate the rotational contribution to the molar entropy of CO_2 at 298 K. Use $\tilde{B}=0.3902\,\text{cm}^{-1}$.
60.4(b) Calculate the rotational contribution to the molar entropy of CS_2 at 298 K. Use $\tilde{B}=0.1091\,\text{cm}^{-1}$.

60.5(a) The ground state of the Co^{2+} ion in $CoSO_4\cdot 7H_2O$ may be regarded as $^4T_{9/2}$. The entropy of the solid at temperatures below 1 K is derived almost entirely from the electron spin. Estimate the molar entropy of the solid at these temperatures.
60.5(b) Estimate the contribution of the spin to the molar entropy of a solid sample of a d-metal complex with $S=\frac{5}{2}$.

60.6(a) Predict the standard molar entropy of methanoic acid (formic acid, HCOOH) at (a) 298 K, (b) 500 K. The normal modes occur at wavenumbers 3570, 2943, 1770, 1387, 1229, 1105, 625, 1033, 638 cm^{-1}.
60.6(b) Predict the standard molar entropy of ethyne at (a) 298 K, (b) 500 K. The normal modes (and their degeneracies in parentheses) occur at wavenumbers 612(2), 729(2), 1974, 3287, and 3374 cm^{-1}.

Problems

60.1 Use the accurate expression for the rotational partition function calculated in Problem 52.6 for HCl(g) to calculate the rotational contribution to the molar entropy over a range of temperature and plot the contribution as a function of temperature.

60.2 Calculate the standard molar entropy of $N_2(g)$ at 298 K from its rotational constant $\tilde{B} = 1.9987\,\text{cm}^{-1}$ and its vibrational wavenumber $\tilde{\nu} = 2358\ \text{cm}^{-1}$. The thermochemical value is 192.1 J K^{-1} mol^{-1}. What does this suggest about the solid at $T = 0$?

60.3‡ J.G. Dojahn, et al. (*J. Phys. Chem.* **100**, 9649 (1996)) characterized the potential energy curves of the ground and electronic states of homonuclear diatomic halogen anions. The ground state of F_2^- is $^2\Sigma_u^+$ with a fundamental vibrational wavenumber of 450.0 cm^{-1} and equilibrium internuclear distance of 190.0 pm. The first two excited states are at 1.609 and 1.702 eV above the ground state. Compute the standard molar entropy of F_2^- at 298 K.

60.4‡ Treat carbon monoxide as a perfect gas and apply equilibrium statistical thermodynamics to the study of its properties, as specified below, in the temperature range 100–1000 K at 1 bar. $\tilde{\nu} = 2169.8\,\text{cm}^{-1}$, $\tilde{B} = 1.931\ \text{cm}^{-1}$, and $hc\tilde{D}_0 = 11.09$ eV; neglect anharmonicity and centrifugal distortion. (a) Examine the probability distribution of molecules over available rotational and vibrational states. (b) Explore numerically the differences, if any, between the rotational molecular partition function as calculated with the discrete energy distribution and that calculated with the classical, continuous energy distribution. (c) Calculate the individual contributions to $U_m(T) - U_m(100\,\text{K})$, $C_{V,m}(T)$, and $S_m(T) - S_m(100\,\text{K})$ made by the translational, rotational, and vibrational degrees of freedom.

60.5 The energy levels of a Morse oscillator (Topic 43) are $E_v = (v+\tfrac{1}{2})hc\tilde{\nu} - (v+\tfrac{1}{2})^2 hcx_e\tilde{\nu}$. Set up the expression for the molar entropy of a collection of Morse oscillators and plot it as a function of temperature for a series of anharmonicities. Take into account only the finite number of bound states. On the same graph plot the entropy of a harmonic oscillator and investigate how the two diverge.

60.6 Explore how the entropy of a collection of two-level systems behaves when the temperature is formally allowed to become negative. You should also construct a graph in which the temperature is replaced by the variable $\beta = 1/kT$. Account for the appearance of the graphs physically.

60.7 Derive the Sackur–Tetrode equation for a monatomic gas confined to a two-dimensional surface, and hence derive an expression for the standard molar entropy of condensation to form a mobile surface film.

60.8 In Problem 58.16 you are invited to consider the expressions

$$q = \sum_j \mathrm{e}^{-\beta\varepsilon_j} \qquad \dot{q} = \sum_j \beta\varepsilon_j \mathrm{e}^{-\beta\varepsilon_j} \qquad \ddot{q} = \sum_j (\beta\varepsilon_j)^2\, \mathrm{e}^{-\beta\varepsilon_j}$$

in the context of the First Law. To see that these expressions are also relevant to the Second Law, derive an expression for the entropy in terms of these three functions. (b) Apply the technique to the calculation of the electronic contribution to the standard molar entropy of magnesium vapour at 5000 K using the following data:

Term	^{1}S	^{3}P$_0$	^{3}P$_1$	^{3}P$_2$	^{1}P$_1$	^{3}S
Degeneracy	1	1	3	5	3	3
$\tilde{\nu}$/cm^{-1}	0	21 850	21 870	21 911	35 051	41 197

Topic 61 The thermodynamic entropy

Discussion question

61.1 Discuss the relationships between the various formulations of the Second Law of thermodynamics.

Exercises

61.1(a) A certain ideal heat engine uses water at the triple point as the hot source and an organic liquid as the cold sink. It withdraws 10.00 kJ of heat from the hot source and generates 3.00 kJ of work. What is the temperature of the organic liquid?

61.1(b) A certain ideal heat engine uses water at the triple point as the hot source and an organic liquid as the cold sink. It withdraws 2.71 kJ of heat from the hot source and generates 0.71 kJ of work. What is the temperature of the organic liquid?

61.2(a) Calculate the change in entropy when 100 kJ of energy is transferred reversibly and isothermally as heat to a large block of copper at (a) 0 °C, (b) 50 °C.

61.2(b) Calculate the change in entropy when 250 kJ of energy is transferred reversibly and isothermally as heat to a large block of lead at (a) 20 °C, (b) 100 °C.

Problems

61.1 Represent the Carnot cycle on a temperature–entropy diagram and show that the area enclosed by the cycle is equal to the work done.

61.2 The cycle involved in the operation of an internal combustion engine is called the *Otto cycle*. Air can be considered to be the working substance and can be assumed to be a perfect gas. The cycle consists of the following steps: (1) Reversible adiabatic compression from A to B, (2) reversible constant-volume pressure increase from B to C due to the combustion of a small amount of fuel, (3) reversible adiabatic expansion from C to D, and (4) reversible and constant-volume pressure decrease back to state A. Determine the change in entropy (of the system and of the surroundings) for each step of the cycle and determine an expression for the efficiency of the cycle, assuming that the heat is supplied in Step 2. Evaluate the efficiency for a compression ratio of 10:1. Assume that in state A, $V = 4.00\,\text{dm}^3$, $p = 1.00$ atm, and $T = 300$ K, that $V_A = 10V_B$, $p_C/p_B = 5$, and $C_{p,m} = \tfrac{7}{2}R$.

61.3 Prove that two reversible adiabatic paths can never cross. Assume that the energy of the system under consideration is a function of temperature only. (*Hint*: Suppose that two such paths can intersect, and complete a cycle with the two paths plus one isothermal path. Consider the changes accompanying

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‡ These problems were supplied by Charles Trapp and Carmen Giunta.

each stage of the cycle and show that they conflict with the Kelvin statement of the Second Law.)

61.4 To calculate the work required to lower the temperature of an object in a Carnot-like device, we need to consider how the coefficient of performance, the ratio of the energy transferred as heat from the cold source to the work required, $c(T) = |q_c|/|w|$, changes with the temperature of the object. (a) Find an expression for the work of cooling an object from T_i to T_f when the refrigerator is in a room at a temperature T_h. *Hint*: Write $dw = dq/c(T)$, relate dq to dT through the heat capacity C_p, and integrate the resulting expression. Assume that the heat capacity is independent of temperature in the range of interest. (b) Use the result in part (a) to calculate the work needed to freeze 250 g of water in a refrigerator at 293 K. How long will it take when the refrigerator operates at 100 W?

61.5 The expressions that apply to the treatment of refrigerators (Problem 61.4) also describe the behaviour of heat pumps treated as Carnot engines, where warmth is obtained from the back of a refrigerator while its front is being used to cool the outside world. Heat pumps are popular home heating devices because they are very efficient. Compare heating of a room at 295 K by each of two methods: (a) direct conversion of 1.00 kJ of electrical energy in an electrical heater, and (b) use of 1.00 kJ of electrical energy to run a reversible heat pump with the outside at 260 K. Discuss the origin of the difference in the energy delivered to the interior of the house by the two methods.

Topic 62 Entropy changes for specific processes

Discussion question

62.1 Account for deviations from Trouton's rule for liquids such as water and ethanol. Is their entropy of vaporization larger or smaller than 85 J K^{-1} mol^{-1}? Why?

Exercises

62.1(a) Which of F_2(g) and I_2(g) is likely to have the higher standard molar entropy at 298 K?
62.1(b) Which of H_2O(g) and CO_2(g) is likely to have the higher standard molar entropy at 298 K?

62.2(a) Calculate the change in entropy when 15 g of carbon dioxide gas is allowed to expand from 1.0 dm^3 to 3.0 dm^3 at 300 K.
62.2(b) Calculate the change in entropy when 4.00 g of nitrogen is allowed to expand from 500 cm^3 to 750 cm^3 at 300 K.

62.3(a) Predict the enthalpy of vaporization of benzene from its normal boiling point, 80.1 °C.
62.3(b) Predict the enthalpy of vaporization of cyclohexane from its normal boiling point, 80.7 °C.

62.4(a) Calculate the molar entropy of a constant-volume sample of neon at 500 K given that it is 146.22 J K^{-1} mol^{-1} at 298 K.
62.4(b) Calculate the molar entropy of a constant-volume sample of argon at 250 K given that it is 154.84 J K^{-1} mol^{-1} at 298 K.

62.5(a) Calculate ΔS (for the system) when the state of 3.00 mol of perfect gas atoms, for which $C_{p,m} = \frac{5}{2}R$, is changed from 25 °C and 1.00 atm to 125 °C and 5.00 atm. How do you rationalize the sign of ΔS?
62.5(b) Calculate ΔS (for the system) when the state of 2.00 mol diatomic perfect gas molecules, for which $C_{p,m} = \frac{7}{2}R$, is changed from 25 °C and 1.50 atm to 135 °C and 7.00 atm. How do you rationalize the sign of ΔS?

62.6(a) A sample consisting of 3.00 mol of diatomic perfect gas molecules at 200 K is compressed reversibly and adiabatically until its temperature reaches 250 K. Given that $C_{V,m} = 27.5$ J K^{-1} mol^{-1}, calculate ΔS.
62.6(b) A sample consisting of 2.00 mol of diatomic perfect gas molecules at 250 K is compressed reversibly and adiabatically until its temperature reaches 300 K. Given that $C_{V,m} = 27.5$ J K^{-1} mol^{-1}, calculate ΔS.

62.7(a) Calculate ΔS_{tot} when two copper blocks, each of mass 1.00 kg, one at 50 °C and the other at 0 °C, are placed in contact in an isolated container. The specific heat capacity of copper is 0.385 J K^{-1} g^{-1} and may be assumed constant over the temperature range involved.
62.7(b) Calculate ΔS_{tot} when two iron blocks, each of mass 10.0 kg, one at 100 °C and the other at 25 °C, are placed in contact in an isolated container. The specific heat capacity of iron is 0.449 J K^{-1} g^{-1} and may be assumed constant over the temperature range involved.

62.8(a) Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when a sample of nitrogen gas of mass 14 g at 298 K and 1.00 bar doubles its volume in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against $p_{ex} = 0$, and (c) an adiabatic reversible expansion.
62.8(b) Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when the volume of a sample of argon gas of mass 21 g at 298 K and 1.50 bar increases from 1.20 dm^3 to 4.60 dm^3 in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against $p_{ex} = 0$, and (c) an adiabatic reversible expansion.

62.9(a) The enthalpy of vaporization of chloroform ($CHCl_3$) is 29.4 kJ mol^{-1} at its normal boiling point of 334.88 K. Calculate (a) the entropy of vaporization of chloroform at this temperature and (b) the entropy change of the surroundings.
62.9(b) The enthalpy of vaporization of methanol is 35.27 kJ mol^{-1} at its normal boiling point of 64.1 °C. Calculate (a) the entropy of vaporization of methanol at this temperature and (b) the entropy change of the surroundings.

62.10(a) Calculate the change in entropy of the system when 10.0 g of ice at −10.0 °C is converted into water vapour at 115.0 °C and at a constant pressure of 1 bar. The constant-pressure molar heat capacity of H_2O(s) and H_2O(l) is 75.291 J K^{-1} mol^{-1} and that of H_2O(g) is 33.58 J K^{-1} mol^{-1}. Enthalpies of phase transitions are given in Table 57.2.
62.10(b) Calculate the change in entropy of the system when 15.0 g of ice at −12.0 °C is converted to water vapour at 105.0 °C at a constant pressure of 1 bar. For data, see the preceding exercise.

Problems

62.1 Calculate the difference in molar entropy (a) between liquid water and ice at −5 °C, (b) between liquid water and its vapour at 95 °C and 1.00 atm. The differences in heat capacities on melting and on vaporization are 37.3 J K^{-1} mol^{-1} and −41.9 J K^{-1} mol^{-1}, respectively. Distinguish between the entropy changes of the sample, the surroundings, and the total system, and discuss the spontaneity of the transitions at the two temperatures.

62.2 The molar heat capacity of chloroform (trichloromethane, $CHCl_3$) in the range 240 K to 330 K is given by $C_{p,m}/(J\,K^{-1}\,mol^{-1}) = 91.47 + 7.5\times10^{-2}\,(T/K)$. In a particular experiment, 1.00 mol $CHCl_3$ is heated from 273 K to 300 K. Calculate the change in molar entropy of the sample.

62.3 A block of copper of mass 2.00 kg ($C_{p,m} = 24.44$ J K^{-1} mol^{-1}) and temperature 0 °C is introduced into an insulated container in which there is 1.00 mol $H_2O(g)$ at 100 °C and 1.00 atm. (a) Assuming all the steam is condensed to water, what will be the final temperature of the system, the heat transferred from water to copper, and the entropy change of the water, copper, and the total system? (b) In fact, some water vapour is present at equilibrium. From the vapour pressure of water at the temperature calculated in (a), and assuming that the heat capacities of both gaseous and liquid water are constant and given by their values at that temperature, obtain an improved value of the final temperature, the heat transferred, and the various entropies. (*Hint*: You will need to make plausible approximations.)

62.4 A sample consisting of 1.00 mol of perfect gas molecules at 27 °C is expanded isothermally from an initial pressure of 3.00 atm to a final pressure of 1.00 atm in two ways: (a) reversibly, and (b) against a constant external pressure of 1.00 atm. Determine the values of q, w, ΔU, ΔH, ΔS, ΔS_{surr}, ΔS_{tot} for each path.

62.5 A block of copper of mass 500 g and initially at 293 K is in thermal contact with an electric heater of resistance 1.00 kΩ and negligible mass. A current of 1.00 A is passed for 15.0 s. Calculate the change in entropy of the copper, taking $C_{p,m} = 24.4$ J K^{-1} mol^{-1}. The experiment is then repeated with the copper immersed in a stream of water that maintains its temperature at 293 K. Calculate the change in entropy of the copper and the water in this case.

62.6 Find an expression for the change in entropy when two blocks of the same substance and of equal mass, one at the temperature T_h and the other at T_c, are brought into thermal contact and allowed to reach equilibrium. Evaluate the change for two blocks of copper, each of mass 500 g, with $C_{p,m} = 24.4$ J K^{-1} mol^{-1}, taking $T_h = 500$ K and $T_c = 250$ K.

62.7 According to Newton's law of cooling, the rate of change of temperature is proportional to the temperature difference between the system and its surroundings. Given that $S(T) - S(T_i) = C\ln(T/T_i)$, where T_i is the initial temperature and C the heat capacity, deduce an expression for the rate of change of entropy of the system as it cools.

62.8 The protein lysozyme unfolds at a transition temperature of 75.5 °C and the standard enthalpy of transition is 509 kJ mol^{-1}. Calculate the entropy of unfolding of lysozyme at 25.0 °C, given that the difference in the constant-pressure heat capacities upon unfolding is 6.28 kJ K^{-1} mol^{-1} and can be assumed to be independent of temperature. *Hint*: Imagine that the transition at 25.0 °C occurs in three steps: (i) heating of the folded protein from 25.0 °C to the transition temperature, (ii) unfolding at the transition temperature, and (iii) cooling of the unfolded protein to 25.0 °C. Because the entropy is a state function, the entropy change at 25.0 °C is equal to the sum of the entropy changes of the steps.

Topic 63 The Third Law

Discussion question

63.1 Discuss why the standard entropies of ions in solution may be positive, negative, or zero.

Exercises

63.1(a) Calculate the residual molar entropy of a solid in which the molecules can adopt (a) three, (b) five, (c) six orientations of equal energy at $T = 0$.
63.1(b) Suppose that the hexagonal molecule $C_6H_nF_{6-n}$ has a residual entropy on account of the similarity of the H and F atoms. Calculate the residual for each value of n.

63.2(a) Calculate the standard reaction entropy at 298 K of
(a) $2\,CH_3CHO(g) + O_2(g) \rightarrow 2\,CH_3COOH(l)$
(b) $2\,AgCl(s) + Br_2(l) \rightarrow 2\,AgBr(s) + Cl_2(g)$
(c) $Hg(l) + Cl_2(g) \rightarrow HgCl_2(s)$
63.2(b) Calculate the standard reaction entropy at 298 K of
(a) $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
(b) $C_{12}H_{22}O_{11}(s) + 12\,O_2(g) \rightarrow 12\,CO_2(g) + 11\,H_2O(l)$

Problems

63.1 The standard molar entropy of $NH_3(g)$ is 192.45 J K^{-1} mol^{-1} at 298 K, and its heat capacity is given by eqn 56.5 with the coefficients given in Table 56.1. Calculate the standard molar entropy at (a) 100 °C and (b) 500 °C.

63.2 The molar heat capacity of lead varies with temperature as follows:

T/K	10	15	20	25	30	50
$C_{p,m}/(J\,K^{-1}\,mol^{-1})$	2.8	7.0	10.8	14.1	16.5	21.4
T/K	70	100	150	200	250	298
$C_{p,m}/(J\,K^{-1}\,mol^{-1})$	23.3	24.5	25.3	25.8	26.2	26.6

Calculate the standard Third-Law entropy of lead at (a) 0 °C and (b) 25 °C.

63.3 From standard enthalpies of formation, standard entropies, and standard heat capacities available from tables in the *Resource section*, calculate the standard enthalpies and entropies at 298 K and 398 K for the reaction $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$. Assume that the heat capacities are constant over the temperature range involved.

63.4 The molar heat capacity of anhydrous potassium hexacyanoferrate(II) varies with temperature as follows:

T/K	10	20	30	40	50	60
$C_{p,m}/(\mathrm{J\ K^{-1}\ mol^{-1}})$	2.09	14.43	36.44	62.55	87.03	111.0
T/K	70	80	90	100	110	150
$C_{p,m}/(\mathrm{J\ K^{-1}\ mol^{-1}})$	131.4	149.4	165.3	179.6	192.8	237.6
T/K	160	170	180	190	200	
$C_{p,m}/(\mathrm{J\ K^{-1}\ mol^{-1}})$	247.3	256.5	265.1	273.0	280.3	

Calculate the molar enthalpy relative to its value at $T=0$ and the Third-Law entropy at each of these temperatures.

63.5 The compound 1,3,5-trichloro-2,4,6-trifluorobenzene is an intermediate in the conversion of hexachlorobenzene to hexafluorobenzene, and its thermodynamic properties have been examined by measuring its heat capacity over a wide temperature range (R.L. Andon and J.F. Martin, *J. Chem. Soc. Faraday Trans. I,* 871 (1973)). Some of the data are as follows:

T/K	14.14	16.33	20.03	31.15	44.08	64.81
$C_{p,m}/(\mathrm{J\ K^{-1}\ mol^{-1}})$	9.492	12.70	18.18	32.54	46.86	66.36
T/K	100.90	140.86	183.59	225.10	262.99	298.06
$C_{p,m}/(\mathrm{J\ K^{-1}\ mol^{-1}})$	95.05	121.3	144.4	163.7	180.2	196.4

Calculate the molar enthalpy relative to its value at $T=0$ and the Third-Law molar entropy of the compound at these temperatures.

63.6‡ Given that $S_m^{\ominus} = 29.79\ \mathrm{J\,K^{-1}mol^{-1}}$ for bismuth at 100 K and the following tabulated heat capacity data (D.G. Archer, *J. Chem. Eng. Data* **40**, 1015 (1995)), compute the standard molar entropy of bismuth at 200 K.

T/K	100	120	140	150	160	180	200
$C_{p,m}/(\mathrm{J\ K^{-1}\ mol^{-1}})$	23.00	23.74	24.25	24.44	24.61	24.89	25.11

Compare the value to the value that would be obtained by taking the heat capacity to be constant at 24.44 J K^{-1} mol^{-1} over this range.

63.7 Derive an expression for the molar entropy of a monatomic solid on the basis of the Einstein and Debye models and plot the molar entropy against the temperature (use T/θ in each case, with θ the Einstein or Debye temperature). Use the following expressions for the temperature dependence of the heat capacities:

$$\text{Einstein}: C_{V,m}(T)=3Rf^{E}(T) \qquad f^{E}(T)=\left(\frac{\theta^{E}}{T}\right)^{2}\left(\frac{e^{\theta^{E}/2T}}{e^{\theta^{E}/T}-1}\right)^{2}$$

$$\text{Debye}: C_{V,m}(T)=3Rf^{D}(T) \qquad f^{D}(T)=3\left(\frac{T}{\theta^{D}}\right)^{2}\int_{0}^{\theta^{D}/T}\frac{x^{4}e^{x}}{(e^{x}-1)^{2}}dx$$

Use mathematical software to evaluate the appropriate expressions.

63.8 An average human DNA molecule has 5×10^8 binucleotides (rungs on the DNA ladder) of four different kinds. If each rung were a random choice of one of these four possibilities, what would be the residual entropy associated with this typical DNA molecule?

Topic 64 Spontaneous processes

Discussion questions

64.1 The following expressions have been used to establish criteria for spontaneous change: $dA_{T,V} < 0$ and $dG_{T,p} < 0$. Discuss the origin, significance, and applicability of each criterion.

64.2 Under what circumstances, and why, can the spontaneity of a process be discussed in terms of the properties of the system alone?

Exercises

64.1(a) Combine the reaction entropies calculated in Exercise 63.2(a) with the reaction enthalpies, and calculate the standard reaction Gibbs energies at 298 K.

64.1(b) Combine the reaction entropies calculated in Exercise 63.2(b) with the reaction enthalpies, and calculate the standard reaction Gibbs energies at 298 K.

64.2(a) Calculate the standard Gibbs energy of the reaction $4\ HI(g) + O_2(g) \rightarrow 2\ I_2(s) + 2\ H_2O(l)$ at 298 K, from the standard entropies and enthalpies of formation given in the *Resource section*.

64.2(b) Calculate the standard Gibbs energy of the reaction $CO(g) + CH_3CH_2OH(l) \rightarrow CH_3CH_2COOH(l)$ at 298 K, from the standard entropies and enthalpies of formation given in the *Resource section*.

64.3(a) Calculate the maximum non-expansion work per mole that may be obtained from a fuel cell in which the chemical reaction is the combustion of methane at 298 K.

64.3(b) Calculate the maximum non-expansion work per mole that may be obtained from a fuel cell in which the chemical reaction is the combustion of propane at 298 K.

64.4(a) A CO_2 molecule is linear, and its vibrational wavenumbers are 1388.2 cm^{-1}, 667.4 cm^{-1}, and 2349.2 cm^{-1}, the last being doubly degenerate and the others non-degenerate. The rotational constant of the molecule is 0.3902 cm^{-1}. Calculate the rotational and vibrational contributions to the molar Gibbs energy at 298 K.

64.4(b) An O_3 molecule is angular, and its vibrational wavenumbers are 1110 cm^{-1}, 705 cm^{-1}, and 1042 cm^{-1}. The rotational constants of the molecule are 3.553 cm^{-1}, 0.4452 cm^{-1}, and 0.3948 cm^{-1}. Calculate the rotational and vibrational contributions to the molar Gibbs energy at 298 K.

64.5(a) The ground level of Cl is $^2P_{3/2}$ and a $^2P_{1/2}$ level lies 881 cm^{-1} above it. Calculate the electronic contribution to the molar Gibbs energy of Cl atoms at (a) 500 K and (b) 900 K.

64.5(b) The first electronically excited state of O_2 is $^1\Delta_g$ and lies 7918.1 cm^{-1} above the ground state, which is $^3\Sigma_g^-$. Calculate the electronic contribution to the molar Gibbs energy of O_2 at 500 K.

Problems

64.1 Consider a perfect gas contained in a cylinder and separated by a frictionless adiabatic piston into two sections A and B. All changes in B are isothermal; that is, a thermostat surrounds B to keep its temperature constant. There is 2.00 mol of the gas in each section. Initially $T_A = T_B = 300$ K, $V_A = V_B = 2.00$ dm^3. Energy is supplied as heat to Section A and the piston moves to the right reversibly until the final volume of Section B is 1.00 L. Calculate (a) ΔS_A and ΔS_B, (b) ΔA_A and ΔA_B, (c) ΔG_A and ΔG_B, (d) ΔS of the total system and its surroundings. If numerical values cannot be obtained, indicate whether the values should be positive, negative, or zero or are indeterminate from the information given. (Assume $C_{V,m} = 20$ J K^{-1} mol^{-1}.)

64.2 Calculate the molar internal energy, molar entropy, and molar Helmholtz energy of a collection of harmonic oscillators and plot your expressions as a function of T/θ^V, where $\theta^V = h\nu/k$.

64.3 In biological cells, the energy released by the oxidation of foods is stored in adenosine triphosphate (ATP or ATP^{4-}). The essence of ATP's action is its ability to lose its terminal phosphate group by hydrolysis and to form adenosine diphosphate (ADP or ADP^{3-}):

$$\text{ATP}^{4-}(\text{aq}) + H_2O(\text{l}) \rightarrow \text{ADP}^{3-}(\text{aq}) + HPO_4^{2-}(\text{aq}) + H_3O^+(\text{aq})$$

At pH = 7.0 and 37 °C (310 K, blood temperature) the enthalpy and Gibbs energy of hydrolysis are $\Delta_r H = -20$ kJ mol^{-1} and $\Delta_r G = -31$ kJ mol^{-1}, respectively. Under these conditions, the hydrolysis of 1 mol ATP^{4-}(aq) results in the extraction of up to 31 kJ of energy that can be used to do non-expansion work, such as the synthesis of proteins from amino acids, muscular contraction, and the activation of neuronal circuits in our brains. (a) Calculate and account for the sign of the entropy of hydrolysis of ATP at pH = 7.0 and 310 K. (b) Suppose that the radius of a typical biological cell is 10 μm and that inside it 10^6 ATP molecules are hydrolysed each second. What is the power density of the cell in watts per cubic metre (1 W = 1 J s^{-1})? A computer battery delivers about 15 W and has a volume of 100 cm^3. Which has the greater power density, the cell or the battery? (c) The formation of glutamine from glutamate and ammonium ions requires 14.2 kJ mol^{-1} of energy input. It is driven by the hydrolysis of ATP to ADP mediated by the enzyme glutamine synthetase. How many moles of ATP must be hydrolysed to form 1 mol glutamine?

64.4‡ The molecule Cl_2O_2, which is believed to participate in the seasonal depletion of ozone over Antarctica, has been studied by several means. Birk, et al. (*J. Chem. Phys.* **91**, 6588 (1989)) report its rotational constants B as 13109.4, 2409.8, and 2139.7 MHz. They also report that its rotational spectrum indicates a molecule with a symmetry number of 2.19. Its vibrational wavenumbers are 753, 542, 310, 127, 646, and 419 cm^{-1}. Compute $G_m^\ominus(200\ \text{K}) - G_m^\ominus(0)$ of Cl_2O_2.

Topic 65 Standard Gibbs energies

Discussion questions

65.1 Describe ways the standard Gibbs energies of formation can be determined.

65.2 Identify the thermodynamic factors responsible for the magnitude of the Gibbs energy of formation of an ion in solution.

Exercises

65.1(a) Use standard Gibbs energies of formation to calculate the standard reaction Gibbs energies at 298 K of the reactions
(a) $2\,CH_3CHO(g) + O_2(g) \rightarrow 2\,CH_3COOH(l)$
(b) $2\,AgCl(s) + Br_2(l) \rightarrow 2\,AgBr(s) + Cl_2(g)$
(c) $Hg(l) + Cl_2(g) \rightarrow HgCl_2(s)$

65.1(b) Use standard Gibbs energies of formation to calculate the standard reaction Gibbs energies at 298 K of the reactions
(a) $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
(b) $C_{12}H_{22}O_{11}(s) + 12\,O_2(g) \rightarrow 12\,CO_2(g) + 11\,H_2O(l)$

65.2(a) The standard enthalpy of combustion of ethyl acetate ($CH_3COOC_2H_5$) is −2231 kJ mol^{-1} at 298 K and its standard molar entropy is 259.4 J K^{-1} mol^{-1}. Calculate the standard Gibbs energy of formation of the compound at 298 K.

65.2(b) The standard enthalpy of combustion of the amino acid glycine (NH_2CH_2COOH) is −969 kJ mol^{-1} at 298 K and its standard molar entropy is 103.5 J K^{-1} mol^{-1}. Calculate the standard Gibbs energy of formation of glycine at 298 K.

Problem

65.1‡ R. Viswanathan, et al. (*J. Phys. Chem.* **100**, 10784 (1996)) studied the thermodynamic properties of several boron–silicon gas-phase species experimentally and theoretically. These species can occur in the high-temperature chemical vapour deposition (CVD) of silicon-based semiconductors. Among the computations they reported was computation of the Gibbs energy of BSi(g) at several temperatures based on a $^4\Sigma^-$ ground state with equilibrium internuclear distance of 190.5 pm and fundamental vibrational wavenumber of 772 cm^{-1} and a $^2P_0$ first excited level 8000 cm^{-1} above the ground level. Compute the standard molar Gibbs energy $G_m^\ominus(2000\ \text{K}) - G_m^\ominus(0)$.

Topic 66 Combining the First and Second Laws

Discussion question

66.1 Suggest a physical interpretation of the dependence of the Gibbs energy on the temperature.

Exercises

66.1(a) Suppose that 2.5 mmol N_2(g) occupies 42 cm^3 at 300 K and expands isothermally to 600 cm^3. Calculate ΔG for the process.
66.1(b) Suppose that 6.0 mmol Ar(g) occupies 52 cm^3 at 298 K and expands isothermally to 122 cm^3. Calculate ΔG for the process.

66.2(a) The change in the Gibbs energy of a certain constant-pressure process was found to fit the expression $\Delta G/\mathrm{J} = -85.40 + 36.5(T/\mathrm{K})$. Calculate the value of ΔS for the process.
66.2(b) The change in the Gibbs energy of a certain constant-pressure process was found to fit the expression $\Delta G/\mathrm{J} = -73.1 + 42.8(T/\mathrm{K})$. Calculate the value of ΔS for the process.

66.3(a) Estimate the change in the Gibbs energy and molar Gibbs energy of 1.0 dm^3 of octane when the pressure acting on it is increased from 1.0 atm to 100 atm. The mass density of octane is 0.703 g cm^{-3}.

66.3(b) Estimate the change in the Gibbs energy and molar Gibbs energy of 100 cm^3 of water when the pressure acting on it is increased from 100 kPa to 500 kPa. The mass density of water is 0.997 g cm^{-3}.

66.4(a) Calculate the change in the molar Gibbs energy of hydrogen gas when its pressure is increased isothermally from 1.0 atm to 100.0 atm at 298 K.
66.4(b) Calculate the change in the molar Gibbs energy of oxygen when its pressure is increased isothermally from 50.0 kPa to 100.0 kPa at 500 K.

66.5(a) Calculate the change in Gibbs energy of 35 g of ethanol (mass density 0.789 g cm^{-3}) when the pressure is increased isothermally from 1 atm to 3000 atm.
66.5(b) Calculate the change in Gibbs energy of 25 g of methanol (mass density 0.791 g cm^{-3}) when the pressure is increased isothermally from 100 kPa to 100 MPa.

Problems

66.1 Calculate $\Delta_r G^{\ominus}(375\ \mathrm{K})$ for the reaction $2\,CO(g) + O_2(g) \rightarrow 2\,CO_2(g)$ from the values of $\Delta_r G^{\ominus}(298\ \mathrm{K})$: and $\Delta_r H^{\ominus}(298\ \mathrm{K})$, and the Gibbs–Helmholtz equation.

66.2 Estimate the standard reaction Gibbs energy of $N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$ at (a) 500 K, (b) 1000 K from its value at 298 K.

66.3 At 298 K the standard enthalpy of combustion of sucrose is −5797 kJ mol^{-1} and the standard Gibbs energy of the reaction is −6333 kJ mol^{-1}. Estimate the additional non-expansion work that may be obtained by raising the temperature to blood temperature, 37 °C.

66.4 Two empirical equations of state of a real gas are as follows:

$$\text{van der Waals:}\ p = \frac{RT}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}^2}$$

$$\text{Dieterici:}\ p = \frac{RT\mathrm{e}^{-a/RTV_\mathrm{m}}}{V_\mathrm{m} - b}$$

Evaluate $(\partial S/\partial V)_T$ for each gas. For an isothermal expansion, for which kind of gas (also consider a perfect gas) will ΔS be greatest? Explain your conclusion.

66.5 Two of the four Maxwell relations were derived in the text, but two were not. Complete their derivation by showing that $(\partial S/\partial V)_T = (\partial p/\partial T)_V$ and $(\partial T/\partial p)_S = (\partial V/\partial S)_p$.

66.6 (a) Use the Maxwell relations to express the derivatives $(\partial S/\partial V)_T$, $(\partial V/\partial S)_p$, $(\partial p/\partial S)_V$, and $(\partial V/\partial S)_p$ in terms of the heat capacities, the expansion coefficient, $\alpha = (1/V)(\partial V/\partial T)_p$, and the isothermal compressibility, $\kappa_T = -(1/V)(\partial V/\partial p)_T$. (b) The Joule coefficient, μ_J, is defined as $\mu_\mathrm{J} = (\partial T/\partial V)_U$. Show that $\mu_\mathrm{J} C_V = p - \alpha T/\kappa_T$.

66.7 Suppose that S is regarded as a function of p and T. Show that $T\mathrm{d}S = C_p\mathrm{d}T - \alpha TV\mathrm{d}p$. Hence, show that the energy transferred as heat when the pressure on an incompressible liquid or solid is increased by Δp is equal to $-\alpha TV\Delta p$, where $\alpha = (1/V)(\partial V/\partial T)_p$. Evaluate q when the pressure acting on 100 cm^3 of mercury at 0 °C is increased by 1.0 kbar. ($\alpha = 1.82 \times 10^{-4}\ \mathrm{K}^{-1}$.)

66.8 Equation 66.5 ($\pi_T = T(\partial p/\partial T)_V - p$) expresses the internal pressure π_T in terms of the pressure and its derivative with respect to temperature. Express π_T in terms of the molecular partition function.

66.9 Explore the consequences of replacing the equation of state of a perfect gas by the van der Waals equation of state for the pressure dependence of the molar Gibbs energy (eqn 66.10). Proceed in three steps. First, consider the case when $a = 0$ and only repulsions are significant. Then consider the case when $b = 0$ and only attractions are significant. For the latter, you should consider making the approximation that the attractions are weak. Finally, explore the full expression by using mathematical software. In each case plot your results graphically and account physically for the deviations from the perfect gas expression.

66.10‡ Nitric acid hydrates have received much attention as possible catalysts for heterogeneous reactions which bring about the Antarctic ozone hole. Worsnop, et al. (*Science* **259**, 71 (1993)) investigated the thermodynamic stability of these hydrates under conditions typical of the polar winter stratosphere. They report thermodynamic data for the sublimation of mono-, di-, and trihydrates to nitric acid and water vapours, $HNO_3{\cdot}nH_2O(s) \rightarrow HNO_3(g) + n\,H_2O(g)$, for $n = 1$, 2, and 3. Given $\Delta_r G^{\ominus}$ and $\Delta_r H^{\ominus}$ for these reactions at 220 K, use the Gibbs–Helmholtz equation to compute $\Delta_r G^{\ominus}$ at 190 K.

n	1	2	3
$\Delta_r G^{\ominus}/(\mathrm{kJ\ mol^{-1}})$	46.2	69.4	93.2
$\Delta_r H^{\ominus}/(\mathrm{kJ\ mol^{-1}})$	127	188	237

Integrated activities

F13.1 Identify as many arguments as you can that confirm the relation $\beta = 1/kT$. Present arguments that show that β is a more appropriate parameter for expressing the temperature than T itself. What is the status of k as a fundamental constant?

F13.2 A gaseous sample consisting of 1.00 mol molecules is described by the equation of state $pV_m = RT(1+Bp)$. Initially at 373 K, it undergoes Joule–Thomson expansion from 100 atm to 1.00 atm. Given that $C_{p,m} = \frac{5}{2}R$, $\mu = 0.21\ \mathrm{K\ atm^{-1}}$, $B = -0.525(\mathrm{K}/T)\ \mathrm{atm^{-1}}$ and that these are constant over the temperature range involved, calculate ΔT and ΔS for the gas.

F13.3 A Carnot cycle uses 1.00 mol of monatomic perfect gas molecules as the working substance from an initial state of 10.0 atm and 600 K. It expands isothermally to a pressure of 1.00 atm (step 1), and then adiabatically to a temperature of 300 K (step 2). This expansion is followed by an isothermal compression (step 3), and then an adiabatic compression (step 4) back to the initial state. Determine the values of q, w, ΔU, ΔH, ΔS, ΔS_{tot}, and ΔG for each stage of the cycle and for the cycle as a whole. Express your answer as a table of values.

F13.4 Suppose that an internal combustion engine runs on octane, for which the enthalpy of combustion is $-5512\ \mathrm{kJ\ mol^{-1}}$, and take the mass of 1 gallon of fuel as 3 kg. What is the maximum height, neglecting all forms of friction, to which a car of mass 1000 kg can be driven on 1.00 gallon of fuel given that the engine cylinder temperature is 2000 °C and the exit temperature is 800 °C?

F13.5 Deduce the result $(\partial U/\partial S)_V = T$ and then use the calculation on which Problem 60.6 is based to draw a graph of U against S (or vice versa) to identify the temperature. *Hint*: Use mathematical software to construct the graph.

F13.6 Use mathematical software, a spreadsheet, or the *Living graphs* (labelled $^{\mathrm{LG}}$) on the website of this book for the following exercises.

(a) Evaluate the change in entropy that accompanies the expansion of 1.00 mol CO_2(g) from $0.0010\ \mathrm{m^3}$ to $0.010\ \mathrm{m^3}$ at 298 K, treated as a van der Waals gas.

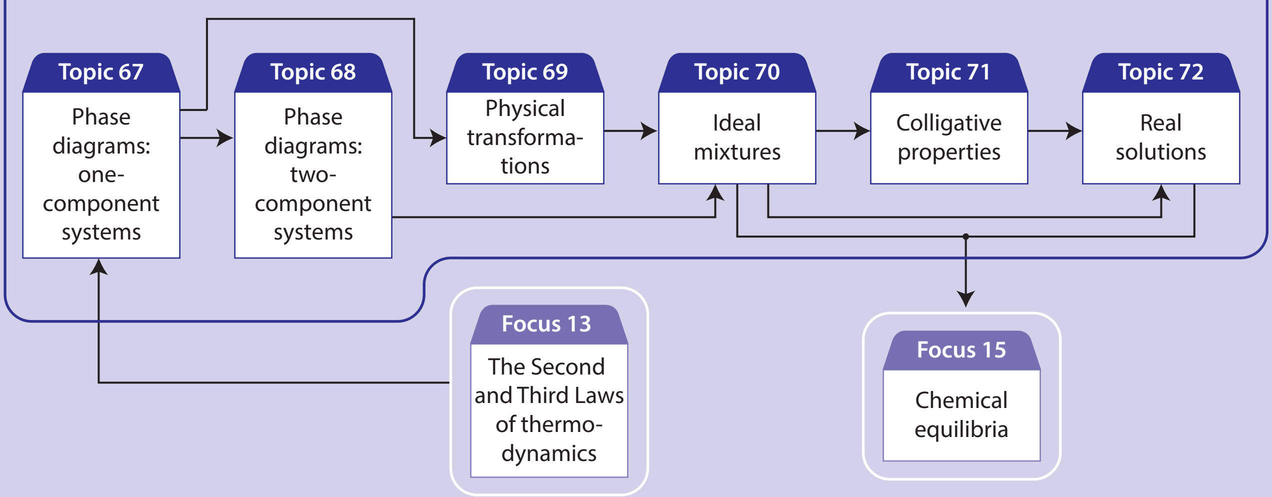
(b) Plot the function $\mathrm{d}S/\mathrm{d}T$, the temperature coefficient of the entropy for a collection of harmonic oscillators, against kT/ε. Is there a temperature at which this coefficient passes through a maximum? If you find a maximum, explain its physical origins.

(c) Plot the change in entropy of a perfect gas of (a) atoms, (b) linear rotors, (c) nonlinear rotors as the sample is heated over the same range under conditions of (i) constant volume, (ii) constant pressure. Use the high-temperature limit for the rotors.

(d)$^{\mathrm{LG}}$ Allow for the temperature dependence of the heat capacity by writing $C = a + bT + c/T^2$, and plot the change in entropy of heating for different values of the three coefficients (including negative values of c).

(e) Show how the first derivative of G, $(\partial G/\partial p)_T$, varies with pressure for a perfect gas, and plot the resulting expression over a pressure range. What is the physical significance of $(\partial G/\partial p)_T$?

FOCUS 14 ON Physical equilibria



Physical equilibria are very important aspects of the properties of matter, for they include phase transitions of pure substances and mixtures. They also provide an introduction to the thermodynamic discussion of how one component can affect the properties of another present in the mixture, and are an essential preliminary to the discussion of *Chemical equilibria*, in which the components can change their chemical identities by reaction.

The equilibria between the various phases of a substance or a mixture of substances can be summarized by constructing a 'phase diagram', a map showing the conditions under which each phase is the most stable. For one-component systems (**Topic 67**) the natural choice of variables for the diagram is the pressure and temperature. For two-component systems (**Topic 68**) there is a wider choice, with temperature and composition or pressure and composition being natural and useful choices. These diagrams also allow us to discuss fractional distillation of liquid mixtures.

The conversion of one phase into another when the conditions change has a thermodynamic basis and can be expressed by drawing on *The Second and Third Laws of thermodynamics*. We show (**Topic 69**) how it is possible to predict the location of phase boundaries (where two phases are in equilibrium) and thus to use thermodynamic criteria to show, for instance, how a change in pressure affects the boiling temperature of a liquid.

Thermodynamics acquires considerable predictive power when the contribution of each substance to the Gibbs energy of a mixture is expressed in terms of the 'chemical potential' (**Topic 70**), one of several 'partial molar quantities'. Equilibria can be expressed in terms of the balancing of chemical potentials between phases. We set up expressions for showing how the chemical potential of a substance in a mixture can be expressed in terms of the composition of the mixture, and in the process introduce the concepts of 'ideal' and 'ideal–dilute' solutions.

The presence of a solute in a solution affects the entropy of the mixture, and through that effect changes various physical properties of the solvent, such as its freezing and boiling temperatures and its osmotic pressure (**Topic 71**). The last of these properties has important applications in biology and macromolecular science.

Ideal solutions, however, are abstractions, and in the final section (**Topic 72**) we see how to transform the equations developed for ideal solutions into similar equations for real solutions by replacing concentrations by 'activities'. Activities are essential for the discussion of electrolyte solutions.

What is the impact of this material?

Almost everything we encounter in the everyday world is a mixture. In the two Impacts referred to here we focus on biology and technology. *Impact* 14.1 describes the importance of osmosis in biology, and in particular its role in maintaining the shape and structural integrity of biological cells. *Impact* 14.2 describes another ubiquitous modern material, the liquid crystals that are common in electronic displays, and explores how the formulation of mixtures affects their optical properties.

To read more about the impact of this material, scan the QR code or go to http://bcs.whfreeman.com/webpub/chemistry/qmc2e/impact/qchem_impact14.html.

TOPIC 67

Phase diagrams: one-component systems

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➤ Why do you need to know this material?

Phase transitions occur widely in nature and industry, and it is important to be able to keep track of them. Phase diagrams are used in materials science and related fields to display the conditions under which each phase of a substance or a mixture is the most stable.

➤ What is the key idea?

When two phases are in equilibrium, their chemical potentials are equal; a consequence is the phase rule, which constrains the freedom to change the conditions while preserving equilibrium.

➤ What do you need to know already?

This Topic draws on the concept of chemical potential (Topic 69), but if you have not encountered that concept, interpret it as the molar Gibbs energy of a substance (Topic 64). Some of the discussion relies on knowledge of concepts in equilibrium (Topic 64) and simple concepts of crystal structure (Topic 37).

A **phase** of a substance is a form of matter that is uniform throughout in chemical composition and physical state. Thus, we speak of solid, liquid, and gas phases of a substance, and of its various solid phases, such as the white and black allotropes of phosphorus. A **phase transition**, the spontaneous conversion of one phase into another phase, occurs at a characteristic temperature for a given pressure. Thus, at 1 atm, ice is the stable phase of water below 0 °C, but above 0 °C liquid water is more stable. This difference indicates that below 0 °C the Gibbs energy (Topic 64) decreases as liquid water changes into ice and that above 0 °C the Gibbs energy decreases as ice changes into liquid water. An empirically constructed **phase diagram** of a substance shows the regions of pressure and temperature at which its various phases are thermodynamically stable (Fig. 67.1). The lines separating the regions, which are called **phase boundaries**, show the values of p and T at which two phases coexist in equilibrium. Similar diagrams can be constructed

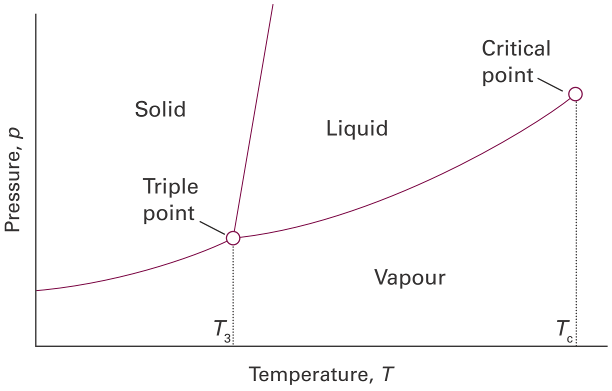

Figure 67.1 The general regions of pressure and temperature where solid, liquid, or gas is stable (that is, has minimum molar Gibbs energy) are shown on this phase diagram. For example, the solid phase is the most stable phase at low temperatures and high pressures. In the following paragraphs we locate the precise boundaries between the regions.

for mixtures (Topic 68), where the regions summarize, for instance, the compositions and temperatures at which the various phases are stable and the boundaries summarize the conditions under which these phases are in equilibrium with one another.

All the properties we describe in this Topic can be traced to the intermolecular interactions that bind the molecules together. Which particular phase is the most stable at a given pressure and at $T=0$, where entropy plays no role, corresponds to the lowest energy that can be achieved as the molecules pack together. At higher temperatures entropy does play a role, and the substance adopts the molecular arrangement that corresponds to lowest Gibbs energy at the prevailing pressure. Although it is difficult to extend the computational techniques of Topics 27–30 to solids and liquids, that can be done, and phase transitions can in some cases be predicted. However, that is beyond the scope of this text: here for the most part we shall simply refer to the qualitative features of intermolecular forces.

67.1 The phase rule

One of the most celebrated results in chemical thermodynamics, the **phase rule**, can be used as a basis for discussing the implications of phase diagrams. The phase rule is a general relation between the variance, F, the number of components, C, and the number of phases at equilibrium, P, for a system of any composition:

$$F=C-P+2 \qquad \text{Phase rule} \qquad (67.1)$$

To count the number of components we first recognize that:

- A **constituent** is a chemical species (an ion or a molecule) that is present.

The term constituent should then be carefully distinguished from 'component', which has a more technical meaning.

- A **component** is a *chemically independent* constituent of a system. The number of components, C, in a system is the minimum number of independent species necessary to define the composition of all the phases present in the system.
- The **variance**, F, of a system is the number of intensive variables that can be changed independently without disturbing the number of phases in equilibrium.

Finally, as stated above and for completeness here,

- A **phase** of a substance is a form of matter that is uniform throughout in chemical composition and physical state. P is the number of phases in mutual equilibrium.

Brief illustration 67.1 Constituents and components

A mixture of ethanol and water has two constituents. A solution of sodium chloride has three constituents: water, Na^+ ions, and Cl^- ions. That solution has only two components: water and sodium chloride, because the amounts of Na^+ and Cl^- ions are constrained to be equal.

Self-test 67.1 How many constituents and components does water have, after allowing for its autoprotolysis? *Hint*: Acknowledge the constraints of equilibria and charge balance.

Answer: 3 constituents (H_2O, H_3O^+, OH^-), 1 component

In a single-component, single-phase system ($C=1$, $P=1$), the pressure and temperature may be changed independently without changing the number of phases, so $F=2$. We say that such a system is **bivariant**, or that it has two **degrees of freedom**. On the other hand, if two phases are in equilibrium (a liquid and its vapour, for instance) in a single-component system ($C=1$, $P=2$), the temperature (or the pressure) can be changed at will, but the change in temperature (or pressure) demands an accompanying change in pressure (or temperature) to preserve the number of phases in equilibrium. That is, the variance of the system has fallen to 1.

To see the origin of eqn 67.1, consider first the special case of a one-component system. We focus on the molar Gibbs energy, G_m, of the substance in each phase. However, in anticipation of extending the discussion to many-component systems, we shall replace this quantity by the 'chemical potential', μ. As far as we are concerned at this stage, $\mu=G_m$; this relation is put on a formal basis in Topic 69.

For two phases α and β in equilibrium, the molar Gibbs energies of the substance are equal and we can write $\mu_J(\alpha)=\mu_J(\beta)$. Each chemical potential is a function of the pressure and temperature, so

$$\mu_J(\alpha;p,T)=\mu_J(\beta;p,T)$$

This is an equation relating p and T, so only one of these variables is independent (just as the equation $x+y=2$ is a relation for y in terms of x: $y=2-x$). That conclusion is consistent with $F=1$. For three phases in mutual equilibrium,

$$\mu_J(\alpha;p,T)=\mu_J(\beta;p,T)=\mu_J(\gamma;p,T)$$

This relation is actually two equations for two unknowns ($\mu_J(\alpha;p,T)=\mu_J(\beta;p,T)$ and $\mu_J(\beta;p,T)=\mu_J(\gamma;p,T)$), and therefore has a solution only for a single value of p and T (just as the pair of equations $x+y=2$ and $3x-y=4$ has the single solution $x=\frac{3}{2}$ and $y=\frac{1}{2}$). That conclusion is consistent with $F=0$. Four phases cannot be in mutual equilibrium in a one-component system because the three equalities

$$\mu_J(\alpha;p,T)=\mu_J(\beta;p,T)$$
$$\mu_J(\beta;p,T)=\mu_J(\gamma,p,T)$$
$$\mu_J(\gamma;p,T)=\mu_J(\delta;p,T)$$

are three equations for two unknowns (p and T) and are not consistent (just as $x+y=2$, $3x-y=4$, and $x+4y=6$ have no solution). The general case is treated in the following *Justification*.

Justification 67.1 The phase rule

We begin by counting the total number of intensive variables. The pressure, p, and temperature, T, count as 2. We can specify the composition of a phase by giving the mole fractions of $C-1$ components. We need specify only $C-1$ and not all C mole fractions because $x_1+x_2+\ldots+x_C=1$, and all mole fractions are known if all except one are specified. Because there are P phases, the total number of composition variables is $P(C-1)$. At this stage, the total number of intensive variables is $P(C-1)+2$.

At equilibrium, the chemical potential of a component J must be the same in every phase:

$$\mu_J(\alpha)=\mu_J(\beta)\ =\ldots\ \text{for } P \text{ phases}$$

That is, there are $P-1$ equations of this kind to be satisfied for each component J. As there are C components, the total number of equations is $C(P-1)$. Each equation reduces our freedom to vary one of the $P(C-1)+2$ intensive variables. It follows that the total number of degrees of freedom is

$$F=P(C-1)+2-C(P-1)=C-P+2$$

which is eqn 67.1.

For a one-component system, such as pure water, $F=3-P$. When only one phase is present, $F=2$ and both p and T can be varied independently without changing the number of phases. In other words, a single phase is represented by an *area* on a phase diagram. When two phases are in equilibrium, $F=1$, which implies that pressure is not freely variable if the temperature is set; indeed, at a given temperature, a liquid has a characteristic vapour pressure. It follows that the equilibrium of two phases is represented by a *line* in the phase diagram. Instead of selecting the temperature, we could select the pressure, but having done so the two phases would be in equilibrium at a single definite temperature. Therefore, freezing (or any other phase transition) occurs at a definite temperature at a given pressure.

When three phases are in equilibrium, $F=0$ and the system is invariant. This special condition can be established only at a definite temperature and pressure that is characteristic of the substance and outside our control. The equilibrium of three phases is therefore represented by a *point*, the triple point, on a phase diagram. Four phases cannot be in equilibrium in a one-component system because F cannot be negative.

67.2 The Ehrenfest classification

Many familiar phase transitions, like fusion and vaporization, are accompanied by changes of enthalpy and volume. These changes have implications for the slopes of the chemical potentials (the molar Gibbs energies) of the phases at either side of the phase transition. Thus, at the transition from a phase α to another phase β,

$$\left(\frac{\partial\mu(\beta)}{\partial p}\right)_T-\left(\frac{\partial\mu(\alpha)}{\partial p}\right)_T=V_m(\beta)-V_m(\alpha)=\Delta_{trs}V \qquad (67.2)$$
$$\left(\frac{\partial\mu(\beta)}{\partial T}\right)_p-\left(\frac{\partial\mu(\alpha)}{\partial T}\right)_p=-S_m(\beta)-(-S_m(\alpha))=-\Delta_{trs}S=-\frac{\Delta_{trs}H}{T_{trs}}$$

We have used eqn 66.7 ($(\partial G/\partial p)_T=V$ and $(\partial G/\partial T)_p=-S$) of Topic 66 to relate the slopes to molar volumes and entropies. Because $\Delta_{trs}V$ and $\Delta_{trs}H$ are nonzero for melting and vaporization, it follows that for such transitions the slopes of the chemical potential plotted against either pressure or temperature are different on either side of the transition (Fig. 67.2a). In other words, the first derivatives of the chemical potentials with respect to pressure and temperature are discontinuous at the transition.

The **Ehrenfest classification** takes note of whether the derivatives in eqn 67.2 are continuous or discontinuous. A transition for which the first derivative of the chemical potential with respect to temperature is discontinuous is classified as a **first-order phase transition**. The constant-pressure heat capacity, C_p, of a substance is the slope of a plot of the enthalpy with respect to temperature. At a first-order phase transition, H changes by a finite amount for an infinitesimal change of temperature. Therefore, at the transition the heat capacity is infinite. The

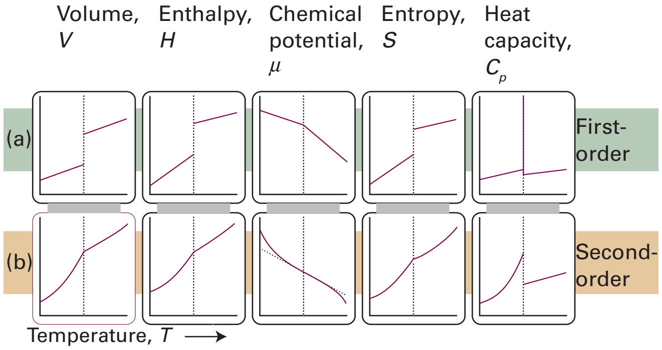

Figure 67.2 The changes in thermodynamic properties accompanying (a) first-order and (b) second-order phase transitions.

physical reason is that heating drives the transition rather than raising the temperature. For example, boiling water stays at the same temperature even though heat is being supplied.

A **second-order phase transition** in the Ehrenfest sense is one in which the first derivative of μ with respect to temperature is continuous but its second derivative is discontinuous. A continuous slope of μ (a graph with the same slope on either side of the transition) implies that the volume and entropy (and hence the enthalpy) do not change at the transition (Fig. 67.2b). The heat capacity is discontinuous at the transition but does not become infinite there. An example of a second-order transition is the conducting–superconducting transition in metals at low temperatures.

Brief illustration 67.2 The Ehrenfest classification

One type of second-order transition is associated with a change in symmetry of the crystal structure of a solid. Thus, suppose the arrangement of atoms in a solid is like that represented in Fig. 67.3a, with one dimension of the tetragonal unit cell longer than the other two, which are equal. Moreover, suppose the two shorter dimensions increase more than the long dimension when the temperature is raised. There may come a stage when the three dimensions become equal. At that point the crystal has cubic symmetry (Fig. 67.3b), and at higher temperatures it will expand equally in all three directions (because there is no longer any distinction between them). The tetragonal → cubic phase transition has occurred, but as it has not involved a discontinuity in the interaction energy between the atoms or the volume they occupy, the transition is not first-order.

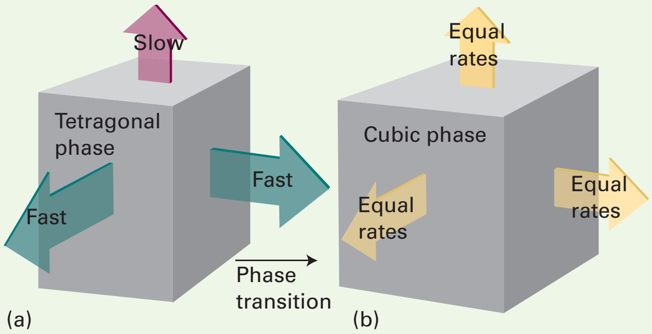

Figure 67.3 One version of a second-order phase transition in which (a) a tetragonal phase expands more rapidly in two directions than a third, and hence becomes a cubic phase, which (b) expands uniformly in three directions as the temperature is raised. There is no rearrangement of atoms at the transition temperature, and hence no enthalpy of transition.

Self-test 67.2 Identify the Ehrenfest order for sublimation.

Answer: first-order; $\Delta_{\text{sub}}V$ and $\Delta_{\text{sub}}S$ nonzero

67.3 One-component systems

We begin exploring the implications of the phase rule and the thermodynamic criteria of equilibrium by considering a liquid sample of a pure substance in a closed vessel. The pressure of a vapour in equilibrium with the liquid is called the **vapour pressure** of the substance (Fig. 67.4). Therefore, the liquid–vapour phase boundary in a phase diagram shows how the vapour pressure of the liquid varies with temperature. Similarly, the solid–vapour phase boundary shows the temperature variation of the **sublimation vapour pressure**, the vapour pressure of the solid phase. The vapour pressure of a substance increases with temperature because at higher temperatures more molecules have sufficient energy to escape from their neighbours.

(a) Phase characteristics

When a liquid is heated in an *open* vessel, the liquid vaporizes from its surface as molecules acquire enough kinetic energy to escape from their neighbours. At the temperature at which its vapour pressure would be equal to the external pressure, vapour can form throughout the bulk of the liquid and can expand freely into the surroundings. The condition of free vaporization throughout the liquid is called **boiling**. The temperature at which the vapour pressure of a liquid is equal to the external pressure is called the **boiling temperature** at that pressure; therefore, the liquid–vapour phase boundary also shows how the boiling temperature varies with external pressure. For the special case of an external pressure of 1 atm, the boiling temperature is called the **normal boiling point**, T_b. With the replacement of 1 atm by 1 bar as standard pressure, there is some advantage in using the **standard boiling point** instead: this is the temperature at which the vapour pressure reaches 1 bar. Because 1 bar is slightly less than 1 atm (1.00 bar = 0.987 atm), the standard boiling point of a liquid is slightly lower than

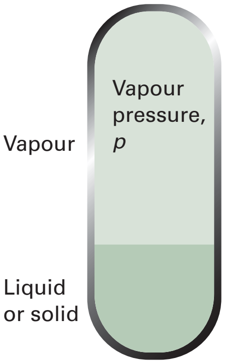

Figure 67.4 The vapour pressure of a liquid or solid is the pressure exerted by the vapour in equilibrium with the condensed phase.

its normal boiling point. The normal boiling point of water is 100.0 °C; its standard boiling point is 99.6 °C.

Boiling does not occur when a liquid is heated in a partly filled, rigid, closed vessel. Instead, the vapour pressure, and hence the density of the vapour, rises as the temperature is raised (Fig. 67.5). At the same time, the density of the liquid decreases slightly as a result of its expansion. There comes a stage when the density of the vapour is equal to that of the remaining liquid and the surface between the two phases disappears. The temperature at which the surface disappears is the **critical temperature**, T_c, of the substance (see Fig. 67.1 again). The vapour pressure at the critical temperature is called the **critical pressure**, p_c. At and above the critical temperature, a single uniform phase called a **supercritical fluid** fills the container and an interface no longer exists. That is, above the critical temperature, the liquid phase of the substance does not exist.

The temperature at which, under a specified pressure, the liquid and solid phases of a substance coexist in equilibrium is called the **melting temperature**. Because a substance melts at exactly the same temperature as it freezes, the melting temperature of a substance is the same as its **freezing temperature**. The freezing temperature when the pressure is 1 atm is called the **normal freezing point**, T_f, and its freezing point when the pressure is 1 bar is called the **standard freezing point**. The normal and standard freezing points are negligibly different for most purposes. The normal freezing point is also called the **normal melting point**.

There is a set of conditions (and, in general, several sets) under which three different phases of a single substance (such as solid, liquid, and vapour) all simultaneously coexist in equilibrium. These conditions are represented by the **triple point**, a point at which the three phase boundaries meet. The temperature at the triple point is denoted T_3 (see Fig. 67.1). The triple point of a pure substance depends on the details of the intermolecular interactions and is outside our control: it occurs at a single definite pressure and temperature characteristic of the substance: because $P=3$ and $C=1$, it follows that $F=0$ and the triple point is invariant.

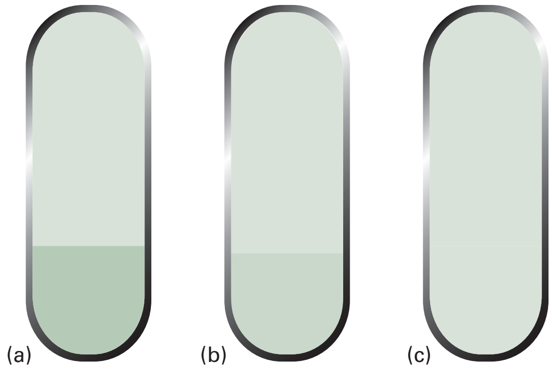

Figure 67.5 (a) A liquid in equilibrium with its vapour. (b) When a liquid is heated in a sealed container, the density of the vapour phase increases and that of the liquid decreases slightly. There comes a stage (c) at which the two densities are equal and the interface between the phases disappears. This disappearance occurs at the critical temperature. The container needs to be strong: the critical temperature of water is 374 °C and the vapour pressure is then 218 atm.

Brief illustration 67.3 Triple points

The triple point of water lies at 273.16 K and 611 Pa (6.11 mbar, 4.58 Torr), and the three phases of water (ice, liquid water, and water vapour) coexist in equilibrium at no other combination of pressure and temperature. This invariance of the triple point was the basis of its use in the now superseded definition of the Kelvin scale of temperature (Topic 61).

Self-test 67.3 How many triple points are present in the (as far as it is known) full phase diagram for water shown later in this Topic in Fig. 67.7?

Answer: 6

As we can see from Fig. 67.1, the triple point marks the lowest pressure at which a liquid phase of a substance can exist. If (as is common) the slope of the solid–liquid phase boundary is as shown in the diagram, then the triple point also marks the lowest temperature at which the liquid can exist; the critical temperature is the upper limit.

(b) Three typical phase diagrams

The phase diagram for carbon dioxide is shown in Fig. 67.6. The features to notice include the positive slope of the solid–liquid boundary (the direction of this line is characteristic of most substances), which indicates that the melting

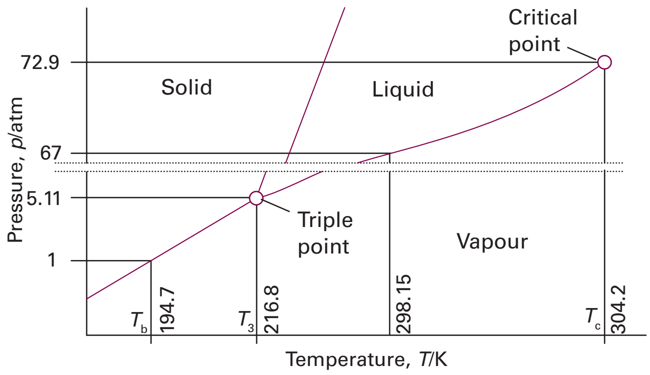

Figure 67.6 The experimental phase diagram for carbon dioxide. Note that, as the triple point lies at pressures well above atmospheric, liquid carbon dioxide does not exist under normal conditions (a pressure of at least 5.1 atm must be applied).

temperature of solid carbon dioxide rises as the pressure is increased. Notice also that as the triple point lies above 1 atm, the liquid cannot exist at normal atmospheric pressures whatever the temperature, and the solid sublimes when left in the open (hence the name 'dry ice'). To obtain the liquid, it is necessary to exert a pressure of at least 5.11 atm. Cylinders of carbon dioxide generally contain the liquid or compressed gas; at 25 °C that implies a vapour pressure of 67 atm if both gas and liquid are present in equilibrium. When the gas squirts through the throttle it cools by the Joule–Thomson effect (Topic 56), so when it emerges into a region where the pressure is only 1 atm, it condenses into a finely divided snow-like solid.

Figure 67.7 is the phase diagram for water. The liquid–vapour boundary in the phase diagram summarizes how the vapour pressure of liquid water varies with temperature. It also summarizes how the boiling temperature varies with pressure: we simply read off the temperature at which the vapour pressure is equal to the prevailing atmospheric pressure. The solid–liquid boundary shows how the melting temperature varies with the pressure. Its very steep slope indicates that enormous pressures are needed to bring about significant changes. Notice that the line has a negative slope up to 2 kbar, which means that the melting temperature falls as the pressure is raised. The reason for this almost unique behaviour can be traced to the decrease in volume that occurs on melting, and hence it being more favourable for the solid to transform into the liquid as the pressure is raised. The decrease in volume is a result of the very open molecular structure of ice: the water molecules are held apart, as well as together, by the hydrogen bonds between them but the structure partially collapses on melting and the liquid is denser than the solid.

Figure 67.7 shows that water has one liquid phase but many different **polymorphs**, or different solid phases, other than ordinary ice ('ice I'). This polymorphic richness is due in large measure to the adaptability of the directional characteristics of hydrogen-bonding interactions, which allow the oxygen atoms to adopt slightly different arrangements throughout the solid in response to changes in pressure and temperature. Some of the phases melt at high temperatures. Ice VII, for instance, melts at 100 °C but exists only above 25 kbar. Note that five more triple points occur in the diagram other than the one where vapour, liquid, and ice I coexist. Each one occurs at a definite pressure and temperature that cannot be changed. The polymorphs of ice differ in the arrangement of the water molecules: under the influence of very high pressures, hydrogen bonds buckle and the H_2O molecules adopt different arrangements. They may be responsible for the advance of glaciers, for ice at the bottom of glaciers experiences very high pressures where it rests on jagged rocks.

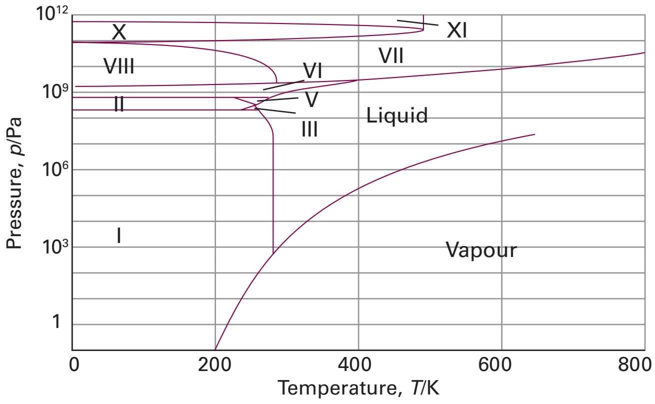

Figure 67.7 The experimental phase diagram for water showing the different solid phases.

Figure 67.8 shows the phase diagram of helium. Helium behaves unusually at low temperatures. For instance, the solid and gas phases of helium are never in equilibrium however low the temperature: the atoms are so light that they vibrate with a large-amplitude motion even at very low temperatures and the solid simply shakes itself apart. Solid helium can be obtained, but only by holding the atoms together by applying pressure. Pure helium-4 has two liquid phases. The phase marked He-I in the diagram behaves like a normal liquid; the other phase, He-II, is a **superfluid**; it is so called because it flows without viscosity. Provided we discount liquid crystalline substances, helium is the only known substance with a liquid–liquid boundary, shown as the **λ-line** (lambda line) in Fig. 67.8. The phase diagram of helium-3 differs from the phase diagram of helium-4, but it also possesses a superfluid phase. Helium-3 is

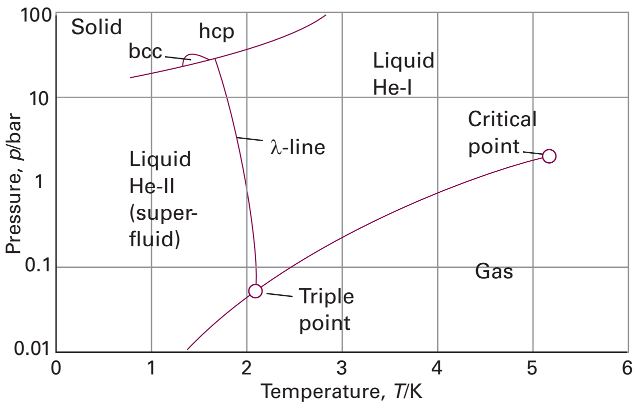

Figure 67.8 The phase diagram for helium (^{4}He). The λ-line marks the conditions under which the two liquid phases are in equilibrium. Helium-II is the superfluid phase. Note that a pressure of over 20 bar must be exerted before solid helium can be obtained. The labels hcp and bcc denote different solid phases in which the atoms pack together differently: hcp denotes hexagonal closed packing and bcc denotes body-centred cubic (see Topic 37 for a description of these structures).

unusual in that the entropy of the liquid is lower than that of the solid, and melting is exothermic.

The existence of superfluid helium is a quantum phenomenon that manifests itself on a macroscopic scale. Because the interatomic forces in helium are so weak, as a first approximation we can treat the liquid as a collection of non-interacting particles in a box. According to Topic 52, many translational states of a particle in a box are occupied provided the separation of particles, $d=(V/N)^{1/3}$ is much larger than their thermal wavelength, $\Lambda=h/(2\pi mkT)^{1/2}$. Given the mass density, ρ, of liquid helium of 0.15 g cm^{-3} and noting that $N/V=\rho/m$, this condition requires $T\gg 6\,\mathrm{K}$ (as you should verify). But the normal boiling point of helium is 4.2 K, so it is not true that many translational states of He atoms are occupied in the liquid and we have to treat the phase as a quantum system. The second important point is that helium-4 atoms are bosons, so that an unrestricted number of them can occupy a single quantum state.

The current view is that helium-II consists of two components. In this **two-fluid model**, below 2.17 K the liquid consists of a normal liquid component and a superfluid component, with the proportions changing as the temperature is lowered and becoming entirely superfluid at $T=0$. Although it is tempting to think of the superfluid phase as consisting of all the atoms in the lowest energy state (corresponding to $n=1$ for a particle in a box) and zero linear momentum, that is not quite right, for neutron scattering experiments have shown that only about 10 per cent of the atoms have zero linear momentum at $T=0$, despite the phase then being entirely superfluid. The ground state is in fact much more complicated, with correlated pairs of atoms with zero overall linear momentum.

Helium-3 forms a superfluid phase despite being a spin-$\frac{1}{2}$ fermion. In its case, pairs of atoms act jointly (like pairs of electrons in superconductivity, Topic 39), and each pair behaves like a single spin-0 boson.

Checklist of concepts

☐ 1. A **phase** is a form of matter that is uniform throughout in chemical composition and physical state.

☐ 2. A **transition temperature** is the temperature at which the two phases are in equilibrium.

☐ 3. A **phase diagram** is a diagram showing the regions of pressure and temperature at which its various phases are thermodynamically stable.

☐ 4. The **phase boundaries** in a phase diagram show the pressures and temperatures at which two phases are in equilibrium.

☐ 5. The **vapour pressure** is the pressure of a vapour in equilibrium with the condensed phase.

☐ 6. The **boiling temperature** is the temperature at which the vapour pressure of a liquid is equal to the external pressure.

☐ 7. The **critical temperature** is the temperature at which a liquid surface disappears and above which a liquid does not exist whatever the pressure. The **critical pressure** is the vapour pressure at the critical temperature.

☐ 8. The **melting temperature** (or freezing temperature) is the temperature at which, under a specified pressure, the liquid and solid phases of a substance coexist in equilibrium.

☐ 9. The **triple point** is a point on a phase diagram at which the three phase boundaries meet and all three phases are in mutual equilibrium.

☐ 10. Phase transitions are categorized by the **Ehrenfest classification**.

Checklist of equations

Property	Equation	Comment	Equation number
Phase rule	$F=C-P+2$	F: variance; C: components; P: phases	67.1

TOPIC 68

Phase diagrams: two-component systems

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➤ Why do you need to know this material?

Most phase diagrams of technological, geological, and chemical interest represent the phase stabilities of systems of more than one component. This Topic shows how to interpret the phase diagrams of two-component systems and use them to discuss the important process of distillation.

➤ What is the key idea?

A two-component phase diagram depicts the phases that are stable under the specified conditions of pressure and temperature.

➤ What do you need to know already?

This Topic develops the introduction of the phase rule in Topic 67 and uses the terms introduced there.

If two components are present in a mixture, there are three variables to consider: the pressure, the temperature, and the composition. Hence, one form of the phase diagram is a map of pressures and compositions at which each phase is stable at a fixed temperature. Alternatively, the pressure could be held constant and the phase diagram depicted in terms of temperature and composition.

68.1 Liquid–vapour systems

The choice of variables under our control, such as pressure or temperature, leads to two types of two-component phase diagram that show the equilibrium composition of the system under the selected conditions.

(a) Pressure–composition diagrams

Figure 68.1 is a typical **pressure–composition diagram** at a fixed temperature. All the points above the diagonal line in the graph correspond to a system under such high pressure that it contains only a liquid phase (the applied pressure is higher than the vapour pressure). All points below the lower curve correspond to a system under such low pressure that it contains only a vapour phase (the applied pressure is lower than the vapour pressure). Points that lie between the two lines correspond to a system in which there are two phases present, one a liquid and the other a vapour.

To see this interpretation in more detail, consider the effect of lowering the pressure on a liquid mixture of overall composition a in Fig. 68.1. The changes to the system do not affect the overall composition, so the state of the system moves down the vertical line that passes through a. This vertical line is called an **isopleth** (from the Greek words for 'equal abundance'). Until

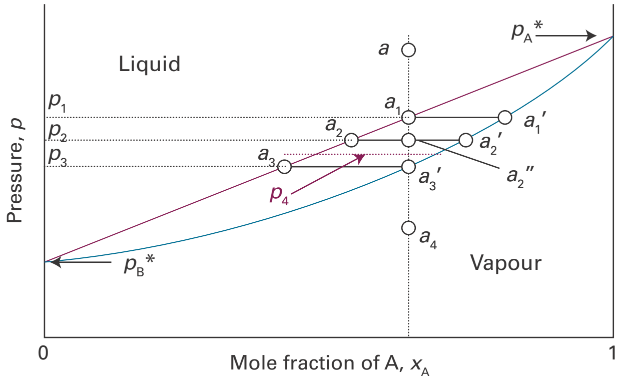

Figure 68.1 A typical phase diagram for a mixture of two volatile liquids. A point between the two lines corresponds to both liquid and vapour being present; outside that region there is only one phase present.

the point a_1 is reached (when the pressure has been reduced to p_1), the sample consists of a single liquid phase. At a_1 the liquid can exist in equilibrium with its vapour of composition a_1'. A line joining two points representing phases in equilibrium is called a **tie line**. The composition of the liquid is the same as initially (a_1 lies on the isopleth through a), so we have to conclude that at this pressure there is virtually no vapour present; however, the tiny amount of vapour that is present has the composition a_1'.

To use a phase diagram to find the relative amounts of two phases α and β that are in equilibrium when the system is in a two-phase region, we measure the distances l_α and l_β along the horizontal tie line, and then use the **lever rule** (Fig. 68.2) which is derived in the following *Justification*:

$$n_\alpha l_\alpha = n_\beta l_\beta \qquad \text{Lever rule} \qquad (68.1)$$

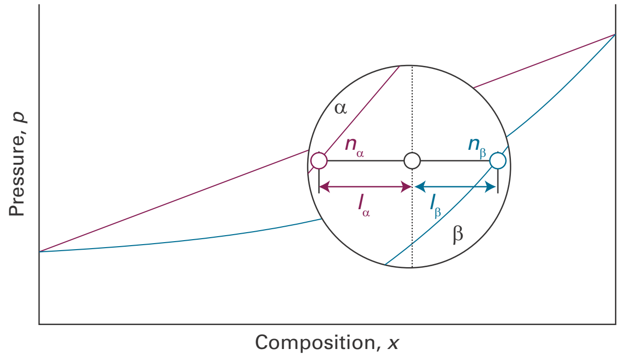

Figure 68.2 The lever rule. The distances l_α and l_β are used to find the proportions of the amounts of phases α (such as vapour) and β (for example, liquid) present at equilibrium. The lever rule is so called because a similar rule relates the masses at two ends of a lever to their distances from a pivot ($m_\alpha l_\alpha = m_\beta l_\beta$ for balance).

Here n_α is the amount of phase α and n_β the amount of phase β. In the case illustrated in Fig. 68.2, because $l_\beta \approx l_\alpha$, the two phases are in equal abundance.

Brief illustration 68.1 The lever rule

At p_1 in Fig. 68.1, the ratio $l_{\text{vap}}/l_{\text{liq}}$ is almost infinite for this tie line, so $n_{\text{liq}}/n_{\text{vap}}$ is also almost infinite, and there is only a trace of vapour present. When the pressure is reduced to p_2, the value of $l_{\text{vap}}/l_{\text{liq}}$ is about 0.5, so $n_{\text{liq}}/n_{\text{vap}} \approx 0.5$ and the amount of liquid is about one-half the amount of vapour. When the pressure has been reduced to p_3, the sample is almost completely gaseous and because $l_{\text{vap}}/l_{\text{liq}} \approx 0$ we conclude that there is only a trace of liquid present.

Self-test 68.1 What is the ratio of abundances of the two phases at p_4?

Answer: $n_{\text{vap}}/n_{\text{liq}} \approx 3.8$

Justification 68.1 The lever rule

To prove the lever rule we write $n = n_\alpha + n_\beta$ and the overall amount of A as nx_A, where x_A is the mole fraction of A in the mixture. The amount of A is also the sum of its amounts in the two phases:

$$nx_A = n_\alpha x_{A,\alpha} + n_\beta x_{A,\beta}$$

where $x_{A,\alpha}$ is the mole fraction of A in phase α and $x_{A,\beta}$ is its mole fraction in phase β. Since also

$$nx_A = (n_\alpha + n_\beta)x_A = n_\alpha x_A + n_\beta x_A$$

by equating these two expressions it follows that

$$n_\alpha(x_{A,\alpha} - x_A) = n_\beta(x_A - x_{A,\beta})$$

which corresponds to eqn 68.1.

(b) Temperature–composition diagrams

A **temperature–composition diagram** is a phase diagram in which the boundaries show the composition of the phases that are in equilibrium at various temperatures (and at a fixed pressure, typically 1 atm). An example is shown in Fig. 68.3. Note that the liquid phase now lies in the lower part of the diagram because all points below the lower curve correspond to a system under such low temperature than it contains only a liquid phase. The region between the lines in Fig. 68.3 is a two-phase region; the regions outside the phase lines correspond to a single phase.

Consider what happens when a liquid of composition a_1 is heated. It boils when the temperature reaches T_2. Then the

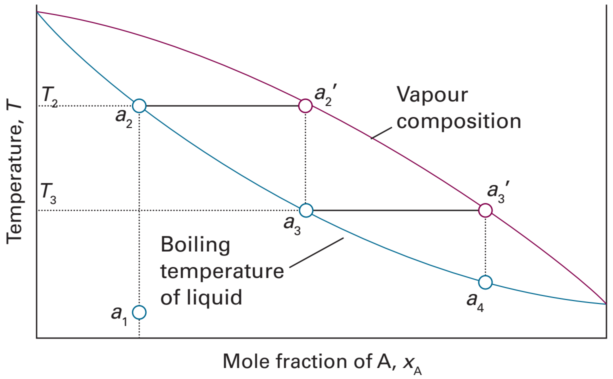

Figure 68.3 The temperature–composition diagram corresponding to an ideal mixture (Topic 70) with the component A more volatile than component B. Successive boilings and condensations of a liquid originally of composition a_1 lead to a condensate that is pure A. The separation technique is called fractional distillation.

liquid has composition a_2 (the same as a_1) and the vapour (which is present only as a trace) has composition a_2'. The vapour is richer in the more volatile component A (the component with the lower boiling point). From the location of a_2', we can state the vapour's composition at the boiling point, and from the location of the tie line joining a_2 and a_2' we can read off the boiling temperature (T_2) of the original liquid mixture.

In a **simple distillation,** the vapour is withdrawn and condensed. This technique is used to separate a volatile liquid from a non-volatile solute or solid. In **fractional distillation**, the boiling and condensation cycle is repeated successively. This technique is used to separate volatile liquids. We can follow the changes that occur by seeing what happens when the first condensate of composition a_3 is reheated. The phase diagram shows that this mixture boils at T_3 and yields a vapour of composition a_3', which is even richer in the more volatile component. That vapour is drawn off, and the first drop condenses to a liquid of composition a_4. The cycle can then be repeated until in due course almost pure A is obtained.

Although many liquids have temperature–composition phase diagrams resembling the version in Fig. 68.3, in a number of important cases there are marked deviations. A maximum in the phase diagram (Fig. 68.4) may occur when the favourable interactions between A and B molecules reduce the vapour pressure of the mixture below the ideal value implied by Raoult's law (Topic 70): in effect, the A–B interactions stabilize the liquid. Examples of this behaviour include trichloromethane/propanone and nitric acid/water mixtures. Phase diagrams showing a minimum (Fig. 68.5) indicate that the mixture is destabilized relative to the ideal solution, the A–B interactions then being unfavourable. Examples include dioxane/water and ethanol/water mixtures.

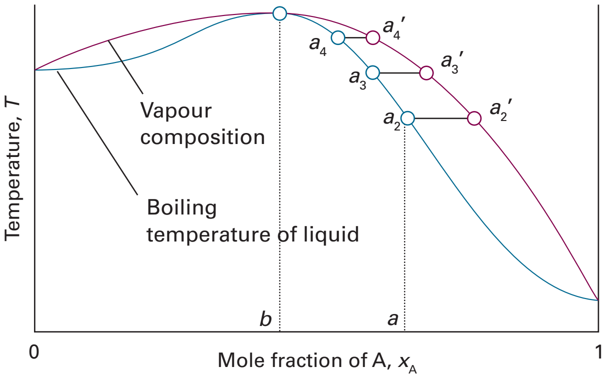

Figure 68.4 A high-boiling azeotrope. When the liquid of composition a is distilled, the composition of the remaining liquid changes towards b but no further.

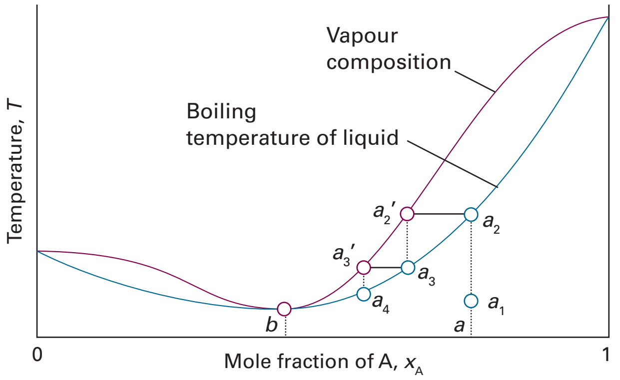

Figure 68.5 A low-boiling azeotrope. When the mixture at a is fractionally distilled, the vapour in equilibrium in the fractionating column moves towards b and then remains unchanged.

Deviations from ideality are not always so strong as to lead to a maximum or minimum in the phase diagram, but when they do there are important consequences for distillation. Consider a liquid of composition a on the right of the maximum in Fig. 68.4. The vapour (at a_2') of the boiling mixture (at a_2) is richer in A. If that vapour is removed (and condensed elsewhere), then the remaining liquid will move to a composition that is richer in B, such as that represented by a_3, and the vapour in equilibrium with this mixture will have composition a_3'. As that vapour is removed, the composition of the boiling liquid shifts to a point such as a_4, and the composition of the vapour shifts to a_4'. Hence, as evaporation proceeds, the composition of the remaining liquid shifts towards B as A is drawn off. The boiling point of the liquid rises, and the vapour becomes richer in B. When so much A has been evaporated that the liquid has reached the composition b, the vapour has the same composition as the liquid. Evaporation then occurs without change of composition. The mixture is said to form an **azeotrope** (from the Greek words for 'boiling without changing').

When the azeotropic composition has been reached, distillation cannot separate the two liquids because the condensate has the same composition as the azeotropic liquid. One example of azeotrope formation is hydrochloric acid/water, which is azeotropic at 80 per cent by mass of water and boils unchanged at 108.6 °C.

Brief illustration 68.2 Azeotropes

The system shown in Fig. 68.5 is azeotropic, but shows its azeotropy in a different way. Suppose we start with a mixture of composition a_1. The mixture boils at a_2 to give a vapour of composition a_2'. This vapour condenses to a liquid of the same composition (now marked a_3). That liquid reaches equilibrium with its vapour at a_3' which condenses to give a liquid of the same composition, which we now call a_4. The distillation therefore shifts the vapour towards the azeotropic composition at *b*, but not beyond, and the azeotropic vapour emerges from the top of the column. An example is ethanol/water, which boils unchanged when the water content is 4 per cent by mass and the temperature is 78 °C.

Self-test 68.2 Consider a liquid of a composition on the left of the maximum in Fig. 68.4. Show that repeated distillations will also result in formation of the azeotrope.

Answer: As evaporation proceeds, the composition of the remaining liquid shifts towards A as B is drawn off

68.2 Liquid–liquid systems

Now we consider temperature–composition diagrams for systems that consist of pairs of **partially miscible** liquids, which are liquids that do not mix in all proportions at all temperatures. An example is hexane and nitrobenzene.

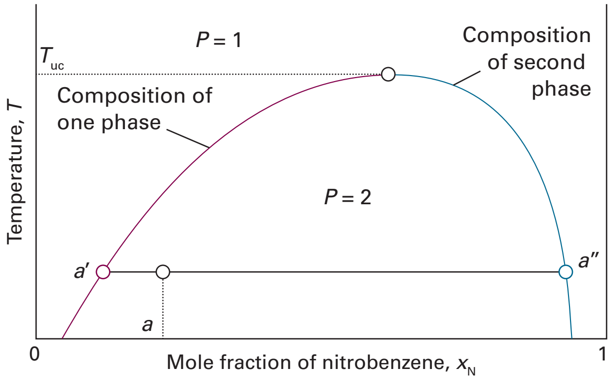

Figure 68.6 The temperature–composition diagram for a system composed of two partially miscible liquids. The region below the curve corresponds to the compositions and temperatures at which the liquids are partially miscible. The upper critical temperature, T_{uc}, is the temperature above which the two liquids are miscible in all proportions. In this and subsequent phase diagrams, *P* is the number of phases. This phase diagram is for A = hexane and B = nitrobenzene, with T_{uc} = 294 K.

Suppose a small amount of a liquid B is added to a sample of another liquid A at a temperature *T*′. It dissolves completely, and the binary system remains a single phase. As more B is added, a stage comes at which no more dissolves. The sample now consists of two phases in equilibrium with each other, the most abundant one consisting of A saturated with B, the minor one a trace of B saturated with A. In the temperature–composition diagram drawn in Fig. 68.6, the composition of the former is represented by the point *a*′ and that of the latter by the point *a*″. The relative abundances of the two phases are given by the lever rule. When more B is added, A dissolves in it slightly. However, the amount of one phase increases at the expense of the other. A stage is reached when so much B is present that it can dissolve all the A, and the system reverts to a single phase. The addition of more B now simply dilutes the solution, and from then on it remains a single phase.

The compositions of the two phases at equilibrium vary with the temperature. For hexane and nitrobenzene, raising the temperature increases their miscibility. The two-phase system therefore becomes less extensive, because each phase in equilibrium is richer in its minor component: the A-rich phase is richer in B and the B-rich phase is richer in A. The phase diagram is constructed by repeating the observations at different temperatures and drawing the envelope of the two-phase region.

The **upper critical solution temperature** (or upper *consolute temperature*), T_{uc}, is the highest temperature at which phase separation occurs. Above the upper critical temperature the two components are fully miscible. This temperature exists because the greater thermal motion overcomes any potential energy advantage in molecules of one type being close together. One example is the nitrobenzene/hexane system shown in Fig. 68.6. Some systems show a **lower critical solution temperature** (or *lower consolute temperature*), T_{lc}, below which they mix in all proportions and above which they form two phases. An example is water and triethylamine (Fig. 68.7). In this case, at low temperatures the two components are more miscible because they form a weak complex; at higher temperatures the complexes break up and the two components are less miscible.

For the thermodynamic treatment of these features, and their modelling in terms of a 'regular solution', see Topic 72.

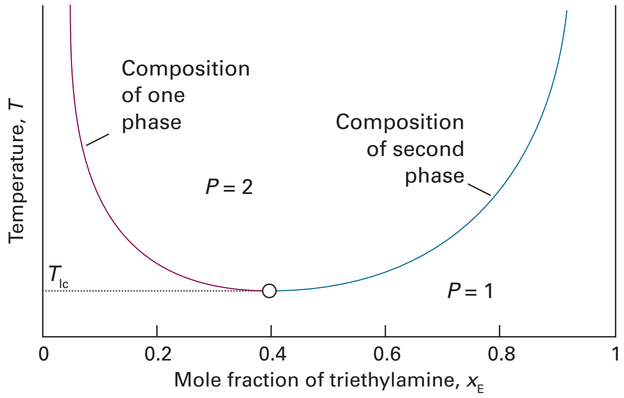

Figure 68.7 The temperature–composition diagram for water and triethylamine. This system shows a lower critical temperature at 292 K. The labels indicate the interpretation of the boundaries.

Example 68.1 Interpreting a liquid–liquid phase diagram

A mixture of 50 g of hexane (0.58 mol C_6H_{14}) and 50 g of nitrobenzene (0.41 mol $C_6H_5NO_2$) was prepared at 290 K. What are the compositions of the phases, and in what proportions do they occur? To what temperature must the sample be heated in order to obtain a single phase?

Method The compositions of phases in equilibrium are given by the points where the tie-line representing the temperature intersects the phase boundary. Their proportions are given by the lever rule (eqn 68.1). The temperature at which the components are completely miscible is found by following the isopleth upwards and noting the temperature at which it enters the one-phase region of the phase diagram.

Answer We denote hexane by H and nitrobenzene by N; refer to Fig. 68.8, which is a more quantitative version of Fig. 68.6. The point $x_N = 0.41$, $T = 290\,\text{K}$ occurs in the two-phase region of the phase diagram. The horizontal tie line cuts the phase boundary at $x_N = 0.35$ and $x_N = 0.83$, so those are the compositions of the two phases. According to the lever rule, the ratio of amounts of each phase is equal to the ratio of the distances l_α and l_β:

$$\frac{n_\alpha}{n_\beta}=\frac{l_\beta}{l_\alpha}=\frac{0.83-0.41}{0.41-0.35}=\frac{0.42}{0.06}=7$$

That is, there is about seven times more hexane-rich phase than nitrobenzene-rich phase. Heating the sample to 292 K takes it into the single-phase region. Because the phase diagram has been constructed experimentally, these conclusions are not based on any assumptions about ideality. They would be modified if the system were subjected to a different pressure.

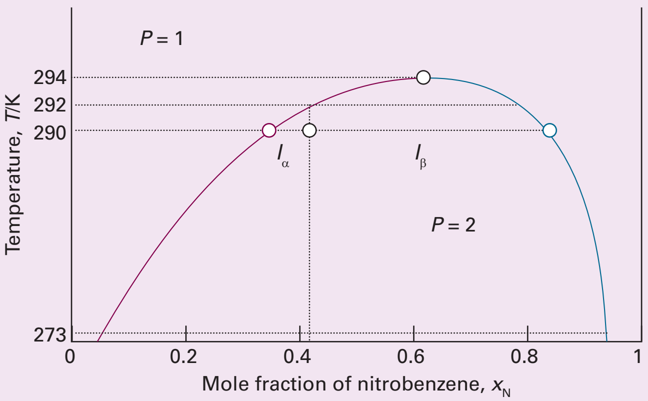

Figure 68.8 The temperature–composition diagram for hexane and nitrobenzene at 1 atm with the points and lengths discussed in Example 68.1.

Self-test 68.3 Repeat the problem for 50 g of hexane and 100 g of nitrobenzene at 273 K.

Answer: $x_N = 0.09$ and 0.95 in ratio 1:1.3; 294 K

68.3 Liquid–solid systems

Finally, we consider a simple example of a two-component mixture that forms both liquid and solid phases. The interpretation of the phase diagram follows the same principles as before. Thus, consider the two-component liquid of composition a_1 in Fig. 68.9. The changes that occur may be expressed as follows:

- $a_1 \rightarrow a_2$. The system enters the two-phase region labelled 'Liquid + B'. Pure solid B begins to come out of solution and the remaining liquid becomes richer in A.
- $a_2 \rightarrow a_3$. More of the solid forms, and the relative amounts of the solid and liquid (which are in equilibrium) are given by the lever rule. At this stage there are roughly equal amounts of each. The liquid phase is richer in A than before (its composition is given by b_3) because some B has been deposited.
- $a_3 \rightarrow a_4$. At the end of this step, there is less liquid than at a_3, and its composition is given by e. This liquid now freezes to give a two-phase system of pure B and pure A.

The isopleth at e in Fig. 68.9 corresponds to the **eutectic** composition, the mixture with the lowest melting point (the name comes from the Greek words for 'easily melted'). A liquid with

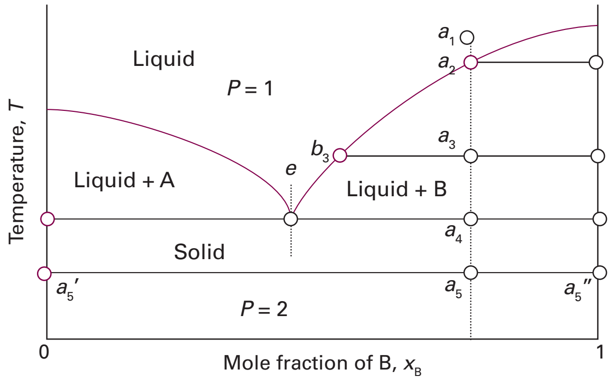

Figure 68.9 The temperature–composition phase diagram for two almost immiscible solids and their completely miscible liquids. The isopleth through *e* corresponds to the eutectic composition, the mixture with lowest melting point.

the eutectic composition freezes at a single temperature, without previously depositing solid A or B. A solid with the eutectic composition melts, without change of composition, at the lowest temperature of any mixture. Solutions of composition to the right of *e* deposit B as they cool, and solutions to the left deposit A: only the eutectic mixture (apart from pure A or pure B) solidifies at a single definite temperature without gradually unloading one or other of the components from the liquid.

Brief illustration 68.3 A binary phase diagram

Figure 68.10 is the phase diagram for silver and tin. The regions have been labelled to show which each one represents. When a liquid of composition *a* is cooled, solid silver with dissolved tin begins to precipitate at a_1 and the sample solidifies completely at a_2.

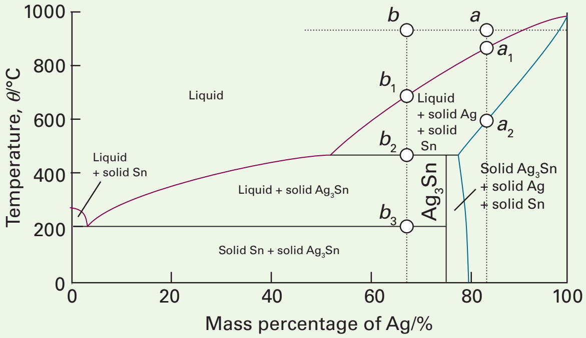

Figure 68.10 The phase diagram for the binary system silver–tin.

Self-test 68.4 Describe what happens when the sample of composition *b* is cooled.

Answer: Solid Ag with dissolved Sn begins to precipitate at b_1, and the liquid becomes richer in Sn as the temperature falls further. At b_2 solid Ag_3Sn begins to precipitate, and the liquid becomes richer in Sn. At b_3 the system has its eutectic composition (a solid solution of Sn and Ag_3Sn) and it freezes without further change in composition.

Checklist of concepts

☐ 1. The **tie line** in a phase diagram joins two points representing phases in equilibrium.
☐ 2. The **lever rule** (see below) allows for the calculation of the relative amounts of two phases in equilibrium.
☐ 3. At the **eutectic composition**, the liquid–solid system has its lowest melting point.
☐ 4. An **azeotrope** is a mixture that boils without change of composition.
☐ 5. The **upper critical solution temperature** is the highest temperature at which phase separation occurs in a binary liquid mixture.
☐ 6. The **lower critical solution temperature** is the temperature below which the components of a binary mixture mix in all proportions and above which they form two phases.

Checklist of equations

Property	Equation	Comment	Equation number
Lever rule	$n_\alpha l_\alpha = n_\beta l_\beta$		68.1

TOPIC 69

Physical transformations

Contents

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➤ Why do you need to know this material?

The chemical potential is a central unifying property for discussing the thermodynamic criteria of equilibrium of all kinds. This Topic defines it, introduces its variation with temperature and pressure, and shows how to use it to discuss the phase equilibria of pure substances.

➤ What is the key idea?

The chemical potentials of a substance are the same in all the phases in which it exists at equilibrium.

➤ What do you need to know already?

This Topic makes use of the properties of the Gibbs energy (Topic 65) and provides a thermodynamic justification of the material in Topic 66. The chemical potential introduced in Topic 67 is developed in greater detail here.

In this Topic we see how thermodynamic considerations can account for the features of the phase diagrams described in Topics 67 and 68. All our considerations are based on the Gibbs energy of the system (Topic 65). At constant temperature and pressure, a system tends towards lowest Gibbs energy: that is, it tends to achieve the greatest total entropy of the system and its surroundings.

69.1 Partial molar quantities

Central to the discussion of mixtures is the concept of 'partial molar quantity'. The easiest partial molar property to visualize is the 'partial molar volume', the contribution that a component of a mixture makes to the total volume of a sample.

(a) Partial molar volume

Imagine a huge volume of pure water at 25 °C. When a further 1 mol H_2O is added, the volume increases by 18 cm^3 and we can report that 18 $cm^3\,mol^{-1}$ is the molar volume of pure water. However, when we add 1 mol H_2O to a huge volume of pure ethanol the volume increases by only 14 cm^3. The reason for the different increase in volume is that the volume occupied by a given number of water molecules depends on the identity of the molecules that surround them. In the latter case, there is so much ethanol present that each H_2O molecule is surrounded by ethanol molecules. The network of hydrogen bonds that normally hold H_2O molecules at certain distances from each other in pure water does not form. The packing of the molecules in the mixture results in the H_2O molecules increasing the volume by only 14 cm³. The quantity 14 cm³ mol⁻¹ is the partial molar volume of water in pure ethanol. In general, the **partial molar volume** of a substance A in a mixture is the change in volume per mole of A added to a large volume of the mixture.

The partial molar volumes of the components of a mixture vary with composition because the environment of each type of molecule changes as the composition changes from pure A to pure B. It is this changing molecular environment, and the consequential modification of the forces acting between molecules, that results in the variation of the thermodynamic properties of a mixture as its composition is changed. The partial molar volumes of water and ethanol across the full composition range at 25 °C are shown in Fig. 69.1.

The partial molar volume, V_J , of a substance J at some general composition is defined formally as follows:

$$V_J = \left(\frac{\partial V}{\partial n_J}\right)_{p,T,n'} \qquad \textit{Definition} \quad \text{Partial molar volume} \qquad (69.1)$$

where the subscript n' signifies that the amounts of all other substances present are constant. The partial molar volume is the slope of the plot of the total volume as the amount of J is changed, the pressure, temperature, and amount of the other components being constant (Fig. 69.2). Its value depends on the composition, as we saw for water and ethanol.

> *A note on good practice* The IUPAC recommendation is to denote a partial molar quantity by $\bar{X}$ but only when there is the possibility of confusion with the quantity X. For instance, to avoid confusion, the partial molar volume of NaCl in water could be written $V(\text{NaCl, aq})$ to distinguish it from the total volume of the solution, V.

The definition in eqn 69.1 implies that when the composition of the mixture is changed by the addition of dn_A of A and dn_B of B, then the total volume of the mixture changes by

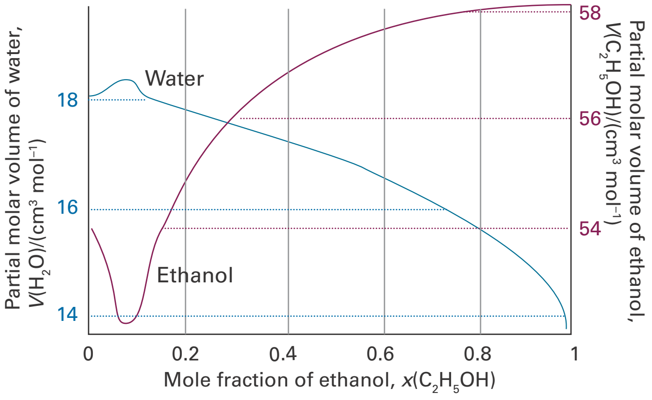

Figure 69.1 The partial molar volumes of water and ethanol at 25 °C. Note the different scales (water on the left, ethanol on the right).

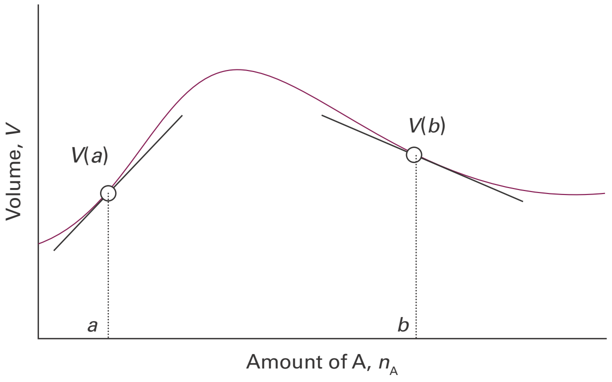

Figure 69.2 The partial molar volume of a substance is the slope of the variation of the total volume of the sample plotted against the composition. In general, partial molar quantities vary with the composition, as shown by the different slopes at the compositions *a* and *b*. Note that the partial molar volume at *b* is negative: the overall volume of the sample decreases as A is added.

$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{p,T,n_A} dn_B = V_A dn_A + V_B dn_B \qquad (69.2)$$

Provided the relative composition is held constant as the amounts of A and B are increased, the partial molar volumes are both constant. In that case we can obtain the final volume by integration, treating V_A and V_B as constants:

$$\begin{aligned} V &= \int_0^{n_A} V_A dn_A + \int_0^{n_B} V_B dn_B = V_A \int_0^{n_A} dn_A + V_B \int_0^{n_B} dn_B \\ &= V_A n_A + V_B n_B \end{aligned} \qquad (69.3)$$

Although we have envisaged the two integrations as being linked (in order to preserve constant relative composition), because V is a state function the final result in eqn 69.3 is valid however the solution is in fact prepared.

Partial molar volumes can be measured in several ways. One method is to measure the dependence of the volume on the composition and to fit the observed volume to a function of the amount of the substance. Once the function has been found, its slope can be determined at any composition of interest by differentiation.

Example 69.1 Determining a partial molar volume

A polynomial fit to measurements of the total volume of a water/ethanol mixture at 25 °C that contains 1.000 kg of water is

$$v = 1002.93 + 54.6664x - 0.363\,94x^2 + 0.028\,256x^3$$

where $v = V/\text{cm}^3$, $x = n_E/\text{mol}$, and n_E is the amount of CH_3CH_2OH present. Determine the partial molar volume of ethanol.

Method Apply the definition in eqn 69.1, taking care to convert the derivative with respect to n to a derivative with respect to x and keeping the units intact.

Answer The partial molar volume of ethanol, V_E, is

$$V_E = \left(\frac{\partial V}{\partial n_E}\right)_{p,T,n_W} = \left(\frac{\partial (V/\text{cm}^3)}{\partial (n_E/\text{mol})}\right)_{p,T,n_W} \frac{\text{cm}^3}{\text{mol}} = \left(\frac{\partial v}{\partial x}\right)_{p,T,n_W} \text{cm}^3\ \text{mol}^{-1}$$

Then, because

$$\frac{dv}{dx} = 54.6664 - 2(0.363\ 94)x + 3(0.028\ 256)x^2$$

we can conclude that

$$V_E/(\text{cm}^3\text{mol}^{-1}) = 54.6664 - 0.72788x + 0.084768x^2$$

Figure 69.3 is a graph of this function.

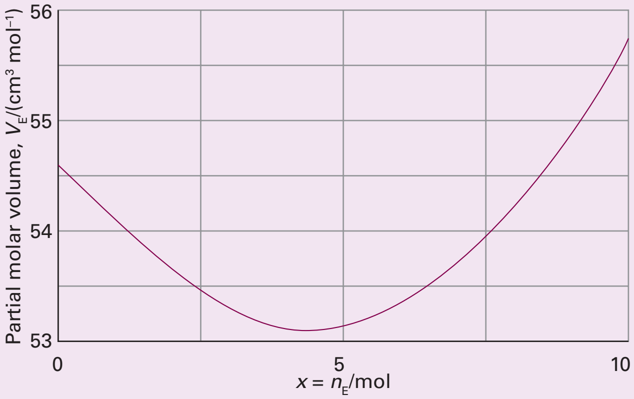

Figure 69.3 The partial molar volume of ethanol as expressed by the polynomial in Example 69 1.

Self-test 69.1 At 25 °C, the density of a 50 per cent by mass ethanol/water solution is $0.914\ \text{g cm}^{-3}$. Given that the partial molar volume of water in the solution is $17.4\ \text{cm}^3\ \text{mol}^{-1}$, what is the partial molar volume of the ethanol?

Answer: $54.6\ \text{cm}^3\ \text{mol}^{-1}$ by the formula above

Molar volumes are always positive, but partial molar quantities need not be. For example, the limiting partial molar volume of $MgSO_4$ in water (its partial molar volume in the limit of zero concentration) is $-1.4\ \text{cm}^3\ \text{mol}^{-1}$, which means that the addition of 1 mol $MgSO_4$ to a large volume of water results in a decrease in volume of $1.4\ \text{cm}^3$. The mixture contracts because the salt breaks up the open structure of water as the Mg^{2+} and SO_4^{2-} ions become hydrated, and it collapses slightly.

(b) Partial molar Gibbs energies

The concept of a partial molar quantity can be extended to any extensive state function. Thus, to discuss the Gibbs energy of a system that in general consists of several components J, each of which contributes to the total Gibbs energy, we introduce the partial molar Gibbs energy of each component. This quantity is so important that it is given its own name, the **chemical potential**, and symbol, μ (mu):

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'} \qquad \textit{Definition} \quad \text{Chemical potential} \qquad (69.4)$$

The n' signifies that the abundances of all the other species in the mixture are held constant; the units of a chemical potential are joules (from G) per mole (from n). For a one-component system, $G = nG_m$, and the chemical potential is simply the molar Gibbs energy of the substance because

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{p,T} = \left(\frac{\partial (nG_m)}{\partial n}\right)_{p,T} = G_m \qquad (69.5)$$

Just like the partial molar volume, the chemical potential of a substance in a mixture varies with the composition of the mixture because the environment of each type of molecule changes as the composition changes. When the composition of a binary (two-component) mixture of A and B molecules is nearly pure A, each A molecule is surrounded almost entirely by A molecules and μ_A has a value characteristic of this environment. When the mixture is almost pure B, each A molecule is surrounded almost entirely by B molecules and now μ_A has a different value, one characteristic of this environment. At intermediate compositions, the environment of A lies between these two extremes, and μ_A has the corresponding value.

By the same argument used for the total volume of a mixture, it follows that the total Gibbs energy of a mixture is simply

$$G = \sum_J n_J \mu_J \qquad \text{Gibbs energy of a mixture} \qquad (69.6)$$

with the chemical potential of each component evaluated at the composition of the mixture. According to this equation, the chemical potential of a substance in a mixture is the contribution of that substance to the total Gibbs energy of the mixture.

69.2 The chemical potential

The name 'chemical potential' is instructive and should be borne in mind. As we develop the concept, we shall see that μ is a measure of the potential—the capacity—that a substance has for producing change in a system. In this Topic, it reflects the potential of a substance to bring about physical change. In Topic 73 it is shown that μ is also the potential of a substance to bring about chemical change.

(a) Changes in the Gibbs energy

Because chemical potentials depend on composition (and the pressure and temperature), the Gibbs energy of a mixture may change when these variables change, and for a system of several components eqn 66.6 ($\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T$) becomes

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T + \sum_J \mu_J \mathrm{d}n_J \tag{69.7}$$

Fundamental equation of chemical thermodynamics

This expression is the **fundamental equation of chemical thermodynamics**. Its implications and consequences are explored and developed in this and other Topics.

At constant pressure and temperature, eqn 69.7 simplifies to

$$\mathrm{d}G_{p,T} = \sum_J \mu_J \mathrm{d}n_J \tag{69.8}$$

However, when the composition is changed infinitesimally from eqn 69.6 we might expect G to change by

$$\mathrm{d}G_{p,T} = \sum_J \mu_J \mathrm{d}n_J + \sum_J n_J \mathrm{d}\mu_J$$

Because G is a state function, the last two equations must be equal, which implies that, at constant temperature and pressure, changes in the chemical potentials of the components of a mixture at equilibrium must satisfy the **Gibbs–Duhem equation**:

$$\sum_J n_J \mathrm{d}\mu_J = 0 \tag{69.9}$$

Constant temperature and pressure Gibbs–Duhem equation

The significance of this equation is that the chemical potential of one component of a mixture cannot change independently of the chemical potentials of the other components. In a binary mixture, if the chemical potential of one component increases, then the other must decrease, with the two changes related by $n_A\mathrm{d}\mu_A + n_B\mathrm{d}\mu_B = 0$, and therefore by

$$\mathrm{d}\mu_B = -\frac{n_A}{n_B}\mathrm{d}\mu_A \tag{69.10}$$

Brief illustration 69.1 The Gibbs–Duhem equation

If the composition of a mixture is such that $n_A = 2n_B$, and a small change in composition results in μ_A changing by $\delta\mu_A = +1\ \mathrm{J\ mol^{-1}}$, μ_B will change by

$$\delta\mu_B = -2\times(1\,\mathrm{J\,mol^{-1}}) = -2\,\mathrm{J\,mol^{-1}}$$

Self-test 69.2 Suppose that $n_A = 0.3n_B$ and a small change in composition results in μ_A changing by $\delta\mu_A = -10\ \mathrm{J\ mol^{-1}}$, by how much will μ_B change?

Answer: $+3\ \mathrm{J\ mol^{-1}}$

(b) The thermodynamic criterion of equilibrium

The importance of the chemical potential for the discussion of phase equilibria is that:

> At equilibrium, the chemical potential of a substance is the same throughout a sample, regardless of how many phases are present.

When the liquid and solid phases of a single substance are in equilibrium, the chemical potential of the substance is the same in both phases and throughout each phase (Fig. 69.4). When two phases of a many-component mixture are in equilibrium the chemical potential of each component is the same in every phase.

To see the validity of this remark, consider a system in which the chemical potential of any one component is μ_1 at one location and μ_2 at another location. The locations may be in the same or in different phases. When an amount $\mathrm{d}n$ of the substance is transferred from one location to the other, the Gibbs energy of the system changes by $-\mu_1\mathrm{d}n$ when material

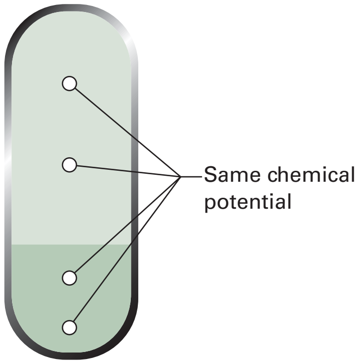

Figure 69.4 When two or more phases are in equilibrium, the chemical potential of a substance (and, in a mixture, a component) is the same in each phase and is the same at all points in each phase.

is removed from location 1, and it changes by $+\mu_2 \mathrm{d}n$ when that material is added to location 2. The overall change is therefore $\mathrm{d}G = (\mu_2 - \mu_1)\mathrm{d}n$. If the chemical potential at location 1 is higher than that at location 2, the transfer is accompanied by a decrease in G, and so has a spontaneous tendency to occur. The spontaneous direction is from high to low chemical potential and the most stable phase is the one of lowest chemical potential under the prevailing conditions. Only if $\mu_1 = \mu_2$ is there no change in G, and only then is the system at equilibrium.

Brief illustration 69.2 Phase equilibria

Consider the two-component, two-phase system in which a mixture of water and ethanol is in equilibrium with its vapour. The chemical potentials of ethanol in the vapour and liquid phases are equal, $\mu_{\text{ethanol}}(\text{g}) = \mu_{\text{ethanol}}(\text{l})$, as are those of water, $\mu_{\text{water}}(\text{g}) = \mu_{\text{water}}(\text{l})$. Because no solid phases are present, they are not the stable phases under the prevailing conditions and therefore $\mu_{\text{ethanol}}(\text{s}) > \mu_{\text{ethanol}}(\text{g})$ and $\mu_{\text{ethanol}}(\text{s}) > \mu_{\text{ethanol}}(\text{l})$ and likewise $\mu_{\text{water}}(\text{s}) > \mu_{\text{water}}(\text{g})$ and $\mu_{\text{water}}(\text{s}) > \mu_{\text{water}}(\text{l})$.

Self-test 69.3 What is the relation between the chemical potentials of the phases of water at 273.16 K and 611 Pa? You might wish to consult the phase diagram (Fig. 67.7), a section of which is reproduced here as Fig. 69.5 for convenience.

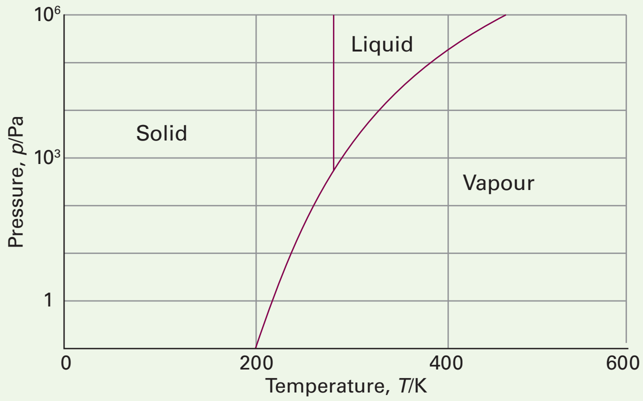

Figure 69.5 A region of the phase diagram for water, extracted from Fig. 67.7 of Topic 67.

Answer: triple point: $\mu_{\text{water}}(\text{s}) = \mu_{\text{water}}(\text{g}) = \mu_{\text{water}}(\text{l})$

(c) The response of the chemical potential to the conditions

The temperature dependence of the Gibbs energy is expressed in terms of the entropy of the system by eqn 66.7 of Topic 66 ($(\partial G/\partial T)_p = -S$). Because, as we have seen, the chemical potential of a pure substance is just another name for its molar Gibbs energy, it follows that

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_{\text{m}} \quad \text{Temperature variation of the chemical potential} \qquad (69.11)$$

This relation shows that as the temperature is raised, the chemical potential of a pure substance decreases: $S_{\text{m}} > 0$ for all substances, so the slope of a plot of μ against T is negative. At first sight it might seem odd that the chemical potential, the capacity to bring about change, decreases as the temperature is raised. However, in Topic 64 it is remarked that an interpretation of the Gibbs energy is that it is the difference between the total energy and the energy stored chaotically: the latter increases with temperature, so the energy 'free' to do work decreases.

Brief illustration 69.3 The variation of chemical potential with temperature

The molar entropy of water vapour at 25 °C is 189 J K^{-1} mol^{-1} (Table 57.4). Therefore, $(\partial \mu/\partial T)_p = -189$ J K^{-1} mol^{-1}. Therefore, an increase in temperature of 1 K *decreases* the chemical potential of $H_2O(g)$ by 189 J mol^{-1}.

Self-test 69.4 Repeat the calculation for liquid water at the same temperature.

Answer: Decreases by 70 J mol^{-1}

Equation 69.11 implies that the slope of a plot of μ against temperature is steeper for gases than for liquids, because $S_{\text{m}}(\text{g}) > S_{\text{m}}(\text{l})$. The slope is also usually steeper for a liquid than the corresponding solid, because $S_{\text{m}}(\text{l}) > S_{\text{m}}(\text{s})$ almost always. These features are illustrated in Fig. 69.6. The steep negative

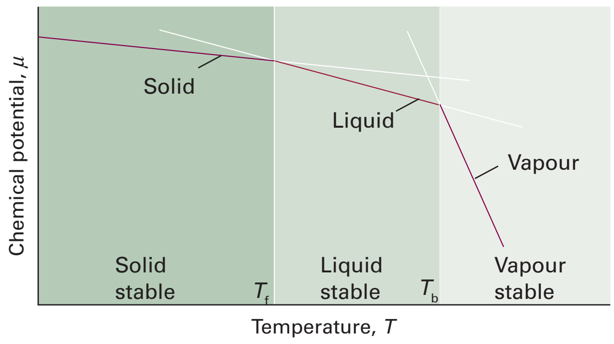

Figure 69.6 The schematic temperature dependence of the chemical potential of the solid, liquid, and gas phases of a substance (in practice, the lines are curved). The phase with the lowest chemical potential at a specified temperature is the most stable one at that temperature. The transition temperatures, the melting and boiling temperatures (T_f and T_b, respectively), are the temperatures at which the chemical potentials of the two phases are equal.

slope of μ(l) results in its falling below μ(s) when the temperature is high enough, and then the liquid becomes the stable phase: the solid melts. The chemical potential of the gas phase plunges steeply downwards as the temperature is raised (because the molar entropy of the vapour is so high), and there comes a temperature at which it lies lowest. Then the gas is the stable phase and vaporization is spontaneous.

As summarized in the phase diagrams in Topic 67, most substances melt at a higher temperature when subjected to pressure. It is as though the pressure is preventing the formation of the less dense liquid phase. Exceptions to this behaviour include water, for which the liquid is denser than the solid. Application of pressure to water encourages the formation of the liquid phase. That is, water freezes at a lower temperature when it is under pressure (see Fig. 69.5).

We can rationalize the response of melting temperatures to pressure as follows. The variation of the chemical potential of a pure substance with pressure is expressed (from the second of eqn 66.7 in Topic 66, $(\partial G/\partial p)_T = V$) by

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m \quad \text{Pressure variation of the chemical potential} \qquad (69.12)$$

This equation shows that the slope of a plot of chemical potential against pressure is equal to the molar volume of the substance. An increase in pressure raises the chemical potential of any pure substance (because $V_m > 0$). In most cases, $V_m(\mathrm{l}) > V_m(\mathrm{s})$ and the equation predicts that an increase in pressure increases the chemical potential of the liquid more than that of the solid. As shown in Fig. 69.7a, the effect of pressure in such a case is to raise the melting temperature slightly, as is seen for carbon dioxide in Fig. 67.6, reproduced for convenience here as Fig. 69.8. For water, however, $V_m(\mathrm{l}) < V_m(\mathrm{s})$, and an increase in pressure increases the chemical potential of the solid more than that of the liquid. In this case, the melting temperature is lowered slightly (Fig. 69.7b), as is seen for water in Fig. 69.5.

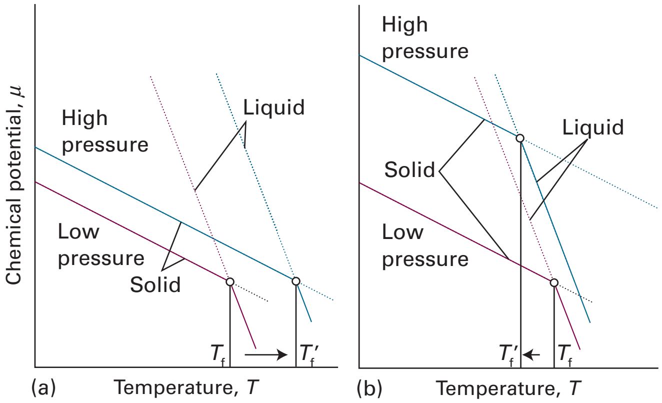

Figure 69.7 The pressure dependence of the chemical potential of a substance depends on the molar volume of the phase. The lines show schematically the effect of increasing pressure on the chemical potential of the solid and liquid phases (in practice, the lines are curved), and the corresponding effects on the freezing temperatures. (a) In this case the molar volume of the solid is smaller than that of the liquid and μ(s) increases less than μ(l). As a result, the freezing temperature rises. (b) Here the molar volume is greater for the solid than the liquid (as for water), μ(s) increases more strongly than μ(l), and the freezing temperature is lowered.

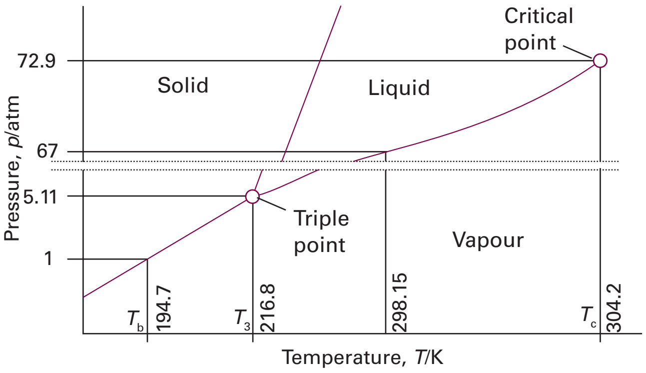

Figure 69.8 The phase diagram for carbon dioxide (from Fig. 67.6).

Brief illustration 69.4 The variation of chemical potential with pressure

The molar volume of water vapour at 25 °C, treated as a perfect gas, is 25 dm^3 mol^{-1}, corresponding to 2.5×10^{-2} m^3 mol^{-1}. Therefore, $(\partial\mu/\partial p)_T = +2.5\times10^{-2}$ m^3 mol^{-1} and an increase in pressure of 1.0 bar (1.0×10^5 Pa) *increases* the chemical potential of H_2O(g) by

$$\begin{aligned}\delta\mu &= (2.5\times10^{-2}\,\mathrm{m^3\,mol^{-1}})\times(1.0\times10^5\,\mathrm{Pa})\\ &= +2.5\times10^3\,\mathrm{Pa\,m^3\,mol^{-1}} = +2.5\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

Self-test 69.5 Repeat the calculation for liquid water at the same temperature, when its mass density is 0.997 g cm^{-3}.

Answer: Increases by 1.8 kJ mol^{-1}

69.3 The structure of one-component phase diagrams

The precise locations of the phase boundaries in a one-component phase diagram—the pressures and temperatures at which any two of its phases can coexist—can be found by making use of the fact that when two phases are in equilibrium, their chemical potentials must be equal. Therefore, where the phases α and β are in equilibrium,

$$\mu(\alpha; p,T) = \mu(\beta; p,T) \qquad (69.13)$$

As we show in the following *Justification*, by solving this equation for p in terms of T, we get the **Clapeyron equation** for the phase boundary:

$$\frac{\mathrm{d}p}{\mathrm{d}T}=\frac{\Delta_{\mathrm{trs}}S}{\Delta_{\mathrm{trs}}V} \quad \text{Clapeyron equation} \quad (69.14)$$

In this expression $\Delta_{\mathrm{trs}}S = S_{\mathrm{m}}(\beta) - S_{\mathrm{m}}(\alpha)$ and $\Delta_{\mathrm{trs}}V = V_{\mathrm{m}}(\beta) - V_{\mathrm{m}}(\alpha)$ are the entropy and volume of transition. The Clapeyron equation is an exact expression for the slope of the phase boundary and applies to any phase equilibrium of any pure substance. It implies that we can use thermodynamic data to predict the appearance of phase diagrams and to understand their form.

Justification 69.1 The Clapeyron equation

It turns out to be simplest to discuss the phase boundaries in terms of their slopes, $\mathrm{d}p/\mathrm{d}T$. Let p and T be changed infinitesimally, but in such a way that the two phases α and β remain in equilibrium. The chemical potentials of the phases are initially equal (the two phases are in equilibrium). They remain equal when the conditions are changed to another point on the phase boundary, where the two phases continue to be in equilibrium (Fig. 69.9). Therefore, the changes in the chemical potentials of the two phases must be equal and we can write $\mathrm{d}\mu(\alpha)=\mathrm{d}\mu(\beta)$. Because, $\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T$, we know that $\mathrm{d}\mu = -S_{\mathrm{m}}\mathrm{d}T + V_{\mathrm{m}}\mathrm{d}p$ for each phase; it follows that

$$-S_{\mathrm{m}}(\alpha)\mathrm{d}T+V_{\mathrm{m}}(\alpha)\mathrm{d}p=-S_{\mathrm{m}}(\beta)\mathrm{d}T+V_{\mathrm{m}}(\beta)\mathrm{d}p$$

where $S_{\mathrm{m}}(\alpha)$ and $S_{\mathrm{m}}(\beta)$ are the molar entropies of the phases and $V_{\mathrm{m}}(\alpha)$ and $V_{\mathrm{m}}(\beta)$ are their molar volumes. Hence

$$\{V_{\mathrm{m}}(\beta)-V_{\mathrm{m}}(\alpha)\}\mathrm{d}p=\{S_{\mathrm{m}}(\beta)-S_{\mathrm{m}}(\alpha)\}\mathrm{d}T$$

which rearranges into eqn 69.14.

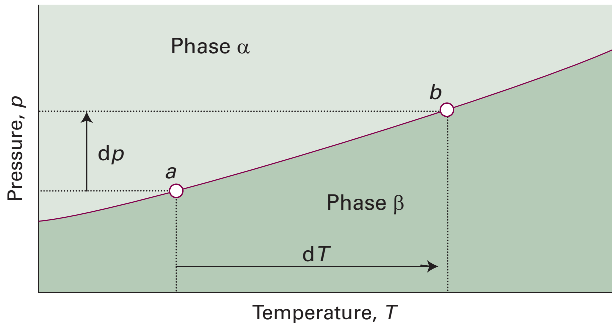

Figure 69.9 When pressure is applied to a system in which two phases are in equilibrium (at *a*), the equilibrium is disturbed. It can be restored by changing the temperature, so moving the state of the system to *b*. It follows that there is a relation between d*p* and d*T* that ensures that the system remains in equilibrium as either variable is changed.

Example 69.2 Estimating the effect of pressure on the boiling temperature

Estimate the typical size of the effect of increasing pressure on the boiling point of a liquid.

Method To use eqn 69.14 we need to estimate the right-hand side. At the boiling point, the term $\Delta_{\mathrm{vap}}S$ is Trouton's constant (Topic 62). Because the molar volume of a gas is so much greater than the molar volume of a liquid, we can write

$$\Delta_{\mathrm{vap}}V=V_{\mathrm{m}}(\mathrm{g})-V_{\mathrm{m}}(\mathrm{l})\approx V_{\mathrm{m}}(\mathrm{g})$$

and take for $V_{\mathrm{m}}(\mathrm{g})$ the molar volume of a perfect gas (at low pressures, at least).

Answer Trouton's constant has the value 85 J K^{-1} mol^{-1}. The molar volume of a perfect gas is about 25 dm^3 mol^{-1} at 1 atm and near but above room temperature. Therefore,

$$\frac{\mathrm{d}p}{\mathrm{d}T}\approx\frac{85\ \mathrm{J\ K^{-1}\ mol^{-1}}}{2.5\times10^{-3}\ \mathrm{m^3\ mol^{-1}}}=3.4\times10^{3}\ \mathrm{J\ m^{-3}\ K^{-1}}$$

Then, because 1 J = 1 Pa m^3, this value corresponds to 3.4 kPa K^{-1} and therefore to about 0.034 atm K^{-1} and hence to $\mathrm{d}T/\mathrm{d}p$ = 29 K atm^{-1}. Therefore, a change of pressure of +0.1 atm can be expected to change a boiling temperature by about +3 K.

Self-test 69.6 Estimate $\mathrm{d}T/\mathrm{d}p$ for water at its normal boiling point using the information in Table 62.2 and $V_{\mathrm{m}}(\mathrm{g}) = RT/p$.

Answer: 28 K atm^{-1}

Melting (fusion) is accompanied by a molar enthalpy change $\Delta_{\mathrm{fus}}H$ and occurs at a temperature T. The molar entropy of melting at T is therefore $\Delta_{\mathrm{fus}}H/T$ (Topic 62), and the Clapeyron equation becomes

$$\frac{\mathrm{d}p}{\mathrm{d}T}=\frac{\Delta_{\mathrm{fus}}H}{T\Delta_{\mathrm{fus}}V} \quad \text{Solid–liquid boundary} \quad (69.15a)$$

where $\Delta_{\mathrm{fus}}V$ is the change in molar volume that occurs on melting. The enthalpy of melting is positive (the only exception is helium-3) and the volume change is usually positive (water being an exception) and always small. Consequently, the slope $\mathrm{d}p/\mathrm{d}T$ is steep and usually positive, as in Fig. 69.8 for carbon dioxide. The entropy of vaporization at a temperature T is equal to $\Delta_{\mathrm{vap}}H/T$; the Clapeyron equation for the liquid–vapour boundary is therefore

$$\frac{\mathrm{d}p}{\mathrm{d}T}=\frac{\Delta_{\mathrm{vap}}H}{T\Delta_{\mathrm{vap}}V} \quad \text{Liquid–vapour boundary} \quad (69.15b)$$

The enthalpy of vaporization is positive; $\Delta_{\mathrm{vap}}V$ is large and positive. Therefore, $\mathrm{d}p/\mathrm{d}T$ is positive, but it is much smaller than for the solid–liquid boundary. It follows that $\mathrm{d}T/\mathrm{d}p$, the inverse of $\mathrm{d}p/\mathrm{d}T$, is large, and hence that the boiling temperature is more responsive to pressure than the freezing temperature, as shown in Figs 69.5 and 69.8. Exactly the same reasoning applies to the solid–vapour boundary, and we can write

$$\frac{dp}{dT}=\frac{\Delta_{\text{sub}}H}{T\Delta_{\text{sub}}V} \qquad \text{Solid–vapour boundary} \qquad (69.15c)$$

where $\Delta_{\text{sub}}H$ and $\Delta_{\text{sub}}V$ are the enthalpy and volume of sublimation (the direct conversion of solid into vapour).

Because the molar volume of a gas is so much greater than the molar volume of a liquid or solid, we can write $\Delta_{\text{vap}}V \approx V_{\text{m}}(\text{g})$ (as in Example 69.2) and similarly $\Delta_{\text{sub}}V \approx V_{\text{m}}(\text{g})$. Moreover, if the gas behaves perfectly, $V_{\text{m}}(\text{g})=RT/p$. These two approximations turn the exact Clapeyron equation into

$$\frac{dp}{dT}\approx\frac{\Delta_{\text{vap}}H}{T(RT/p)}=\frac{p\Delta_{\text{vap}}H}{RT^2}$$

with a similar expression for the solid–vapour boundary. Because $dp/p=d\ln p$, this expression rearranges into the **Clausius–Clapeyron equation** for the variation of vapour pressure with temperature:

$$\frac{d\ln p}{dT}=\frac{\Delta_{\text{vap}}H}{RT^2} \qquad \textit{Vapour is a perfect gas} \qquad \text{Clausius–Clapeyron equation} \qquad (69.16)$$

Like the Clapeyron equation, the Clausius–Clapeyron equation is used to understand the location and shape of the liquid–vapour and solid–vapour phase boundaries of one-component phase diagrams (Topic 67). The only difference between the solid–vapour boundary and liquid–vapour boundary is the replacement of the enthalpy of vaporization by the enthalpy of sublimation, $\Delta_{\text{sub}}H$. Because the enthalpy of sublimation is greater than the enthalpy of vaporization ($\Delta_{\text{sub}}H=\Delta_{\text{fus}}H+\Delta_{\text{vap}}H$ at a given temperature), the equation predicts a steeper slope for the sublimation curve than for the vaporization curve at similar temperatures, which is near where they meet at the triple point. This behaviour can be seen in Figs 69.5 and 69.8.

Because the boiling temperature of a liquid is the temperature at which the vapour pressure matches the external pressure, the Clausius–Clapeyron equation can also be interpreted as an expression for the variation in boiling temperature with applied pressure. This interpretation is illustrated in the following Example.

Example 69.3 Estimating a boiling temperature

The vapour pressure of dichloromethane at 24.1 °C is 53.3 kPa and its enthalpy of vaporization is 28.7 kJ mol^{-1}. Estimate its boiling temperature when the external pressure is 80.0 kPa.

Method We need to determine the temperature at which the vapour pressure matches the external pressure. Convert the Clausius–Clapeyron equation into an expression for the vapour pressures at two temperatures by integration on the assumption that the enthalpy of vaporization is independent of temperature, and solve it for the temperature at which the vapour pressure matches the stated external pressure.

Answer The integration of eqn 69.16 proceeds as follows:

$$\int_{\ln p_1}^{\ln p_2} d\ln p=\int_{T_1}^{T_2}\frac{\Delta_{\text{vap}}H}{RT^2}dT=\frac{\Delta_{\text{vap}}H}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

Therefore

$$\ln\frac{p_2}{p_1}=\frac{\Delta_{\text{vap}}H}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

On rearranging to find an expression for the temperature T_2 at which the vapour pressure is p_2, we find

$$T_2=\frac{\Delta_{\text{vap}}H/R}{\Delta_{\text{vap}}H/RT_1-\ln(p_2/p_1)}=\frac{T_1}{1-(RT_1/\Delta_{\text{vap}}H)\ln(p_2/p_1)}$$

From the data ($T_1=297.3\,\text{K}$, $\Delta_{\text{vap}}H=28.7\text{ kJ mol}^{-1}$, $p_1=53.3\,\text{kPa}$, $p_2=80.0\,\text{kPa}$), we find

$$T_2=\frac{297.3\,\text{K}}{1-\dfrac{(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})\times(297.3\,\text{K})}{2.87\times10^4\,\text{J}\,\text{mol}^{-1}}\ln\left(\dfrac{80.0\,\text{kPa}}{53.3\,\text{kPa}}\right)}=308\,\text{K}$$

The boiling temperature is therefore predicted to be 35 °C.

Self-test 69.7 The vapour pressure of a substance at 20.0 °C is 48.4 kPa and its enthalpy of vaporization is 34.7 kJ mol^{-1}. Estimate its boiling temperature when the external pressure is 58.0 kPa.

Answer: 23.8 °C

Checklist of concepts

☐ 1. The **partial molar volume** is the contribution (per mole) that a substance makes to the total volume of a mixture.

☐ 2. The **chemical potential** is the partial molar Gibbs energy of a species.

☐ 3. The **temperature variation** of the chemical potential is governed by the molar entropy.

☐ 4. The **pressure variation** of the chemical potential is governed by the molar volume.

☐ 5. The chemical potential is the same for all phases of a component throughout a system at equilibrium.

☐ 6. The slope of a phase boundary is given by the **Clapeyron equation** (see below).

☐ 7. The dependence of the vapour pressure of a condensed phase is given by the **Clausius–Clapeyron equation** (see below).

Checklist of equations

Property	Equation	Comment	Equation number
Partial molar volume	$V_J=(\partial V/\partial n_J)_{p,T,n'}$	Definition	69.1
Total volume of a mixture	$V=n_AV_A+n_BV_B$		69.3
Chemical potential	$\mu_J=(\partial G/\partial n_J)_{p,T,n'}$	Definition	69.4
Total Gibbs energy of a mixture	$G=\sum_J n_J\mu_J$		69.6
Fundamental equation of chemical thermodynamics	$\mathrm{d}G=V\mathrm{d}p-S\mathrm{d}T+\sum_J \mu_J\mathrm{d}n_J$		69.7
Gibbs–Duhem equation	$\sum_J n_J\mathrm{d}\mu_J=0$	Constant temperature and pressure	69.9
Temperature variation of μ	$(\partial\mu/\partial T)_p=-S_m$		69.11
Pressure variation of μ	$(\partial\mu/\partial p)_T=V_m$		69.12
Clapeyron equation	$\mathrm{d}p/\mathrm{d}T=\Delta_{trs}S/\Delta_{trs}V$		69.14
	$\mathrm{d}p/\mathrm{d}T=\Delta_{trs}H/T\Delta_{trs}V$		69.15
Clausius–Clapeyron equation	$\mathrm{d}\ln p/\mathrm{d}T=\Delta_{vap}H/RT^2$	Vapour a perfect gas	69.16

TOPIC 70

Ideal mixtures

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➤ Why do you need to know this material?

Mixtures are a hugely important aspect of chemistry, for chemical reactions start when reagents are mixed and the products are also typically mixtures. Even mixtures of non-reactive substances are important, for the presence of solutes can affect their physical properties. This Topic establishes the groundwork for this type of discussion.

➤ What is the key idea?

The changes in thermodynamic properties when substances mix are established by considering how the chemical potential of each component varies with composition.

➤ What do you need to know already?

This Topic makes use of the properties of the chemical potential (Topic 69). It draws on the variation of Gibbs energy with temperature and pressure (Topic 66).

To start our investigation of the thermodynamics of mixtures, we consider the act of mixing itself, and begin with the simplest possible case, the mixing of two perfect gases.

70.1 The mixing of perfect gases

We show in the following *Justification* that the Gibbs energy of mixing of two perfect gases at a temperature T is

$$\Delta_{\text{mix}}G = nRT(x_A \ln x_A + x_B \ln x_B) \quad \textit{Perfect gases} \quad \text{Gibbs energy of mixing} \qquad (70.1)$$

where the x_J are the mole fractions of the gases in the mixture and n is the total amount of molecules of gas. Because mole fractions are never greater than 1, the logarithms in this equation are negative, and $\Delta_{\text{mix}}G < 0$ (Fig. 70.1). The conclusion that $\Delta_{\text{mix}}G$ is negative for all compositions confirms that perfect gases mix spontaneously in all proportions. However, the equation extends common sense by allowing us to discuss the process quantitatively.

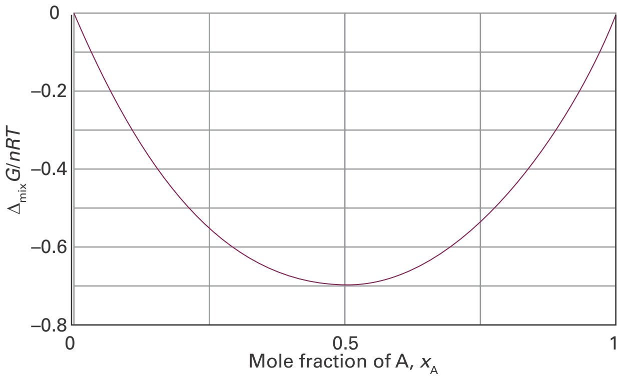

Figure 70.1 The Gibbs energy of mixing of two perfect gases and (as discussed later) of two liquids that form an ideal solution. The Gibbs energy of mixing is negative for all compositions and temperatures, so perfect gases mix spontaneously in all proportions.

Justification 70.1 The Gibbs energy of mixing

Let the amounts of two perfect gases in the two containers be n_A and n_B; both are at a temperature T and a pressure p (Fig. 70.2). At this stage, the chemical potentials of the two gases have their 'pure' values. It then follows from eqn 66.13 of Topic 66 ($G_m(p) = G_m^{\ominus} + RT\ln(p/p^{\ominus})$), with $\mu_J = G_m(J)$, that for each gas J

$$\mu_J = \mu_J^{\ominus} + RT\ln\frac{p}{p^{\ominus}}$$

where $\mu_J^{\ominus}$ is the standard chemical potential, the chemical potential of the pure gas J at 1 bar (that is, its standard molar Gibbs energy). The initial Gibbs energy of the total system is then given by eqn 69.6 ($G = n_A\mu_A + n_B\mu_B$) as

$$G_i = n_A\left(\mu_A^{\ominus} + RT\ln\frac{p}{p^{\ominus}}\right) + n_B\left(\mu_B^{\ominus} + RT\ln\frac{p}{p^{\ominus}}\right)$$

After mixing, the partial pressures of the gases are p_A and p_B, with $p_A + p_B = p$. The total Gibbs energy changes to

$$G_f = n_A\left(\mu_A^{\ominus} + RT\ln\frac{p_A}{p^{\ominus}}\right) + n_B\left(\mu_B^{\ominus} + RT\ln\frac{p_B}{p^{\ominus}}\right)$$

The difference $G_f - G_i$, the Gibbs energy of mixing, $\Delta_{mix}G$, is therefore

$$\Delta_{mix}G = n_A RT\ln\frac{p_A}{p} + n_B RT\ln\frac{p_B}{p}$$

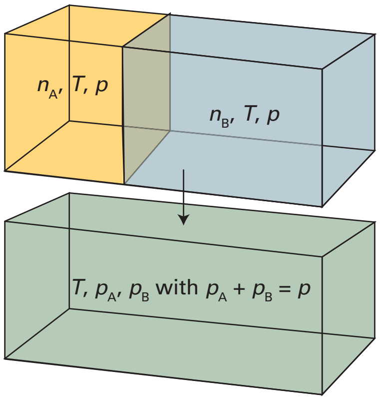

Figure 70.2 The arrangement for calculating the thermodynamic functions of mixing of two perfect gases.

At this point we can replace n_J by $x_J n$, where n is the total amount of A and B and $x_J = n_J/n$ is the mole fraction of J, and use the definition of partial pressure in terms of the mole fraction (see *The chemist's toolkit* 70.1), $p_J = x_J p$, to write $p_J/p = x_J$ for each component, which gives eqn 70.1.

The chemist's toolkit 70.1 Mole fraction

The mole fraction of a component J in a mixture is defined as

$$x_J = \frac{n_J}{n} \qquad n = \sum_J n_J$$

where n_J is the amount of atoms or molecules of the substance J. For a binary mixture,

$$x_A + x_B = 1$$

The partial pressure, p_J, of a gas J (perfect or real) in a mixture of gases is defined as

$$p_J = x_J p$$

where p is the total pressure. When all the gases in the mixture are perfect, $p = nRT/V$ and

$$p_J = \frac{x_J nRT}{V} = \frac{n_J RT}{V}$$

To relate the mole fraction of a solute B in a solution of molality b we note that $b = n_B/(1\text{ kg})$, where 1 kg is the mass of solvent. If the solvent has molar mass M, then the amount of solvent (A) molecules present is $n_A = (1\text{ kg})/M$, so $b = n_B/n_A M$ and $n_A = n_B/bM$. It follows that the mole fraction of B is

$$x_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{n_B/bM + n_B} = \frac{bM}{1 + bM}$$

If $bM \ll 1$, $x_B \approx bM$.

Example 70.1 Calculating a Gibbs energy of mixing

A container is divided into two equal compartments (Fig. 70.3). One contains 3.0 mol $H_2(g)$ at 25 °C; the other contains 1.0 mol $N_2(g)$ at 25 °C. Calculate the Gibbs energy of mixing when the partition is removed. Assume perfect behaviour.

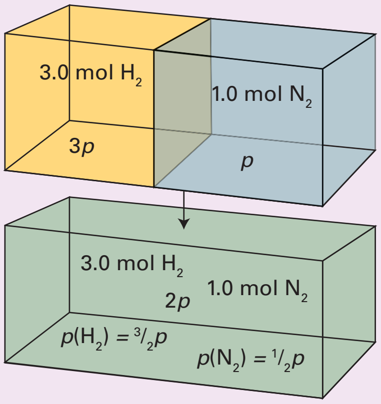

Figure 70.3 The initial and final states considered in the calculation of the Gibbs energy of mixing of gases at different initial pressures in Example 70.1.

Method Equation 70.1 cannot be used directly because the two gases are initially at different pressures. We proceed by calculating the initial Gibbs energy from the chemical potentials. To do so, we need the pressure of each gas. Write the pressure of nitrogen as p; then the pressure of hydrogen as a multiple of p can be found from the gas laws. Next, calculate the Gibbs energy for the system when the partition is removed. The volume occupied by each gas doubles, so its initial partial pressure is halved.

Answer: Given that the pressure of nitrogen is p, the pressure of hydrogen is $3p$; therefore, the initial Gibbs energy is

$$\begin{aligned}G_i = {} & (3.0\,\text{mol})\{\mu^{\ominus}(\text{H}_2)+RT\ln\tfrac{3p}{p^{\ominus}}\}+\\ & (1.0\,\text{mol})\{\mu^{\ominus}(\text{N}_2)+RT\ln\tfrac{p}{p^{\ominus}}\}\end{aligned}$$

When the partition is removed and each gas occupies twice the original volume, the partial pressure of nitrogen falls to $\frac{1}{2}p$ and that of hydrogen falls to $\frac{3}{2}p$. Therefore, the Gibbs energy changes to

$$\begin{aligned}G_f = {} & (3.0\,\text{mol})\{\mu^{\ominus}(\text{H}_2)+RT\ln\tfrac{3p}{2p^{\ominus}}\}+\\ & (1.0\,\text{mol})\{\mu^{\ominus}(\text{N}_2)+RT\ln\tfrac{p}{2p^{\ominus}}\}\end{aligned}$$

The Gibbs energy of mixing is the difference of these two quantities:

$$\begin{aligned}\Delta_{\text{mix}}G &= (3.0\,\text{mol})RT\ln\left(\frac{\frac{3}{2}p}{3p}\right)+(1.0\,\text{mol})RT\ln\left(\frac{\frac{1}{2}p}{p}\right)\\ &= -(3.0\,\text{mol})RT\ln 2-(1.0\,\text{mol})RT\ln 2\\ &= -(4.0\,\text{mol})RT\ln 2 = -6.9\,\text{kJ}\end{aligned}$$

In this Example, the value of $\Delta_{\text{mix}}G$ is the sum of two contributions: the mixing itself, and the changes in pressure of the two gases to their final total pressure, $2p$. When 3.0 mol H_2 mixes with 1.0 mol N_2 at the same pressure, with the volumes of the vessels adjusted accordingly, the change of Gibbs energy is −5.6 kJ.

Self-test 70.1 Suppose that 2.0 mol H_2 at 2.0 atm and 25 °C and 4.0 mol N_2 at 3.0 atm and 25 °C are mixed at constant volume. Calculate $\Delta_{\text{mix}}G$. What would be the value of $\Delta_{\text{mix}}G$ had the pressures been identical initially?

Answer: −9.7 kJ, −9.5 kJ

Once we have an expression for the Gibbs energy of mixing we can find expressions for other mixing functions. Thus, because $(\partial G/\partial T)_{p,n} = -S$, it follows that the **entropy of mixing** is

$$\Delta_{\text{mix}}S = -\left(\frac{\partial \Delta_{\text{mix}}G}{\partial T}\right)_p$$

On substituting eqn 70.1 we obtain

$$\Delta_{\text{mix}}S = -nR(x_{\text{A}}\ln x_{\text{A}} + x_{\text{B}}\ln x_{\text{B}}) \qquad (70.2)$$

Perfect gases Entropy of mixing

Because $\ln x < 0$, it follows that $\Delta_{\text{mix}}S > 0$ for all compositions (Fig. 70.4). For equal amounts of gas, for instance, we set $x_{\text{A}} = x_{\text{B}} = \frac{1}{2}$, and obtain $\Delta_{\text{mix}}S = nR\ln 2$, with n the total amount of gas molecules. In this case, $\Delta_{\text{mix}}S/n = +5.76\ \text{J K}^{-1}\ \text{mol}^{-1}$. An increase in entropy is what we expect when one gas disperses into the other and the disorder increases.

We can calculate **enthalpy of mixing**, $\Delta_{\text{mix}}H$, the enthalpy change accompanying mixing, of two perfect gases from $\Delta G = \Delta H - T\Delta S$. It follows from eqns 70.1 and 70.2 that

$$\Delta_{\text{mix}}H = 0 \qquad (70.3)$$

Perfect gases Enthalpy of mixing

The enthalpy of mixing is zero, as we should expect for a system in which there are no interactions between the molecules forming the gaseous mixture. It follows that the whole of the driving force for mixing comes from the increase in entropy of the system, because the entropy of the surroundings is unchanged.

In statistical terms we can understand the spontaneity of mixing of perfect gases as the molecular tendency to populate the new energy levels that become available when the volume accessible to the molecules of each becomes larger (Fig. 70.5). We show in the following *Justification* that this statistical interpretation leads to the same conclusion as the thermodynamic analysis.

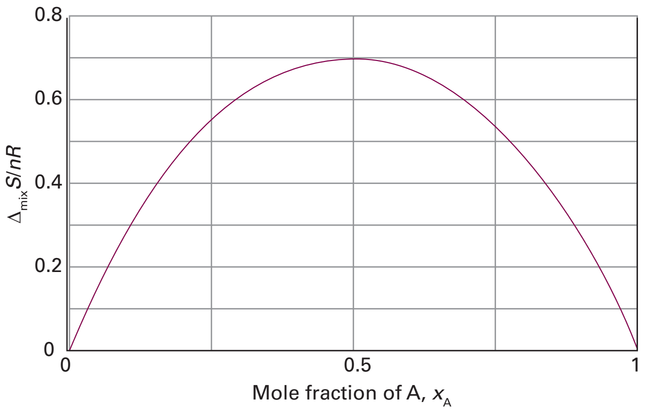

Figure 70.4 The entropy of mixing of two perfect gases and (as discussed later) of two liquids that form an ideal solution. The entropy increases for all compositions and temperatures, so perfect gases mix spontaneously in all proportions. Because there is no transfer of heat to the surroundings when perfect gases mix, the entropy of the surroundings is unchanged. Hence, the graph also shows the total entropy of the system plus the surroundings when perfect gases mix.

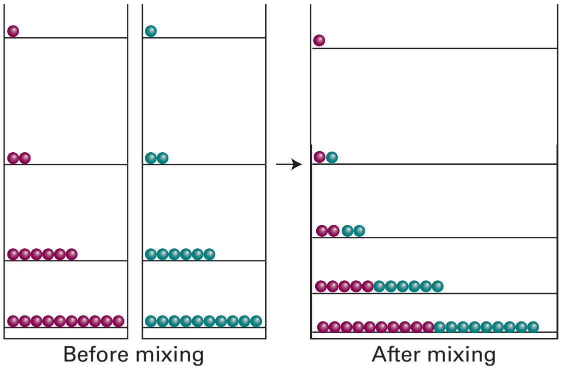

Figure 70.5 The molecular interpretation of the entropy of mixing. Before mixing, each collection of gas molecules occupies the available energy levels with a Boltzmann distribution of populations. After mixing, more levels are accessible to the molecules as they occupy a greater volume (with the same temperature).

Justification 70.2 The statistical thermodynamic description of mixing

This statistical picture is expressed quantitatively by using the relation between the Gibbs energy and the molecular partition function in (eqn 64.12 of Topic 64, $G=G(0)-nRT\times\ln(q/N)$). Thus, initially, when the partition function of gas J is $q_J=V_J/\Lambda_J^3$, where Λ_J is the thermal wavelength of J (eqn 52.7b, $\Lambda_J=h/(2\pi m_J kT)^{1/2}$), the total Gibbs energy is

$$G_i=\left\{G_A(0)-n_A RT\ln\left(\overbrace{\frac{V_A}{N_A\Lambda_A^3}}^{q/N\text{ for A}}\right)\right\}+\left\{G_B(0)-n_B RT\ln\left(\overbrace{\frac{V_B}{N_B\Lambda_B^3}}^{q/N\text{ for B}}\right)\right\}$$
$$=G_A(0)+G_B(0)-n_A RT\ln\left(\frac{kT}{p\Lambda_A^3}\right)-n_B RT\ln\left(\frac{kT}{p\Lambda_B^3}\right)$$

In the second line we have used $V_J/N_J=kT/p$. To simplify the appearance of this and the next equation we write it as

$$G_i=G_A(0)+G_B(0)-n_A RT\ln\left(\frac{A}{p}\right)-n_B RT\ln\left(\frac{B}{p}\right)$$

where $A=kT/\Lambda_A^3$ and $B=kT/\Lambda_B^3$. In the final state of the system, each type of molecule has access to the total volume, V_A+V_B, and the partial pressures are p_J; so

$$G_f=\left\{G_A(0)-n_A RT\ln\left(\frac{V_A+V_B}{N_A\Lambda_A^3}\right)\right\}+\left\{G_B(0)-n_B RT\ln\left(\frac{V_A+V_B}{N_B\Lambda_B^3}\right)\right\}$$
$$=G_A(0)+G_B(0)-n_A RT\ln\left(\frac{kT}{p_A\Lambda_A^3}\right)-n_B RT\ln\left(\frac{kT}{p_B\Lambda_B^3}\right)$$

We have used $(V_A+V_B)/N_J=kT/p_J$ in the second line. This expression has the form

$$G_f=G_A(0)+G_B(0)-n_A RT\ln\left(\frac{A}{p_A}\right)-n_B RT\ln\left(\frac{B}{p_B}\right)$$

The difference G_f-G_i is

$$\Delta_{\text{mix}}G=-n_A RT\ln\left(\frac{p}{p_A}\right)-n_B RT\ln\left(\frac{p}{p_B}\right)$$

which we recognize as eqn 70.1 once we write $p_J=x_J p$ and $n_J=x_J n$. This result confirms that spontaneous mixing is just the hunt of the molecules for the configuration of the greatest weight, their most probable distribution in the system.

70.2 The mixing of liquids

To discuss the equilibrium properties of liquid mixtures we need to know how the Gibbs energy of a liquid varies with composition. To calculate its value, we use the fact that, at equilibrium, the chemical potential of a substance present as a vapour must be equal to its chemical potential in the liquid.

(a) Raoult's law

We shall denote quantities relating to pure substances by a superscript *, so the chemical potential of pure A is written μ_A^*, and as $\mu_A^*(\text{l})$ when we need to emphasize that A is a liquid. Because the vapour pressure of the pure liquid is p_A^*, it follows from the relation of chemical potential and pressure (eqn 66.13 of Topic 66, $G_m(p)=G_m^{\ominus}+RT\ln(p/p^{\ominus})$, with $\mu=G_m$) that the chemical potential of A in the vapour (treated as a perfect gas) is $\mu_A^{\ominus}+RT\,\mathrm{In}(p_A^*/p^{\ominus})$. These two chemical potentials are equal at equilibrium (Fig. 70.6), so we can write

$$\mu_A^*(\text{l})=\mu_A^{\ominus}+RT\ln(p_A^*/p^{\ominus}) \qquad (70.4\text{a})$$

If another substance, a solute, is also present in the liquid, the chemical potential of A in the liquid is changed to μ_A, its vapour pressure is changed to p_A, and the chemical potential of the vapour becomes $\mu_A^{\ominus}+RT\ln(p_A/p^{\ominus})$. The vapour and solvent are still in equilibrium, so we can write

$$\mu_A(\text{l})=\mu_A^{\ominus}+RT\ln(p_A/p^{\ominus}) \qquad (70.4\text{b})$$

Next, we combine these two equations to eliminate the standard chemical potential of the gas. To do so, we write eqn 70.4a as $\mu_A^{\ominus}=\mu_A^*(\text{l})-RT\ln(p_A^*/p_A^{\ominus})$ and substitute this expression into eqn 70.4b to obtain

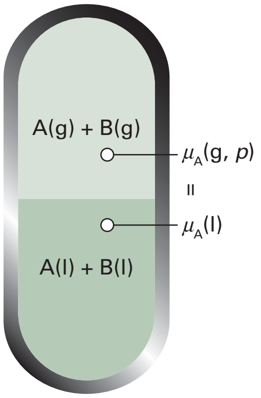

Figure 70.6 At equilibrium, the chemical potential of the gaseous form of a substance A is equal to the chemical potential of its condensed phase. The equality is preserved if a solute is also present. Because the chemical potential of A in the vapour depends on its partial vapour pressure, it follows that the chemical potential of liquid A can be related to its partial vapour pressure.

$$\begin{aligned}\mu_A(l) &= \mu_A^*(l) - RT\ln(p_A^*/p^\ominus) + RT\ln(p_A/p^\ominus) \\ &= \mu_A^*(l) + RT\ln\frac{p_A}{p_A^*}\end{aligned} \qquad (70.5)$$

In the final step we draw on additional experimental information about the relation between the ratio of vapour pressures and the composition of the liquid. In a series of experiments on mixtures of closely related liquids (such as benzene and methylbenzene), the French chemist François Raoult found that the ratio of the partial vapour pressure of each component to its vapour pressure as a pure liquid, p_A/p_A^*, is approximately equal to the mole fraction of A in the liquid mixture. That is, he established what we now call **Raoult's law**:

$$p_A = x_A p_A^* \qquad (70.6)$$

Ideal solution Raoult's law

Raoult's law is illustrated in Fig. 70.7. Some mixtures obey Raoult's law very well, especially when the components are structurally similar. Mixtures that obey the law throughout the composition range from pure A to pure B for both components are called **ideal solutions**. Some solutions depart significantly from Raoult's law. Nevertheless, even in these cases the law is obeyed increasingly closely for the component in excess (the solvent) as it approaches purity. The law is therefore a good approximation for the properties of the solvent if the solution is dilute.

Brief illustration 70.1 Raoult's law

The vapour pressure of benzene at 20 °C is 75 Torr and that of methylbenzene is 21 Torr at the same temperature. In an equimolar mixture $x_{\text{benzene}} = x_{\text{methylbenzene}} = \frac{1}{2}$ so the vapour pressure of each one in the mixture is

$$p_{\text{benzene}} = \tfrac{1}{2} \times 75\text{ Torr} = 38\text{ Torr}$$
$$p_{\text{methylbenzene}} = \tfrac{1}{2} \times 21\text{ Torr} = 11\text{ Torr}$$

The total vapour pressure of the mixture is 49 Torr. Given the two partial vapour pressures, it follows from the definition of partial pressure in *The chemist's toolkit* 70.1 that the mole fractions in the vapour are $x_{\text{vap,benzene}} = (38\text{ Torr})/(49\text{ Torr}) = 0.78$ and $x_{\text{vap,methylbenzene}} = (11\text{ Torr})/(49\text{ Torr}) = 0.22$. The vapour is richer in the more volatile component (benzene).

Self-test 70.2 At 90 °C the vapour pressure of 1,2-dimethylbenzene is 20 kPa and that of 1,3-dimethylbenzene is 18 kPa. What is the composition of the vapour when the liquid mixture has the composition $x_{12} = 0.33$ and $x_{13} = 0.67$?

Answer: $x_{\text{vap,12}} = 0.35$, $x_{\text{vap,13}} = 0.65$

The molecular origin of Raoult's law is the effect of the solute on the entropy of the solution. In the pure solvent, the molecules have a certain disorder and a corresponding entropy; the vapour pressure then represents the tendency of the system and its surroundings to reach a higher entropy. When a solute is present, the solution has a greater disorder than the pure solvent because we cannot be sure that a molecule chosen at random will be a solvent molecule. Because the entropy of the solution is higher than that of the pure solvent, the solution has a lower tendency to acquire an even higher entropy by the solvent vaporizing. In other words, the vapour pressure of the solvent in the solution is lower than that of the pure solvent.

For an ideal solution, it follows from eqns 70.5 and 70.6 that

$$\mu_A(l) = \mu_A^*(l) + RT\ln x_A \qquad (70.7)$$

Ideal solution Chemical potential of solvent

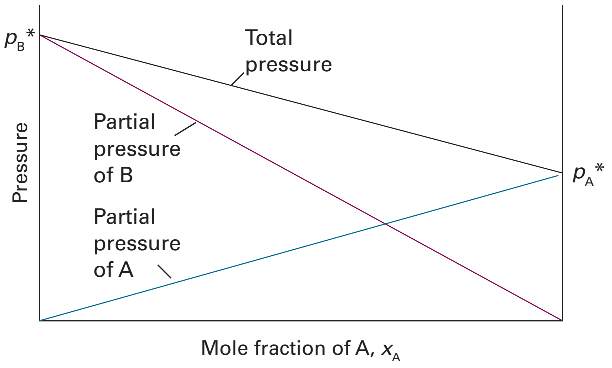

Figure 70.7 The total vapour pressure and the two partial vapour pressures of an ideal binary mixture are proportional to the mole fractions of the components.

This important equation can be used as the *definition* of an ideal solution (so that it implies Raoult's law rather than stemming from it). It is in fact a better definition than eqn 70.6 because it does not assume that the vapour pressure is a perfect gas.

(b) Henry's law

In ideal solutions the solute, as well as the solvent, obeys Raoult's law. However, the English chemist William Henry found experimentally that for real solutions at low concentrations, although the vapour pressure of the solute is proportional to its mole fraction, the constant of proportionality is not the vapour pressure of the pure substance (Fig. 70.8). **Henry's law** is

$$p_B = x_B K_B$$ *Ideal–dilute solution* Henry's law (70.8a)

In this expression x_B is the mole fraction of the solute B and K_B is an empirical constant (with the dimensions of pressure) chosen so that the plot of the vapour pressure of B against its mole fraction is tangent to the experimental curve at $x_B = 0$. In practice, a polynomial is fitted to the vapour pressure data and the slope of the curve at $x_B = 0$ is determined by differentiation or equivalently by identifying the coefficient of the term that is proportional to x_B. In practical applications of Henry's law it is often more convenient to express it in terms of the molality, b, of the solute, in which case we write

$$p_B = b_B K_B$$ *Ideal–dilute solution* Henry's law (70.8b)

Table 70.1 gives a selection of values of the Henry's law constant for this convention.

Mixtures for which the solute obeys Henry's law and the solvent obeys Raoult's law are called **ideal–dilute solutions**. We shall also label equations with a blue number when they have been derived from Henry's law. The difference in behaviour of the solute and solvent at low concentrations (as expressed by Henry's and Raoult's laws, respectively) arises from the fact that in a dilute solution the solvent molecules are in an environment very much like the one they have in the pure liquid (Fig. 70.9). In contrast, the solute molecules are surrounded by solvent molecules, which is entirely different from their environment when pure. Thus, the solvent behaves like a slightly modified pure liquid, but the solute behaves entirely differently from its pure state unless the solvent and solute molecules happen to be very similar. In the latter case, the solute also obeys Raoult's law. This point is taken further in Topic 72; in this Topic, we confine attention to ideal solutions.

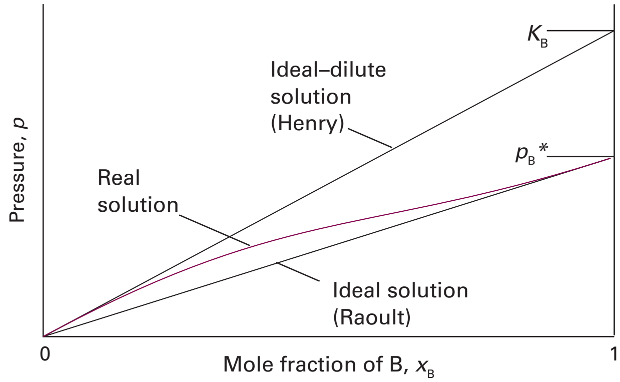

Figure 70.8 When a component (the solvent) is nearly pure, it has a vapour pressure that is proportional to mole fraction with a slope p_B^* (Raoult's law). When it is the minor component (the solute) its vapour pressure is still proportional to the mole fraction, but the constant of proportionality is now K_B (Henry's law).

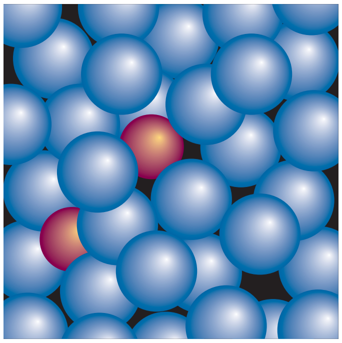

Figure 70.9 In a dilute solution, the solvent molecules (the blue spheres) are in an environment that differs only slightly from that of the pure solvent. The solute particles (the purple spheres), however, are in an environment totally unlike that of the pure solute.

Table 70.1* Henry's law constants for gases in water at 298 K

	K_B/(kPa kg mol^{-1})
CO_2	3.01×10^3
H_2	1.28×10^5
N_2	1.56×10^5
O_2	7.92×10^4

* More values are given in the *Resource section*.

Example 70.2 Investigating the validity of Raoult's and Henry's laws

The vapour pressures of each component in a mixture of propanone (acetone, A) and trichloromethane (chloroform, C) were measured at 35 °C with the following results:

x_C	0	0.20	0.40	0.60	0.80	1
p_C/kPa	0	4.7	11	18.9	26.7	36.4
p_A/kPa	46.3	33.3	23.3	12.3	4.9	0

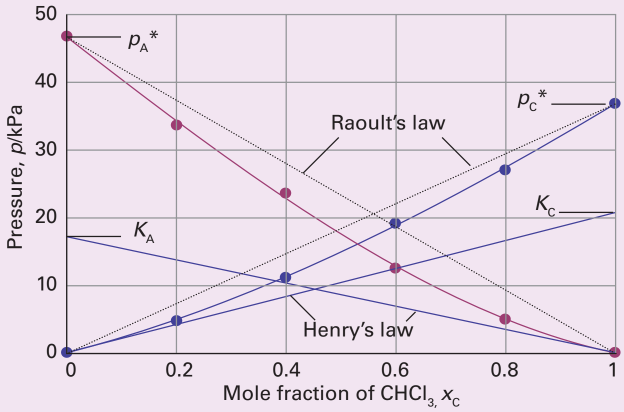

Figure 70.10 The plots of the data in Example 70.2 and the fitted curves.

Confirm that the mixture conforms to Raoult's law for the component in large excess and to Henry's law for the minor component. Find the Henry's law constants.

Method Both Raoult's and Henry's laws are statements about the form of the graph of partial vapour pressure against mole fraction. Therefore, plot the partial vapour pressures against mole fraction. Raoult's law is tested by comparing the data with the straight line $p_J = x_J p_J^*$ for each component in the region in which it is in excess (and acting as the solvent). Henry's law is tested by finding a straight line $p_J = x_J K_J$ that is tangent to each partial vapour pressure at low x, where the component can be treated as the solute. For the best results, use mathematical software to fit the data and determine the slopes of the tangent lines by differentiation.

Answer The data are plotted in Fig. 70.10 with best-fit lines of the form $a+bx+cx^2+dx^3$ together with the Raoult's law lines. The tangent lines have slope $b+2cx+3dx^2$ evaluated at $x=0$ or 1 for each component. Henry's law then requires $K_A = 16.9$ kPa for propanone and $K_C = 20.4$ kPa for trichloromethane (which are taken from the intercepts of the Henry's law lines with the vertical axes). Notice how the system deviates from both Raoult's and Henry's laws even for quite small departures from $x=1$ and $x=0$, respectively. We deal with these deviations in Topic 72.

Self-test 70.3 The vapour pressure of chloromethane at various mole fractions in a mixture at 25 °C was found to be as follows:

x	0.005	0.009	0.019	0.024
p/kPa	27.3	48.4	101	126

Estimate the Henry's law constant.

Answer: 5 MPa

(c) The thermodynamics of ideal solutions

The Gibbs energy of mixing of two liquids to form an ideal solution is calculated in exactly the same way as for two gases. The total Gibbs energy before liquids are mixed is

$$G_i = n_A\mu_A^* + n_B\mu_B^*$$

When they are mixed, the individual chemical potentials are given by eqn 70.7 and the total Gibbs energy is

$$G_f = n_A\{\mu_A^* + RT\ln x_A\} + n_B\{\mu_B^* + RT\ln x_B\}$$

Consequently, the Gibbs energy of mixing is

$$\Delta_{\text{mix}}G = nRT\{x_A\ln x_A + x_B\ln x_B\} \qquad \textit{Ideal solution} \qquad \text{Gibbs energy of mixing} \qquad (70.9a)$$

where $n = n_A + n_B$. As for gases, it follows that the ideal entropy of mixing of two liquids is

$$\Delta_{\text{mix}}S = -nR\{x_A\ln x_A + x_B\ln x_B\} \qquad \textit{Ideal solution} \qquad \text{Entropy of mixing} \qquad (70.9b)$$

and because $\Delta_{\text{mix}}H = \Delta_{\text{mix}}G + T\Delta_{\text{mix}}S = 0$, the ideal enthalpy of mixing is zero:

$$\Delta_{\text{mix}}H = 0 \qquad \textit{Ideal solution} \qquad \text{Enthalpy of mixing} \qquad (70.9c)$$

The ideal volume of mixing, the change in volume on mixing, is also zero because it follows from eqn 66.7 ($(\partial G/\partial p)_T = V$) that $\Delta_{\text{mix}}V = (\partial\Delta_{\text{mix}}G/\partial p)_T$, but $\Delta_{\text{mix}}G$ in eqn 70.9a is independent of pressure, so the derivative with respect to pressure is zero.

Brief illustration 70.2 The thermodynamics of mixing of liquids

Suppose an equimolar mixture of benzene and methylbenzene (toluene), which form a nearly ideal solution, is prepared. The mole fractions of the components of the mixture are $x_A = x_B = \tfrac{1}{2}$, and suppose the total amount of molecules is 1.0 mol; then at 25 °C

$$\Delta_{\text{mix}}G = (1.0\ \text{mol})\times(8.3145\ \text{J K}^{-1}\text{mol}^{-1})\times(298\ \text{K})$$
$$\times\left\{\overbrace{\tfrac{1}{2}\ln\tfrac{1}{2}+\tfrac{1}{2}\ln\tfrac{1}{2}}^{-\ln 2}\right\} = -1.7\ \text{kJ}$$

$$\Delta_{\text{mix}}S = -(1.0\ \text{mol})\times(8.3145\ \text{J K}^{-1}\text{mol}^{-1})$$
$$\times\left\{\overbrace{\tfrac{1}{2}\ln\tfrac{1}{2}+\tfrac{1}{2}\ln\tfrac{1}{2}}^{-\ln 2}\right\} = +5.8\ \text{J K}^{-1}$$

Self-test 70.4 Repeat the calculation for a mixture in which the mole ratio of components is 2:1.

Answer: $\Delta_{\text{mix}}G = -1.6$ kJ, $\Delta_{\text{mix}}S = +5.3$ J K^{-1}

Equation 70.9 is the same as that for two perfect gases and all the conclusions drawn there are valid here: the driving force for mixing is the increasing entropy of the system as the molecules mingle and the enthalpy of mixing is zero. The variation of the Gibbs energy and entropy of mixing with composition is the same as that already depicted for gases in Figs 70.1 and 70.4. It should be noted, however, that solution ideality means something different from gas perfection. In a perfect gas there are no forces acting between molecules. In ideal solutions there are interactions, but the average energy of A–B interactions in the mixture is the same as the average energy of A–A and B–B interactions in the pure liquids.

A note on good practice It is on the basis of this difference that the term 'perfect gas' is preferable to the more common 'ideal gas'. However, it must be admitted that the battle is almost lost, for almost everyone uses the inferior term 'ideal gas' and thus obscures a subtle but in our view important distinction.

Checklist of concepts

☐ 1. An **ideal solution** is a solution in which all components obey Raoult's law throughout the composition range.

☐ 2. An **ideal–dilute solution** is a solution for which the solute obeys Henry's law and the solvent obeys Raoult's law.

☐ 3. The enthalpy of mixing is zero for ideal solutions and mixtures of perfect gases.

Checklist of equations

Property	Equation	Comment	Equation number
Gibbs energy of mixing	$\Delta_{\text{mix}}G=nRT(x_A \ln x_A+x_B \ln x_B)$	Perfect gas; ideal solution	70.1
Entropy of mixing	$\Delta_{\text{mix}}S=-nR(x_A \ln x_A+x_B \ln x_B)$	Perfect gas; ideal solution	70.2
Enthalpy of mixing	$\Delta_{\text{mix}}H=0$	Perfect gas; ideal solution	70.3
Raoult's law	$p_J=x_J p_J^*$	Both components, ideal solution	70.6
Chemical potential	$\mu_J(\text{l})=\mu_J^*(\text{l})+RT\ln x_J$	Both components; ideal solution	70.7
Henry's law	$p_B=x_B K_B$	Solute; ideal–dilute solution	70.8a

TOPIC 71

Colligative properties

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➤ Why do you need to know this material?

The determination of molar mass by the technique of osmometry is important in the field of polymeric materials and macromolecules, where other techniques might not be viable.

➤ What is the key idea?

Colligative properties, properties of solutions that depend only on the number of solute particles, result from the effect of the solute on the chemical potential of the solvent.

➤ What do you need to know already?

You need to be aware of the concept of chemical potential (Topic 69) and its role as the criterion of equilibrium between phases. You need to be aware of the properties of ideal and ideal–dilute solutions (Topic 70).

The presence of a solute modifies the physical properties of the solvent, such as its vapour pressure, boiling point, and freezing point. It also introduces a new property, the 'osmotic pressure'. In dilute solutions these properties depend only on the number of solute particles present, not their identity. For this reason, they are called **colligative properties** (denoting 'depending on the collection').

71.1 The origin of colligative properties

All the colligative properties stem from the reduction of the chemical potential of the liquid solvent as a result of the presence of solute (Topics 69 and 70). For an ideal–dilute solution, the reduction is from μ_A^* for the pure solvent to $\mu_A^* + RT\ln x_A$ when a solute is present ($\ln x_A$ is negative because $x_A < 1$). There is no direct influence of the solute on the chemical potential of the solvent vapour and the solid solvent because the solute, which is assumed to be non-volatile and insoluble in the solid solvent, appears in neither the vapour nor the solid. As can be seen from Fig. 71.1, the reduction in chemical potential of the solvent implies that the liquid–vapour equilibrium occurs at a higher temperature (the boiling point is raised) and the solid–liquid equilibrium occurs at a lower temperature (the freezing point is lowered).

The molecular origin of the lowering of the chemical potential is the effect of the solute on the entropy of the solution. The pure liquid solvent has a characteristic entropy and its vapour pressure reflects the tendency of the system towards greater entropy, which can be achieved if the liquid vaporizes to form a gas. When a solute is present, there is an additional contribution to the entropy of the liquid, even in an ideal solution, because in a blind selection of molecules we cannot predict with certainty that we will draw a solvent or a solute molecule. Because the entropy of the liquid is already higher than that of the pure liquid, there is a weaker tendency to form the gas in the sense that less has to vaporize to maximize the total entropy (Fig. 71.2). As a result, the vapour pressure of the solvent is

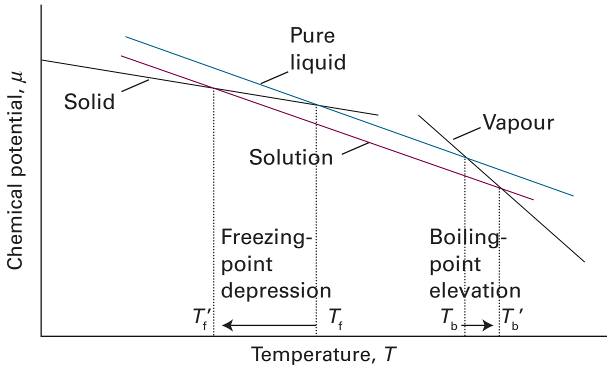

Figure 71.1 The chemical potential of a solvent in the presence of a solute. The lowering of the liquid's chemical potential has a greater effect on the freezing point than on the boiling point because of the angles at which the lines intersect.

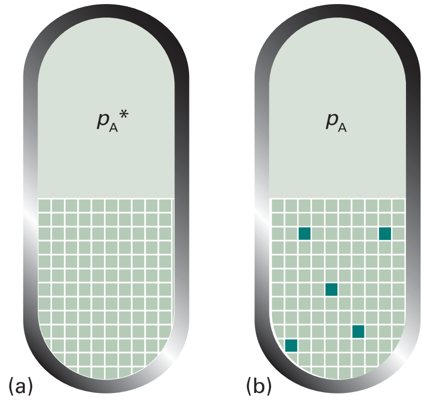

Figure 71.2 The vapour pressure of a pure liquid represents a balance between the increase in disorder arising from vaporization and the decrease in disorder of the surroundings. (a) Here the structure of the liquid is represented highly schematically by the grid of squares. (b) When solute (the dark squares) is present, the disorder of the condensed phase is higher than that of the pure liquid, and there is a decreased tendency to acquire the disorder characteristic of the vapour.

lowered and hence its boiling point is raised. Similarly, the enhanced molecular randomness of the solution opposes the tendency to freeze. Consequently, a lower temperature must be reached before equilibrium between solid and solution is achieved. Hence, the freezing point is lowered.

A thermodynamic analysis of the depression of freezing point and the elevation of boiling point[1] gives expressions for the two effects in terms of the properties of the solvent. More useful are the empirical expressions

$$\Delta T_{\mathrm{f}} = K_{\mathrm{f}} b \qquad \text{Depression of freezing point} \tag{71.1}$$

$$\Delta T_{\mathrm{b}} = K_{\mathrm{b}} b \qquad \text{Elevation of boiling point} \tag{71.2}$$

where b is the molality of the solute. The two empirical constants are known as the **cryoscopic constant** (K_{f}) and the **ebullioscopic constant** (K_{b}). However, because the effect is so small, these expressions are no longer of practical importance and apart from illustrating their relative values we shall not dwell on them.

When assessing colligative properties it is essential to focus on the solute particles that are present, not just the identity of the solute. Thus, when an ionic solute dissolves, it gives rise to cations and anions, both of which count as 'solute particles'. It is commonly supposed in elementary work that an ionic solute is fully dissociated in solution, although this is by no means reliably the case.

Brief illustration 71.1 Cryoscopic and ebullioscopic effects

For water as solvent, $K_{\mathrm{f}} = 1.86\,\mathrm{K\,kg\,mol^{-1}}$ and $K_{\mathrm{b}} = 0.513\,\mathrm{K\,kg\,mol^{-1}}$. Therefore, in a solution in which the molality of a nonelectrolyte (such as glucose) is $0.10\,\mathrm{mol\,kg^{-1}}$,

$$\Delta T_{\mathrm{f}} = (1.86\ \mathrm{K\ kg\ mol^{-1}}) \times (0.10\ \mathrm{mol\ kg^{-1}}) = 0.19\ \mathrm{K}$$
$$\Delta T_{\mathrm{b}} = (0.513\ \mathrm{K\ kg\ mol^{-1}}) \times (0.10\ \mathrm{mol\ kg^{-1}}) = 0.051\ \mathrm{K}$$

Self-test 71.1 The observed depression of freezing point of $0.25\,\mathrm{mol\,kg^{-1}}$ $\mathrm{CaCl_2(aq)}$ is 1.27 K. What can be inferred?

Answer: Presence of 3 ions for each formula unit; electrostatic interaction probably important

It is commonly stated that the depression of freezing point is an important colligative property because, for instance, it accounts for the use of antifreeze in engines. Antifreeze, however, is used in much higher concentration than can justify its effect as a colligative property; its effect is to interfere with the solidification of water molecules. The use of salt on highways is also at concentrations far outside the range of this discussion. The effect of impurities on the melting points of organic compounds is more complex, as the impurity is dissolved in the solid, a situation excluded in the treatment of colligative properties. Boiling-point elevation is too small to be of any practical significance. No one, except perhaps as a laboratory exercise, any longer uses the depression of freezing point or elevation of boiling point to determine molar mass.

71.2 Osmosis

The only colligative property of real importance is **osmosis** (from the Greek word for 'push'), the spontaneous passage of

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[1] For details, see our other *Physical chemistry* (2014).

a pure solvent into a solution separated from it by a **semipermeable membrane**, a membrane permeable to the solvent but not to the solute (Fig. 71.3). The **osmotic pressure**, Π, is the pressure that must be applied to the solution to stop the influx of solvent. Important examples of osmosis include transport of fluids through cell membranes, dialysis, and **osmometry**, the determination of molar mass by the measurement of osmotic pressure. Osmometry is widely used to determine the molar masses of macromolecules.

In the simple arrangement shown in Fig. 71.4, the opposing pressure arises from the column of solution that the osmosis itself produces. Equilibrium is reached when the hydrostatic pressure of the column of solution matches the osmotic pressure. The complicating feature of this arrangement is that the entry of solvent into the solution results in its dilution, and so it is more difficult to treat than the arrangement in Fig. 71.3, in which there is no flow and the concentrations remain unchanged.

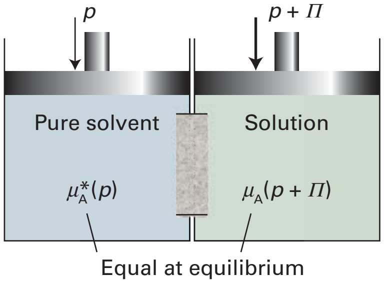

Figure 71.3 The equilibrium involved in the calculation of osmotic pressure, Π, is between pure solvent A at a pressure p on one side of the semipermeable membrane and A as a component of the mixture on the other side of the membrane, where the pressure is $p+\Pi$.

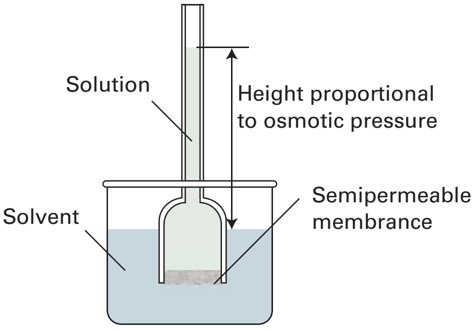

Figure 71.4 In a simple version of the osmotic pressure experiment, A is at equilibrium on each side of the membrane when enough has passed into the solution to cause a hydrostatic pressure difference.

(a) The van 't Hoff equation

The thermodynamic treatment of osmosis depends on noting that, at equilibrium, the chemical potential of the solvent must be the same on each side of the membrane. The chemical potential of the solvent is lowered by the solute, but is restored to its 'pure' value by the application of pressure. As shown in the following *Justification*, this equality implies that for dilute solutions the osmotic pressure is given by the **van 't Hoff equation**:

$$\Pi = [\mathrm{B}]RT \qquad \text{van't Hoff equation} \qquad (71.3)$$

where $[\mathrm{B}] = n_\mathrm{B}/V$ is the molar concentration of the solute.

Brief illustration 71.2 The van 't Hoff equation

We saw in *Brief illustration* 71.1 that an 0.10 mol kg^{-1} non-electrolyte solution has only tiny effects on the freezing and boiling points of water. The osmotic pressure of the same solution at 25 °C, assuming that the molar concentration is 0.10 mol dm^{-3}, corresponding to 1.0×10^2 mol m^{-3} (which is the case if the density of the solution differs insignificantly from that of pure water), is

$$\begin{aligned}\Pi &= (1.0\times10^2\,\mathrm{mol\,m^{-3}})\times(8.3145\,\mathrm{J\,K^{-1}mol^{-1}})\times(298\,\mathrm{K})\\ &= 2.5\times10^5\,\mathrm{J\,m^{-3}}\end{aligned}$$

or 2.5 bar (because 1 J m^{-3} = 1 Pa and 1 bar = 10^5 Pa). This is a huge and easily measured pressure: it would drive water to a height of 25 m.

Self-test 71.2 Use the information in Self-test 71.1 to estimate the osmotic pressure of 0.25 mol kg^{-1} $\mathrm{CaCl_2(aq)}$ at 25 °C. Assume that the density of the solution is that of pure water.

Answer: 17 bar

Justification 71.1 The van 't Hoff equation

On the pure solvent side the chemical potential of the solvent, which is at a pressure p, is $\mu_\mathrm{A}^*(p)$. On the solution side, the chemical potential is lowered by the presence of the solute, which reduces the mole fraction of the solvent from 1 to x_A. However, the chemical potential of A is raised on account of the greater pressure, $p+\Pi$, that the solution experiences. At equilibrium the chemical potential of A is the same in both compartments, and we can write

$$\mu_\mathrm{A}^*(p) = \mu_\mathrm{A}(x_\mathrm{A}, p+\Pi)$$

The presence of solute is taken into account in the normal way (Topic 70):

$$\mu_\mathrm{A}(x_\mathrm{A}, p+\Pi) = \mu_\mathrm{A}^*(p+\Pi) + RT\ln x_\mathrm{A}$$

We saw in Topic 69 (specifically eqn 69.12) how to take the effect of pressure into account. Thus, because $(\partial\mu_A/\partial p)_T = V_{A,m}$, for pure A, we can write $d\mu_A = V_{A,m}dp$, and on integration obtain

$$\mu_A^{\star}(p+\Pi) = \mu_A^{\star}(p) + \int_p^{p+\Pi} V_m dp$$

where V_m is the molar volume of the pure solvent A (which we assume to be negligibly different from its 'partial molar volume', $V_{A,m}$, the contribution that A makes to the total volume of the sample). When these three equations are combined and equivalent terms cancelled we get

$$-RT\ln x_A = \int_p^{p+\Pi} V_m dp$$

This expression enables us to calculate the additional pressure Π that must be applied to the solution to restore the chemical potential of the solvent to its 'pure' value and thus to restore equilibrium across the semipermeable membrane. For dilute solutions, $\ln x_A$ may be replaced by $\ln(1 - x_B) \approx -x_B$, and the left-hand side of this expression becomes simply RTx_B. We may also assume that the pressure range in the integration is so small that the molar volume of the almost incompressible solvent is a constant. That being so, V_m may be taken outside the integral, giving

$$RTx_B = \Pi V_m$$

When the solution is dilute, $x_B \approx n_B/n_A$. Moreover, because $n_AV_m = V$, the total volume of the solvent, the equation simplifies to eqn 71.3.

(b) Osmometry

Because the effect of osmotic pressure is so readily measurable and large, one of the most common applications of osmometry is to the measurement of molar masses of macromolecules, such as proteins and synthetic polymers. As these huge molecules dissolve to produce solutions that are far from ideal, it is assumed that the van 't Hoff equation is only the first term of a virial-like expansion:

$$\Pi = [J]RT\{1 + B[J] + \ldots\} \quad \text{Osmotic virial equation} \quad (71.4)$$

where we have denoted the solute by J to avoid too many different Bs in this expression. The additional terms take the nonideality into account; the empirical constant B is called the **osmotic virial coefficient**.

Example 71.1 Using osmometry to determine the molar mass of a macromolecule

The osmotic pressures of solutions of poly(vinyl chloride), PVC, in cyclohexanone at 298 K are given below. The pressures are expressed in terms of the heights of solution (of mass density $\rho = 0.980\,\text{g cm}^{-3}$) in balance with the osmotic pressure. Determine the molar mass of the polymer.

$c/(\text{g dm}^{-3})$	1.00	2.00	4.00	7.00	9.00
h/cm	0.28	0.71	2.01	5.10	8.00

Method The osmotic pressure is measured at a series of mass concentrations, c, and a plot of Π/c against c is used to determine the molar mass of the polymer. We use eqn 71.4 with $[J] = c/M$, where c is the mass concentration of the polymer and M is its molar mass. The osmotic pressure is related to the hydrostatic pressure by $\Pi = \rho gh$ with $g = 9.81\,\text{m s}^{-2}$. With these substitutions, eqn 71.4 becomes

$$\overbrace{\rho gh}^{\Pi} = \overbrace{\frac{c}{M}}^{[J]} \times RT\left\{1 + \frac{c}{M}B + \cdots\right\}$$

and then

$$\overbrace{\frac{h}{c}}^{y} = \overbrace{\frac{RT}{\rho gM}}^{b} + \overbrace{\frac{RTB}{\rho gM^2}}^{m}\overbrace{c}^{x} + \cdots$$

This expression, truncated after the second term on the right, has the form of a straight line, $y = b + mx$. Therefore, to find M, plot h/c against c, and expect a straight line with intercept $RT/\rho gM$ at $c = 0$.

Answer The data give the following values for the quantities to plot:

$c/(\text{g dm}^{-3})$	1.00	2.00	4.00	7.00	9.00
$(h/c)/(\text{cm g}^{-1}\,\text{dm}^3)$	0.28	0.36	0.503	0.729	0.889

The points are plotted in Fig. 71.5. The intercept from a least-squares analysis is at 0.21. Therefore,

$$\begin{aligned} M &= \frac{RT}{\rho g} \times \frac{1}{0.21\,\text{cm g}^{-1}\,\text{dm}^3} \\ &= \frac{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})}{(980\,\text{kg m}^{-3}) \times (9.81\,\text{m s}^{-2})} \times \frac{1}{2.1\times10^{-3}\,\text{m}^4\,\text{kg}^{-1}} \\ &= 1.2\times10^2\,\text{kg mol}^{-1} \end{aligned}$$

where we have used $1\,\text{kg m}^2\,\text{s}^{-2} = 1\,\text{J}$. Modern osmometers give readings of osmotic pressure in pascals, so the analysis

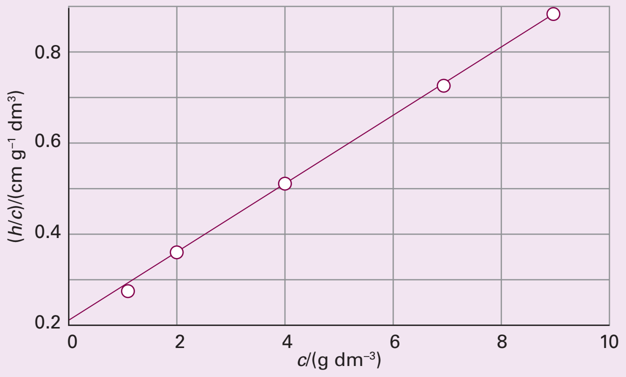

Figure 71.5 The plot involved in the determination of molar mass by osmometry in Example 71.1. The molar mass is calculated from the intercept at $c=0$.

of the data is more straightforward and eqn 71.4 can be used directly.

Self-test 71.3 The osmotic pressures of solutions of polystyrene in methylbenzene at 293 K are given below. Determine the molar mass of the polymer.

$c/(\mathrm{g\,dm^{-3}})$	1.00	2.00	4.00	7.00	9.00
Π/Pa	17.7	35.5	70.8	125.0	162.0

Answer: 140 kg mol⁻¹

(c) Molar mass averages

Care must be taken in the interpretation of molar masses determined by osmosis. Thus, although a pure protein is almost **monodisperse**, meaning that it has a single, definite molar mass (although there may be small variations, such as one amino acid replacing another, depending on the source of the sample), a synthetic polymer is **polydisperse**, in the sense that a sample is a mixture of molecules with various chain lengths and molar masses. The **number-average molar mass**, $\bar{M}_n$, is the value obtained by weighting each molar mass by the number of molecules of that mass present in the sample:

$$\bar{M}_n = \frac{1}{N}\sum_i N_i M_i \qquad (71.5a)$$

Definition Number-average molar mass

where N_i is the number of molecules with molar mass M_i and there are N molecules in all. The **weight-average molar mass**, $\bar{M}_w$, is the average calculated by weighting the molar masses of the molecules by the mass of each one present in the sample:

$$\bar{M}_w = \frac{1}{m}\sum_i m_i M_i \qquad (71.5b)$$

Definition Weight-average molar mass

In this expression, m_i is the total mass of molecules of molar mass M_i and m is the total mass of the sample. Because $m_i = N_i M_i / N_A$ and $m = \Sigma_i N_i M_i$ we can also express this average as

$$\bar{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \qquad (71.5c)$$

This expression shows that the weight-average molar mass is proportional to the mean square molar mass. In practice, osmometry gives the number-average molar mass and light scattering experiments give the weight-average molar mass.

Example 71.2 Calculating number- and weight-average molar masses

Determine the number-average and the weight-average molar masses for a sample of poly(vinyl chloride) from the following data:

Molar mass interval/(kg mo1⁻¹)	Average molar mass within interval/(kg mo1⁻¹)	Mass of sample within interval/g
5–10	7.5	9.6
10–15	12.5	8.7
15–20	17.5	8.9
20–25	22.5	5.6
25–30	27.5	3.1
30–35	32.5	1.7

Method The relevant equations are eqns 71.5a and 71.5b. Calculate the two averages by weighting the molar mass within each interval by the number and mass, respectively, of the molecule in each interval. Obtain the numbers in each interval by dividing the mass of the sample in each interval by the average molar mass for that interval. Because number of molecules is proportional to amount of substance (the number of moles), the number-weighted average can be obtained directly from the amounts in each interval. Use a spreadsheet to evaluate the sums (but here we show the calculation explicitly).

Answer The amounts in each interval are as follows:

Interval	5–10	10–15	15–20	20–25	25–30	30–35
Molar mass/(kg mol⁻¹)	7.5	12.5	17.5	22.5	27.5	32.5
Amount/(10⁻³ mo1)	1.3	0.7	0.51	0.25	0.11	0.052
					Total:	2.92

The number-average molar mass is therefore

$$\bar{M}_{\rm n}/({\rm kg\,mol^{-1}}) = \frac{1}{2.92}\begin{pmatrix}1.3\times7.5+0.70\times12.5+0.51\times17.5+0.25\times22.5\\ +0.11\times27.5+0.052\times32.5\end{pmatrix} = 13$$

where the factor 10^{-3} cancels. The weight-average molar mass is calculated directly from the data after noting that the total mass of the sample is 37.6 g:

$$\bar{M}_{\rm w}/({\rm kg\,mol^{-1}}) = \frac{1}{37.6}\begin{pmatrix}9.6\times7.5+8.7\times12.5+8.9\times17.5+5.6\times22.5+3.1\times27.5\\ +1.7\times32.5\end{pmatrix} = 16$$

Note the significantly different values of the two averages. In this instance, $\bar{M}_{\rm w}/\bar{M}_{\rm n}=1.2$.

Self-test 71.4 The *Z-average molar mass* is defined as

$$\bar{M}_Z = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2} \qquad \textit{Definition} \qquad \textit{Z}\text{-average molar mass} \qquad (71.5\text{d})$$

and can be interpreted in terms of the mean cubic molar mass. Evaluate the Z-average molar mass of the sample described in this Example.

Answer: 19 kg mol^{-1}

The ratio $\bar{M}_{\rm w}/\bar{M}_{\rm n}$ is called the **heterogeneity index** (or 'polydispersity index', PDI). In the determination of protein molar masses we expect the various averages to be the same because the sample is monodisperse (unless there has been degradation). A synthetic polymer normally spans a range of molar masses and the different averages yield different values. Typical synthetic materials have $\bar{M}_{\rm w}/\bar{M}_{\rm n}\approx 4$. The term 'monodisperse' is conventionally applied to synthetic polymers in which this index is less than 1.1; commercial polyethylene samples might be much more heterogeneous, with a ratio close to 30. One consequence of a narrow molar mass distribution for synthetic polymers is often a higher degree of three-dimensional long-range order in the solid and therefore higher density and melting point. The spread of values is controlled by the choice of catalyst and reaction conditions. In practice, it is found that long-range order is determined more by structural factors (branching, for instance) than by molar mass.

Checklist of concepts

☐ 1. **Colligative properties** are properties that depend on the relative number but not the identity of the solute particles.

☐ 2. Colligative properties include the depression of freezing point, the elevation of boiling point, and osmosis.

☐ 3. All three colligative properties stem from the effect of the solute on the entropy of the solution.

☐ 4. **Osmosis** is the only colligative effect of practical importance; it is used to determine the molar masses of macromolecules in solution.

☐ 5. **Osmometry** gives the number-average molar mass and light scattering experiments give the weight-average molar mass.

☐ 6. The **heterogeneity index**, $\bar{M}_{\rm w}/\bar{M}_{\rm n}$, is an indication of the range of molar masses present in a sample.

Checklist of equations

Property	Equation	Comment	Equation number
Depression of freezing point	$\Delta T_{\rm f}=K_{\rm f}b$	Empirical; dilute solution	71.1
Elevation of boiling point	$\Delta T_{\rm b}=K_{\rm b}b$	Empirical; dilute solution	71.2
van 't Hoff equation	$\Pi=[{\rm B}]RT$	Ideal solution	71.3

Property	Equation	Comment	Equation number
Osmotic virial equation	$\Pi = [\mathrm{J}]RT\{1 + B[\mathrm{J}] + \ldots\}$	Empirical extension	71.4
Number-average molar mass	$\bar{M}_{\mathrm{n}} = (1/N)\sum_i N_i M_i$	Definition	71.5a
Weight-average molar mass	$\bar{M}_{\mathrm{w}} = (1/m)\sum_i m_i M_i$	Definition	71.5b

TOPIC 72

Real solutions

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➤ Why do you need to know this material?

All actual solutions are real solutions, and to describe their thermodynamic properties it is important to be able to go beyond the primitive model of ideal solutions and take intermolecular and interionic interactions into account.

➤ What is the key idea?

The activity of a component in solution is its effective concentration, taking into account the effects of intermolecular and interionic interactions.

➤ What do you need to know already?

You need to be familiar with the properties of ideal solutions, specifically Henry's and Raoult's laws (Topic 70), and the dependence of chemical potential on concentration (Topic 69). This Topic extends the discussion of the enthalpy, entropy, and Gibbs energy of mixing of ideal solutions (Topic 70).

Ideal solutions are treated in Topic 70: they are solutions in which A–A, A–B, and B–B interactions are all the same, where A denotes the solvent and B the solute. **Real solutions** are composed of particles for which A–A, A–B, and B–B interactions are all different. Not only may there be enthalpy and volume changes when liquids mix, but there may also be an additional contribution to the entropy arising from the way in which the molecules of one type might cluster together instead of mingling freely with the others. If the enthalpy change is large and positive or if the entropy change is adverse (because of a reorganization of the molecules that results in an orderly mixture), then the Gibbs energy might be positive for mixing. In that case, separation is spontaneous and the liquids may be immiscible. Alternatively, the liquids might be **partially miscible**, which means that they are miscible only over a certain range of compositions.

72.1 Activities

Real solutions differ from ideal solutions as a result of differences in intermolecular interactions between their components and how the molecules aggregate. These differences are taken into account by replacing the concentrations in expressions for the chemical potential by effective concentrations known as 'activities'.

(a) The solvent activity

The general form of the chemical potential of a real or ideal solvent is given by a straightforward modification of eqn 70.5 (that $\mu_A = \mu_A^\star + RT\ln(p_A/p_A^\star)$), where $p_A^\star$ is the vapour pressure of pure A and p_A is the vapour pressure of A when it is a component of a solution. For an ideal solution, as is shown in Topic 70, the solvent obeys Raoult's law at all concentrations and we can express this relation as eqn 70.7 (that is, as $\mu_A = \mu_A^\star + RT\ln x_A$). The form of this relation can be preserved when the solution does not obey Raoult's law by writing

$$\mu_A = \mu_A^\star + RT\ln a_A \qquad \textit{Definition} \quad \text{Solvent activity} \qquad (72.1)$$

The quantity a_A is the **activity** of A, a kind of 'effective' mole fraction.

Because the expression that $\mu_A = \mu_A^* + RT\ln(p_A/p_A^*)$ is true for both real and ideal solutions, we can conclude by comparing it with eqn 72.1 that

$$a_A = \frac{p_A}{p_A^*} \qquad \text{Solvent activity} \qquad (72.2)$$

Note—and this is a very important point—that it follows that the activity of a pure substance (when $p_A = p_A^*$) is 1. We see that there is nothing mysterious about the activity of a solvent: it can be determined experimentally simply by measuring the vapour pressure and then using eqn 72.2.

Brief illustration 72.1 The solvent activity

The vapour pressure of 0.500 M $KNO_3(aq)$ at 100 °C (when the vapour pressure of pure water is 1 atm, or 101.3 kPa) is 99.95 kPa, so the activity of water in the solution at this temperature is

$$a_A = \frac{99.95\,\text{kPa}}{101.3\,\text{kPa}} = 0.9867$$

Self-test 72.1 The vapour pressure of water at 20 °C is 2.339 kPa and that of a saturated solution of KBr in water at the same temperature is 1.853 kPa. What is the activity of water in this solution?

Answer: 0.7922

Because all solvents obey Raoult's law (that $p_A/p_A^* = x_A$, eqn 70.6 of Topic 70) increasingly closely as the concentration of solute approaches zero, the activity of the solvent approaches the mole fraction as $x_A \rightarrow 1$:

$$a_A \rightarrow x_A \quad \text{as } x_A \rightarrow 1 \qquad (72.3)$$

A convenient way of expressing this convergence is to introduce the **activity coefficient**, γ, by the definition

$$a_A = \gamma_A x_A \quad \gamma_A \rightarrow 1 \quad \text{as } x_A \rightarrow 1 \qquad \textit{Definition} \qquad \text{Activity coefficient} \qquad (72.4)$$

at all temperatures and pressures. The chemical potential of the solvent is then

$$\mu_A = \mu_A^* + RT\ln x_A + RT\ln \gamma_A \qquad (72.5)$$

and all the deviation from ideal behaviour is expressed by $RT\ln\gamma_A$. The standard state of the solvent, the pure liquid solvent at 1 bar, is established when $x_A = 1$.

(b) The solute activity

The problem with defining activity coefficients and standard states for solutes is that they approach ideal–dilute (Henry's law, Topic 70) behaviour as $x_B \rightarrow 0$, not as $x_B \rightarrow 1$ (corresponding to pure solute). We shall show how to set up the definitions for a solute that obeys Henry's law exactly, and then show how to allow for deviations.

The vapour pressure of a solute B that satisfies Henry's law is given by $p_B = K_B x_B$, where K_B is an empirical constant. In this case, it follows from the general expression $\mu_B = \mu_B^* + RT\ln(p_B/p_B^*)$ that the chemical potential of B is

$$\mu_B = \mu_B^* + RT\ln\frac{K_B x_B}{p_B^*} = \mu_B^* + RT\ln\frac{K_B}{p_B^*} + RT\ln x_B$$

Both K_B and p_B^* are characteristics of the solute independent of its abundance, so the second term on the right may be combined with the first to give a new standard chemical potential:

$$\mu_B^{\ominus} = \mu_B^* + RT\ln\frac{K_B}{p_B^*} \qquad \textit{Definition} \qquad \text{Standard chemical potential of solute} \qquad (72.6)$$

If the solution is ideal, $K_B = p_B^*$ and eqn 72.6 reduces to $\mu_B^{\ominus} = \mu_B^*$, as we should expect. It now follows that the chemical potential of a solute in an ideal–dilute solution is related to its mole fraction by

$$\mu_B = \mu_B^{\ominus} + RT\ln x_B \qquad \textit{Ideal–dilute solution} \qquad \text{Chemical potential of solute} \qquad (72.7)$$

We now permit deviations from ideal–dilute, Henry's law behaviour. For the solute, we introduce a_B in place of x_B in eqn 72.7, and obtain

$$\mu_B = \mu_B^{\ominus} + RT\ln a_B \qquad \textit{Definition} \qquad \text{Activity of solute} \qquad (72.8)$$

The standard state remains unchanged in this last stage, and all the deviations from ideality are captured in the activity a_B. The value of the activity at any concentration can be obtained in the same way as for the solvent, but in place of eqn 72.2 we use

$$a_B = \frac{p_B}{K_B} \qquad \text{Solute activity} \qquad (72.9)$$

As for the solvent, it is sensible to introduce an activity coefficient through

$$a_B = \gamma_B x_B \qquad \textit{Definition} \qquad \text{Solute activity coefficient} \qquad (72.10)$$

Table 72.1 Activities and standard states

Component	Basis	Standard state	Activity	Limits
Solid or liquid		Pure	$a=1$	
Solvent	Raoult	Pure solvent	$a=p/p^*$, $a=\gamma x$	$\gamma\rightarrow1$ as $x\rightarrow1$ (pure solvent)
Solute	Henry	(1) A hypothetical state of the pure solute	$a=p/K$, $a=\gamma x$	$\gamma\rightarrow1$ as $x\rightarrow0$
		(2) A hypothetical state of the solute at molality $b^\ominus=1\,\text{mol kg}^{-1}$	$a=\gamma b/b^\ominus$	$\gamma\rightarrow1$ as $b\rightarrow0$

In each case, $\mu=\mu^\ominus+RT\ln a$.

Now all the deviations from ideality are captured in the activity coefficient γ_B. Because the solute obeys Henry's law as its concentration goes to zero, it follows that

$$a_B\rightarrow x_B \text{ and } \gamma_B\rightarrow1 \text{ as } x_B\rightarrow0 \qquad (72.11)$$

at all temperatures and pressures. Deviations of the solute from ideality disappear as zero concentration is approached.

The conventions for activities, activity coefficients, and standard states are summarized in Table 72.1.

Example 72.1 Measuring activity

Calculate the activity and activity coefficient of chloroform (trichloromethane) in acetone (propanone) at 25 °C, treating it first as a solvent and then as a solute, given the following data for the partial pressures p_C of chloroform and p_A of acetone as a function of chloroform mole fraction x_C.

x_C	0	0.20	0.40	0.60	0.80	1
p_C/kPa	0	4.7	11	18.9	26.7	36.4
p_A/kPa	46.3	33.3	23.3	12.3	4.9	0

The Henry's law constant K_C is 22.0 kPa for chloroform at 25 °C.

Method For the activity of chloroform as a solvent (the Raoult's law activity), form $ac=p_C/p^*_C$ and $\gamma_C=a_C/x_C$. For its activity as a solute (the Henry's law activity), form $a_C=p_C/K_C$ and $\gamma_C=a_C/x_C$.

Answer Because $p^*_C=36.4\,\text{kPa}$ and $K_C=22.0\,\text{kPa}$, we can construct the following tables. For instance, at $x_C=0.20$, in the Raoult's law case we find $a_C=(4.7\,\text{kPa})/(36.4\,\text{kPa})=0.13$ and $\gamma_C=0.13/0.20=0.65$; likewise, in the Henry's law case, $a_C=(4.7\,\text{kPa})/(22.0\,\text{kPa})=0.21$ and $\gamma_C=0.21/0.20=1.05$.

From Raoult's law (chloroform regarded as the solvent):

a_C	0	0.13	0.30	0.52	0.73	1.00
γ_C		0.65	0.75	0.87	0.91	1.00

From Henry's law (chloroform regarded as the solute):

a_C	0	0.21	0.50	0.86	1.21	1.65
γ_C	1	1.05	1.25	1.43	1.51	1.65

These values are plotted in Fig. 72.1. Notice that $\gamma_C\rightarrow1$ as $x_C\rightarrow1$ in the Raoult's law case, but that $\gamma_C\rightarrow1$ as $x_C\rightarrow0$ in the Henry's law case.

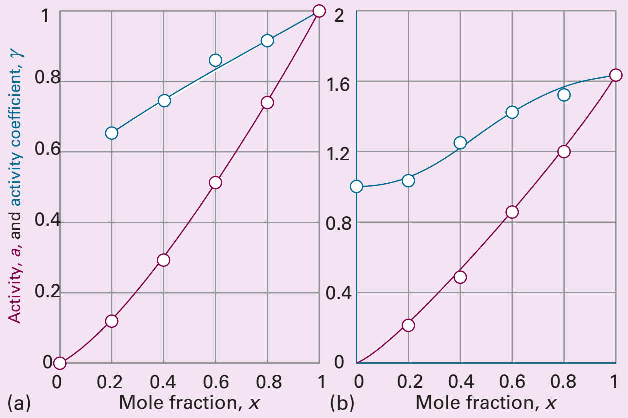

Figure 72.1 The variation of activity and activity coefficient of chloroform (trichloromethane) and acetone (propanone) with composition according to (a) Raoult's law, (b) Henry's law.

Self-test 72.2 Calculate the activities and activity coefficients for acetone according to the two conventions (K_A is 23.3 kPa).

Answer: At $x_A=0.60$, for instance, $a_R=0.50$, $\gamma_R=0.83$, $a_H=1.00$, $\gamma_H=1.67$

72.2 Model systems: regular solutions

The thermodynamic properties of real solutions are commonly expressed in terms of the **excess functions**, X^E, the difference between the observed thermodynamic function of mixing and the function for an ideal solution. The **excess entropy**, S^E, for example, is defined as

$$S^E=\Delta_{mix}S-\Delta_{mix}S^{ideal} \qquad (72.12)$$

Definition Excess entropy

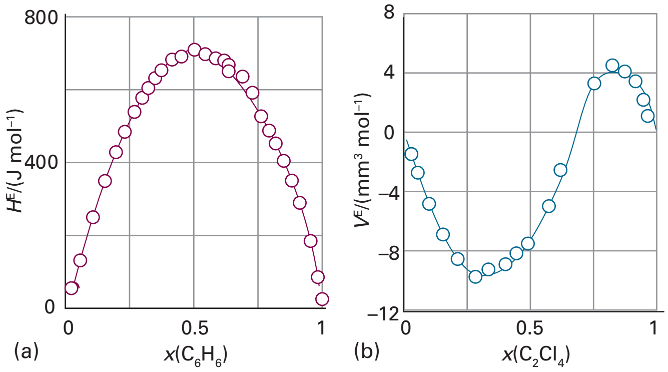

Figure 72.2 Experimental excess functions at 25 °C. (a) H^E for benzene/cyclohexane; this graph shows that the mixing is endothermic (because $\Delta_{mix}H = 0$ for an ideal solution). (b) The excess volume, V^E, for tetrachloroethene/cyclopentane; this graph shows that there is a contraction at low tetrachloroethene mole fractions, but an expansion at high mole fractions (because $\Delta_{mix}V = 0$ for an ideal mixture).

where $\Delta_{mix}S^{ideal}$ is given by eqn 70.2 ($\Delta_{mix}S^{ideal} = -nR(x_A \ln x_A + x_B \ln x_B)$). The excess enthalpy and volume are both equal to the observed enthalpy and volume of mixing, because the ideal values are zero in each case. Figure 72.2 shows two examples of the composition dependence of molar excess functions.

Deviations of the excess energies from zero indicate the extent to which the solutions are non-ideal. In this connection a useful model system is the **regular solution**, a solution for which $H^E \neq 0$ but $S^E = 0$. We can think of a regular solution as one in which the two kinds of molecules are distributed randomly (as in an ideal solution) but have different energies of interactions with each other.

To express this model quantitatively, we suppose that the excess enthalpy depends on composition as

$$H^E = n\xi RTx_A x_B \tag{72.13}$$

where ξ (xi) is a dimensionless parameter that is a measure of the energy of AB interactions relative to that of the A–A and B–B interactions; for an ideal solution, $\xi = 0$. The function given by eqn 72.13 is plotted in Fig. 72.3 and we see it resembles the experimental curve in Fig. 72.2. If $\xi < 0$, mixing is exothermic and the solute–solvent interactions are more favourable than the solvent–solvent and solute–solute interactions. If $\xi > 0$, then the mixing is endothermic. Because for a regular solution the entropy of mixing has its ideal value, the excess Gibbs energy is equal to the excess enthalpy, and the Gibbs energy of mixing is

$$\Delta_{mix}G = nRT(x_A \ln x_A + x_B \ln x_B + \xi x_A x_B) \tag{72.14}$$

with $x_B = 1 - x_A$.

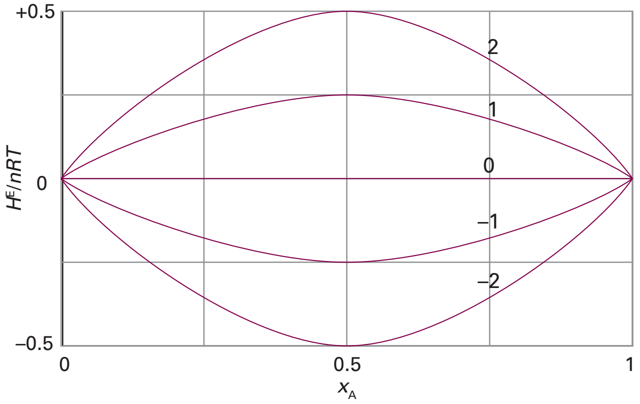

Figure 72.3 The excess enthalpy according to a model in which it is proportional to $\xi x_A x_B$ for different values of the parameter ξ.

Brief illustration 72.2 Regular solutions

When $x_A = x_B = \frac{1}{2}$ the excess enthalpy is $H^E/n = \frac{1}{4}\xi RT$. From the graph in Fig. 72.2 for a mixture of benzene and cyclohexane at 25 °C, we see that this point corresponds to +700 J. It follows that for this mixture

$$\xi = \frac{4 \times (700\,\mathrm{J\,mol^{-1}})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})} = +1.13$$

We shall use this value as this section develops.

Self-test 72.3 In another mixture of two liquids at 20 °C, the excess enthalpy was found to be equal to −420 J mol^{-1} when the mole fraction of one component was 0.333. What is the value of ξ for this mixture?

Answer: −0.776

Figure 72.4 shows how $\Delta_{mix}G$ varies with composition for different values of ξ. The important feature is that for $\xi > 2$ the graph shows two minima separated by a maximum. The implication of this observation is that, provided $\xi > 2$, the system will separate spontaneously into two phases with compositions corresponding to the two minima, for that separation corresponds to a reduction in Gibbs energy. This behaviour is what is summarized by the experimentally determined two-component liquid mixture in Fig. 68.1.

We can take this analysis further and identify the upper critical solution temperature (Topic 68). The compositions corresponding to the two minima in Fig. 72.4 are obtained by looking for the conditions at which $\partial\Delta_{mix}G/\partial x_A = 0$, and a simple manipulation of eqn 72.14 shows that we have to solve

$$\ln \frac{x_A}{1 - x_A} + \xi(1 - 2x_A) = 0$$

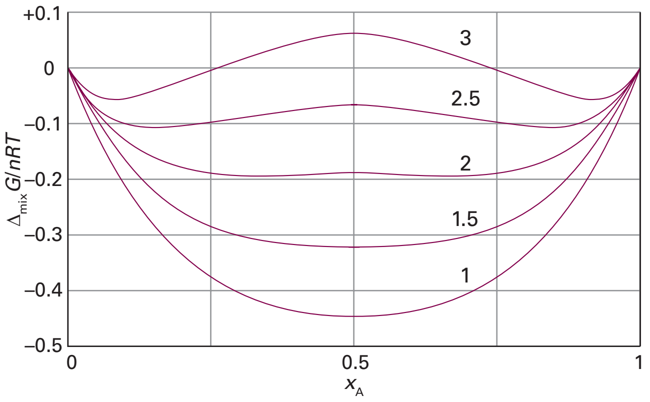

Figure 72.4 The Gibbs energy of mixing for different values of the parameter ξ.

This expression is an example of a 'transcendental equation', an equation that does not have a solution that can be expressed in a closed form. The solutions can be found numerically by using mathematical software or by plotting the first term against the second and identifying the points of intersection as ξ is changed.

The solutions are plotted in Fig. 72.5. We see that the two minima move together as ξ decreases and merge when $\xi=2$. Because $H^E \propto \xi RT$, for constant excess enthalpy (corresponding to the effect of intermolecular forces being constant as the temperature is raised) a decrease in ξ can be interpreted as an increase in temperature, so the vertical axis in Fig. 72.5 can be interpreted as indicating the temperature, and so the topmost point of the curve corresponds to the upper critical solution temperature.

The concept of a regular solution gives further insight into the origin of deviations from Raoult's law and its relation to activity coefficients. We show in the following *Justification* that for a regular solution modelled by the parameter ξ the activity coefficients are given by the **Margules equations**:

$$\ln\gamma_A = \xi x_B^2 \quad \ln\gamma_B = \xi x_A^2 \qquad \textit{Regular solution} \qquad \text{Margules equations} \tag{72.15}$$

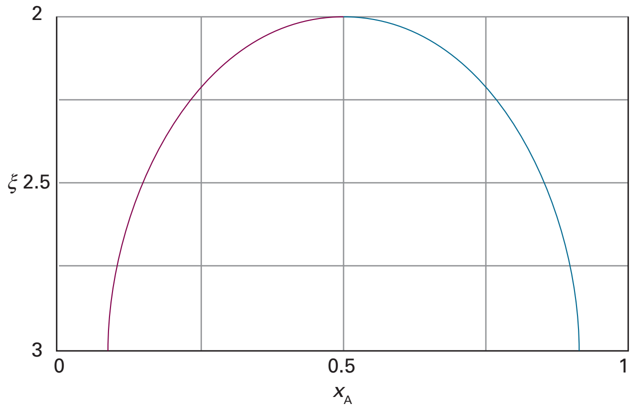

Figure 72.5 The location of the phase boundary as computed on the basis of the ξ-parameter model.

Brief illustration 72.3 The Margules equations

For the mixture of benzene and cyclohexane illustrated in Fig. 72.2 and treated in *Brief illustration* 72.2 on the basis of being a regular solution we know that $\xi=1.13$. It follows that the activity coefficient of benzene when $x_{\text{benzene}} = 0.250$ (and $x_{\text{cyclohexane}}=0.750$) is given by

$$\ln\gamma_{\text{benzene}} = \xi x_{\text{cyclohexane}}^2 = 1.13\times 0.750^2 = 0.636$$

which implies that $\gamma_{\text{benzene}} = e^{0.636} = 1.89$ for this solution.

Self-test 72.4 What is the activity coefficient of A for the solution treated in Self-test 72.3 when $x_A=0.333$?

Answer: 0.708

Justification 72.1 The Margules equations

The Gibbs energy of mixing to form a non-ideal solution is

$$\Delta_{\text{mix}}G = nRT(x_A\ln a_A + x_B\ln a_B)$$

This relation follows from the derivation of eqn 70.1 for ideal solutions with activities in place of mole fractions. When each activity is replaced by $\gamma_J x_J$, this expression becomes

$$\Delta_{\text{mix}}G = nRT(x_A\ln x_A + x_B\ln x_B + x_A\ln\gamma_A + x_B\ln\gamma_B)$$

Now we introduce the two expressions in eqn 72.15, and use $x_A+x_B=1$, which gives

$$\begin{aligned}\Delta_{\text{mix}}G &= nRT(x_A\ln x_A + x_B\ln x_B + \xi x_A x_B^2 + \xi x_B x_A^2)\\ &= nRT\{x_A\ln x_A + x_B\ln x_B + \xi x_A x_B(x_A+x_B)\}\\ &= nRT(x_A\ln x_A + x_B\ln x_B + \xi x_A x_B)\end{aligned}$$

as required by eqn 72.14. Note, moreover, that the activity coefficients behave correctly for dilute solutions: $\gamma_A\to 1$ as $x_B\to 0$ and $\gamma_B\to 1$ as $x_A\to 0$.

At this point we can use the Margules equations to write the activity of A as

$$a_A = \gamma_A x_A = e^{\xi x_B^2}x_A = e^{\xi(1-x_A)^2}x_A \tag{72.16}$$

with a similar expression for a_B. The activity of A, though, is just the ratio of the vapour pressure of A in the solution to the vapour pressure of pure A (eqn 72.2, $a_A = p_A/p_A^*$), so we can write

$$p_A = \left\{e^{\xi(1-x_A)^2}x_A\right\}p_A^* \qquad \textit{Regular solution} \qquad \text{Vapour pressure} \tag{72.17}$$

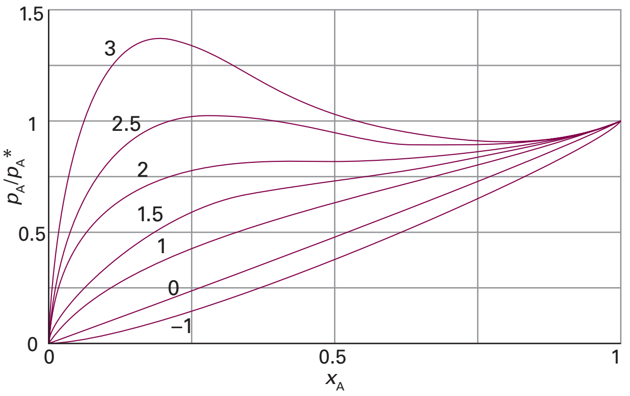

Figure 72.6 The vapour pressure of a mixture based on a model in which the excess enthalpy is proportional to $\xi x_A x_B$. An ideal solution corresponds to $\xi=0$ and gives a straight line, in accord with Raoult's law. Positive values of ξ give vapour pressures higher than ideal. Negative values of ξ give a lower vapour pressure.

This function is plotted in Fig. 72.6. We see that $\xi=0$, corresponding to an ideal solution, gives a straight line, in accord with Raoult's law (indeed, when $\xi=0$, eqn 72.17 becomes $p_A = x_A p_A^*$, which is Raoult's law). Positive values of ξ (endothermic mixing, unfavourable solute–solvent interactions) give vapour pressures higher than ideal. Negative values of ξ (exothermic mixing, favourable solute–solvent interactions) give a lower vapour pressure. All the curves approach linearity and coincide with the Raoult's law line as $x_A \rightarrow 1$ and the exponential function in eqn 72.17 approaches 1. When $x_A \ll 1$, eqn 72.17 approaches

$$p_A = x_A e^{\xi} p_A^* \tag{72.18}$$

This expression has the form of Henry's law once we identify K with $e^{\xi} p_A^*$, which is different for each solute–solvent system.

Brief illustration 72.4 The vapour pressure of a regular solution

The vapour pressure of benzene at 25 °C is 13.8 kPa. For a mixture of benzene and cyclohexane at that temperature we know from *Brief illustration* 72.2 that $\xi=1.13$. The value of Henry's law constant for benzene in this mixture is therefore predicted to be

$$K = e^{1.13} \times 13.8\ \text{kPa} = 42.7\ \text{kPa}$$

Self-test 72.5 Given that the vapour pressure of pure A in the mixture treated in Self-test 72.3 is 22.0 kPa, what is the value of its Henry's law constant?

Answer: 10.1 kPa

72.3 Model systems: ionic solutions

Solutions of ionic compounds are central to much of chemistry and we need to be able to discuss them thermodynamically. However, the Coulombic interactions between ions are so strong that the approximation of replacing activities by mole fractions or molalities is valid only in very dilute solutions (less than 10^{-3} mol kg^{-1} in total ion concentration), and in precise work activities themselves must be used. We need, therefore, to pay special attention to the activities of ions in solution, especially in preparation for the discussion of electrochemical phenomena.

(a) The mean activity coefficient

If the chemical potential of a univalent cation M^+ is denoted μ_+ and that of a univalent anion X^- is denoted μ_-, the total molar Gibbs energy of the ions in the electrically neutral solution is the sum of these two quantities. The molar Gibbs energy of an *ideal* solution is

$$G_m^{\text{ideal}} = \mu_+^{\text{ideal}} + \mu_-^{\text{ideal}} \tag{72.19a}$$

However, for a *real* solution of M^+ and X^- of the same molality,

$$\begin{aligned} G_m &= \mu_+ + \mu_- = \mu_+^{\text{ideal}} + \mu_-^{\text{ideal}} + RT\ln\gamma_+ + RT\ln\gamma_- \\ &= G_m^{\text{ideal}} + RT\ln\gamma_+\gamma_- \end{aligned} \tag{72.19b}$$

All the deviations from ideality are contained in the last term.

There is no experimental way of separating the product $\gamma_+\gamma_-$ into contributions from the cations and the anions. The best we can do experimentally is to assign responsibility for the nonideality equally to both kinds of ion. Therefore, for an electrolyte of the form MX we introduce the **mean activity coefficient** as the geometric mean of the individual coefficients (the geometric mean of x^p and y^q is $(x^p y^q)^{1/(p+q)}$):

$$\gamma_\pm = (\gamma_+\gamma_-)^{1/2} \tag{72.20}$$

Definition; 1:1 electrolyte Mean activity coefficient

and express the individual chemical potentials of the ions as

$$\mu_+ = \mu_+^{\text{ideal}} + RT\ln\gamma_\pm \qquad \mu_- = \mu_-^{\text{ideal}} + RT\ln\gamma_\pm \tag{72.21}$$

The sum of these two chemical potentials is the same as before, eqn 72.19b, but now the non-ideality is shared equally.

We can generalize this approach to the case of a compound M_pX_q that dissolves to give a solution of p cations and q anions from each formula unit. The molar Gibbs energy of the ions is the sum of their partial molar Gibbs energies:

$$G_m = p\mu_+ + q\mu_- = G_m^{\text{ideal}} + pRT\ln\gamma_+ + qRT\ln\gamma_- \tag{72.22}$$

If we introduce the mean activity coefficient

$$\gamma_\pm = (\gamma_+^p\gamma_-^q)^{1/s} \quad s=p+q \qquad \textit{Definition; } M_pX_q \textit{ electrolyte} \quad \text{Mean activity coefficient} \qquad (72.23)$$

and write the chemical potential of each ion as

$$\mu_i = \mu_i^{\text{ideal}} + RT\ln\gamma_\pm \qquad \text{Mean ionic chemical potential} \qquad (72.24)$$

we get the same expression as in eqn 72.22 for G_m when we write

$$G_m = p\mu_+ + q\mu_- \qquad (72.25)$$

However, both types of ion now share equal responsibility for the non-ideality.

Brief illustration 72.5 The mean activity coefficient

In a certain solution of $CaCl_2$ the activity coefficients of the Ca^{2+} and Cl^- ions were calculated as 0.874 and 0.981, respectively. For this solute, $p=1$, $q=2$, and $s=3$. The mean activity coefficient for the solute is therefore

$$\gamma_\pm = \{(0.874)(0.981)^2\}^{1/3} = 0.944$$

Self-test 72.6 In a solution of a salt that dissolved as the ions A^{2+} and B^{3-} the activity coefficients were 0.872 and 0.789, respectively. What is the mean activity coefficient of the solute?

Answer: 0.838

(b) The Debye–Hückel theory

The long range and strength of the Coulombic interaction between ions means that it is likely to be primarily responsible for the departures from ideality in ionic solutions and to dominate all the other contributions to non-ideality. This domination is the basis of the **Debye–Hückel theory** of ionic solutions, which was devised by Peter Debye and Erich Hückel in 1923. We give here a qualitative account of the theory and its principal quantitative conclusions.[1]

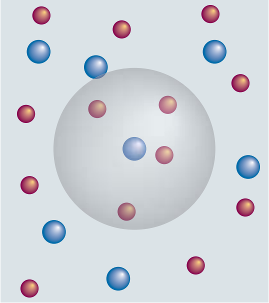

Figure 72.7 The picture underlying the Debye–Hückel theory is of a tendency for anions to be found around cations, and of cations to be found around anions (one such local clustering region is shown by the grey sphere). The ions are in ceaseless motion, and the diagram represents a snapshot of their motion. The solutions to which the theory applies are far less concentrated than shown here.

Oppositely charged ions attract one another. As a result, anions are more likely to be found near cations in solution, and vice versa (Fig. 72.7). Overall the solution is electrically neutral, but near any given ion there is an excess of counter-ions (ions of opposite charge). Averaged over time, counter-ions are more likely to be found near any given ion. This time-averaged, spherical haze around the central ion, in which counter-ions outnumber ions of the same charge as the central ion, has a net charge equal in magnitude but opposite in sign to that on the central ion, and is called its **ionic atmosphere**. The energy, and therefore the chemical potential, of any given central ion is lowered as a result of its electrostatic interaction with its ionic atmosphere. This lowering of energy appears as the difference between the molar Gibbs energy G_m and the ideal value G_m^{ideal} of the solute, and hence can be identified with $RT \ln \gamma_\pm$. (That the Gibbs energy is involved rather than the internal energy is clarified in the formal derivation of the theory, where we see that we need to consider the electrical work of charging the ion: as shown in Topic 64, non-expansion work is equal to the change in Gibbs energy.) The stabilization of ions by their interaction with their ionic atmospheres is part of the explanation for why chemists commonly use dilute solutions, in which the stabilization is less important, to achieve precipitation of ions from electrolyte solutions.

The model leads to the result that at very low concentrations the activity coefficient can be calculated from the **Debye–Hückel limiting law**:

$$\log\gamma_\pm = -|z_+z_-|AI^{1/2} \qquad \text{Debye–Hückel limiting law} \qquad (72.26)$$

where $A=0.509$ for an aqueous solution at 25 °C and I is the dimensionless **ionic strength** of the solution:

$$I = \frac{1}{2}\sum_i z_i^2 b_i/b^\ominus \qquad \textit{Definition} \quad \text{Ionic strength} \qquad (72.27)$$

In this expression z_i is the charge number of an ion i (positive for cations and negative for anions) and b_i is its molality, with $b^\ominus = 1\ \text{mol kg}^{-1}$. The ionic strength occurs widely wherever ionic solutions are discussed, as we shall see. The sum extends over all the ions present in the solution. For solutions consisting of two types of ion at molalities b_+ and b_-,

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[1] For details of the calculation, see our other *Physical chemistry* (2014).

Table 72.2 Ionic strength and molality, $I = kb/b^{\ominus}$

k	X^-	X^{2-}	X^{3-}	X^{4-}
M^+	1	3	6	10
M^{2+}	3	4	15	12
M^{3+}	6	15	9	42
M^{4+}	10	12	42	16

For example, the ionic strength of an M_2X_3 solution of molality b, which is understood to give M^{3+} and X^{2-} ions in solution, is $15b/b^{\ominus}$.

$$I = \tfrac{1}{2}(b_+z_+^2 + b_-z_-^2)/b^{\ominus} \qquad (72.28)$$

The ionic strength emphasizes the charges of the ions because the charge numbers occur as their squares. Table 72.2 summarizes the relation of ionic strength and molality in an easily usable form.

Brief illustration 72.6 The ionic strength

The mean activity coefficient of 5.0 mmol kg⁻¹ KCl(aq) at 25 °C is calculated by writing

$$I = \tfrac{1}{2}(b_+ + b_-)/b^{\ominus} = b/b^{\ominus}$$

where b is the molality of the solution (and $b_+ = b_- = b$). Then, from eqn 72.26,

$$\log \gamma_\pm = -0.509 \times (5.0 \times 10^{-3})^{1/2} = -0.036$$

Hence, $\gamma_\pm = 0.92$. The experimental value is 0.927.

Self-test 72.7 Calculate the ionic strength and the mean activity coefficient of 1.00 mmol kg⁻¹ $CaCl_2$(aq) at 25 °C.

Answer: 3.00×10^{-3}, 0.880

The name 'limiting law' is applied to eqn 72.26 because ionic solutions of moderate molalities may have activity coefficients that differ from the values given by this expression, yet all solutions are expected to conform as $b \to 0$. Table 72.3 lists some experimental values of activity coefficients for salts of various valence types. Figure 72.8 shows some of these values plotted against $I^{1/2}$, and compares them with the theoretical straight lines calculated from the limiting law. The agreement at very low molalities (less than about 1 mmol kg⁻¹, depending on charge type) is impressive, and convincing evidence in support of the model. Nevertheless, the departures from the theoretical curves above these molalities are large, and show that the approximations are valid only at very low concentrations.

Table 72.3 Mean activity coefficients in water at 298 K

$b/b^{\ominus}$	KCl	$CaCl_2$
0.001	0.966	0.888
0.01	0.902	0.732
0.1	0.770	0.524
1.0	0.607	0.725

* More values are given in the *Resource section*.

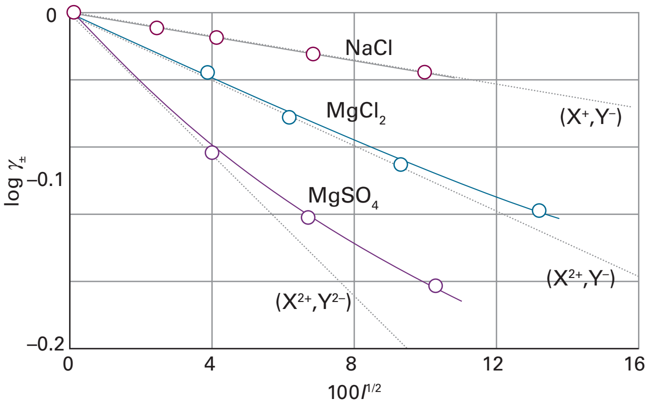

Figure 72.8 An experimental test of the Debye–Hückel limiting law. Although there are marked deviations for moderate ionic strengths, the limiting slopes as $I \to 0$ are in good agreement with the theory, so the law can be used for extrapolating data to very low molalities.

When the ionic strength of the solution is too high for the limiting law to be valid, the activity coefficient may be estimated from the **Davies equation**:

$$\log \gamma_\pm = -\frac{A|z_+z_-|I^{1/2}}{1 + BI^{1/2}} + CI \qquad \text{Davies equation} \qquad (72.29)$$

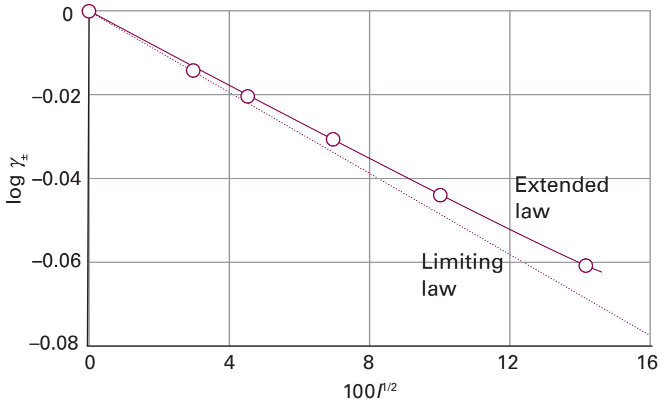

Figure 72.9 The extended Debye–Hückel law gives agreement with experiment (as indicated by the circles) over a wider range of molalities (as shown here for an MX electrolyte, such as NaCl), but it fails at higher molalities.

where *A*, *B*, and *C* are dimensionless constants. The same expression but without the term *CI* is called the **extended Debye–Hückel law**. Although *B* can be interpreted as a measure of the closest approach of the ions, it (like *C*) is best regarded as an adjustable empirical parameter. A curve drawn in this way is shown in Fig. 72.9. It is clear that eqn 72.29 accounts for some activity coefficients over a moderate range of dilute solutions (up to about 0.1 mol kg^{-1}); nevertheless it remains very poor near 1 mol kg^{-1}.

Current theories of activity coefficients for ionic solutes take an indirect route. They set up a theory for the dependence of the activity coefficient of the solvent on the concentration of the solute, and then use the Gibbs–Duhem equation (eqn 69.9 of Topic 69, $\sum_J n_J \mathrm{d}\mu_J = 0$) to estimate the activity coefficient of the solute. The results are reasonably reliable for solutions with molalities greater than about 0.1 mol kg^{-1} and are valuable for the discussion of mixed salt solutions, such as sea-water.

Checklist of concepts

☐ 1. An **activity** is the effective mole fraction of a species.

☐ 2. **Activity coefficients** are based on Raoult's law for the solvent and on Henry's law for the solute.

☐ 3. Activity coefficients approach 1 as $x_{\text{solute}} \rightarrow 0$ and as $x_{\text{solvent}} \rightarrow 1$.

☐ 4. An **excess function** (X^{E}) is the difference between the observed thermodynamic function of mixing and the function for an ideal solution.

☐ 5. A **regular solution** is a solution for which $H^{\mathrm{E}} \neq 0$ but $S^{\mathrm{E}} = 0$.

☐ 6. The **mean activity coefficient** is the geometric mean of the individual coefficients.

☐ 7. The **Debye–Hückel theory** of activity coefficients of electrolyte solutions is based on the assumption that Coulombic interactions between ions are dominant.

☐ 8. A key idea of the Debye–Hückel theory is that of an **ionic atmosphere**.

Checklist of equations

Property	Equation	Comment	Equation number
Solvent activity	$\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^{*} + RT \ln a_{\mathrm{A}}$		72.1
	$a_{\mathrm{A}} = p_{\mathrm{A}}/p_{\mathrm{A}}^{*}$	Practical determination	72.2
Solute activity	$\mu_{\mathrm{B}} = \mu_{\mathrm{B}}^{\ominus} + RT \ln a_{\mathrm{B}}$		72.8
	$a_{\mathrm{B}} = p_{\mathrm{B}}/K_{\mathrm{B}}$	Practical determination	72.9
Activity coefficient	$\gamma_{\mathrm{B}} = a_{\mathrm{B}}/x_{\mathrm{B}}$	Definition; see Table 72.1	72.10
Excess function	$X^{\mathrm{E}} = \Delta_{\mathrm{mix}}X - \Delta_{\mathrm{mix}}X^{\mathrm{ideal}}$	Definition	72.12
Model of regular solution	$H^{\mathrm{E}} = n\xi RTx_{\mathrm{A}}x_{\mathrm{B}}$	Model	72.13
Margules equations	$\ln \gamma_{\mathrm{A}} = \xi x_{\mathrm{B}}^2, \ \ln \gamma_{\mathrm{B}} = \xi x_{\mathrm{A}}^2$	Regular solution	72.15
Vapour pressure	$p_{\mathrm{A}} = \{\mathrm{e}^{\xi(1-x_{\mathrm{A}})^2} x_{\mathrm{A}}\} p_{\mathrm{A}}^{*}$	Regular solution	72.17
Mean activity coefficient	$\gamma_{\pm} = (\gamma_{+}{}^{p}\gamma_{-}{}^{q})^{1/(p+q)}$	Salt of the form $\mathrm{M}_p\mathrm{X}_q$	72.23
Debye–Hückel law	$\log \gamma_{\pm} = -\lvert z_{+}z_{-}\rvert AI^{1/2}$	Limiting law, $A = 0.509$ for aqueous solution at 298 K	72.26
Ionic strength	$I = \frac{1}{2}\sum_i z_i^2 b_i/b^{\ominus}$	Dimensionless	72.27

Focus 14 on Physical equilibria

Topic 67 Phase diagrams: one-component systems

Discussion questions

67.1 Discuss what would be observed as a sample of water is taken along a path in its phase diagram that encircles and is close to its critical point.

67.2 Distinguish between a first-order phase transition, a second-order phase transition, and a λ-transition at both molecular and macroscopic levels.

67.3 Define and provide examples of the following terms: phase, constituent, component, and degree of freedom.

67.4 Explain why four phases cannot be in equilibrium in a one-component system.

Exercises

67.1(a) How many phases are present at the points marked *a* and *b* in Fig. F14.1?
67.1(b) How many phases are present at the points marked *c* and *d* in Fig. F14.1?

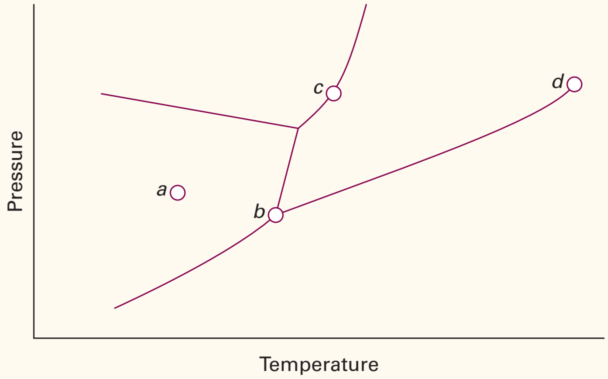

Figure F14.1 The phase diagram referred to in Exercises 67.1(a) and (b).

Problem

67.1 In a theoretical study of a protein, the temperature–composition diagram shown in Fig. F14.2 was obtained. It shows three structural regions: the native form, the unfolded form, and a 'molten globule' form, a partially unfolded but still compact form of the protein. (i) Is the molten globule form ever stable when the denaturant concentration is below 0.1? (ii) Describe what happens to the polymer as the native form is heated in the presence of denaturant at concentration 0.15.

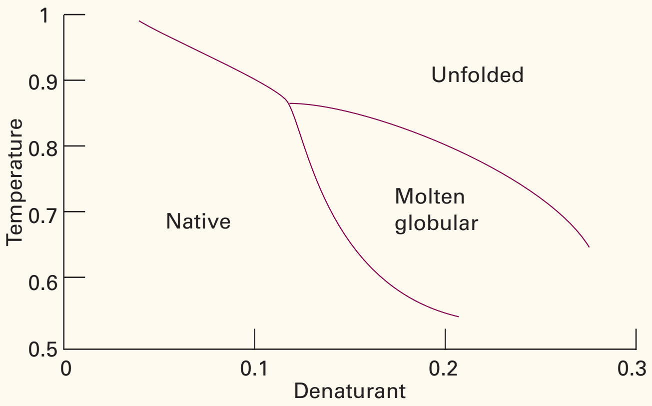

Figure F14.2 The phase diagram for the conformations of a model protein.

For more problems relating to one-component phase diagrams, see the Integrated activities section of this collection.

Topic 68 Phase diagrams: two-component systems

Discussion questions

68.1 What factors determine the number of theoretical plates required to achieve a desired degree of separation in fractional distillation?

68.2 What molecular features determine whether a mixture of two liquids will show high- and low-boiling azeotropic behaviour?

Exercises

68.1(a) Methyl ethyl ether (A) and diborane, B_2H_6 (B), form a compound which melts congruently at 133 K. The system exhibits two eutectics, one at 25 mol per cent B and 123 K and a second at 90 mol per cent B and 104 K. The melting points of pure A and B are 131 K and 110 K, respectively. Sketch the phase diagram for this system. Assume negligible solid–solid solubility.

68.1(b) Sketch the phase diagram of the system NH_3/N_2H_4 given that the two substances do not form a compound with each other, that NH_3 freezes at −78 °C and N_2H_4 freezes at +2 °C, and that a eutectic is formed when the mole fraction of N_2H_4 is 0.07 and that the eutectic melts at −80 °C.

68.2(a) Figure F14.3 shows the phase diagram for water (A) and 2-methyl-1-propanol (B). Describe what will be observed when a mixture of composition $x_B = 0.8$ is heated, at each stage giving the number, composition, and relative amounts of the phases present.

68.2(b) Refer to Fig. F14.3 again. Describe what will be observed when a mixture of composition $x_B = 0.3$ is heated, at each stage giving the number, composition, and relative amounts of the phases present.

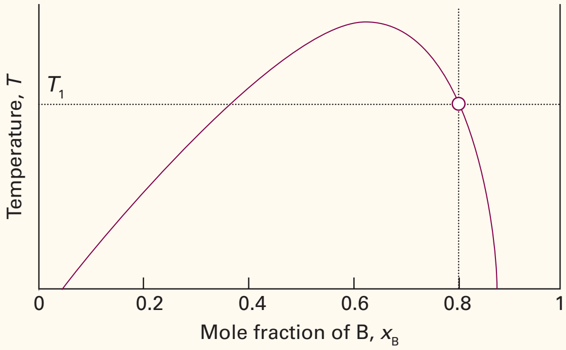

Figure F14.3 The phase diagram for two partially miscible liquids.

Problems

68.1 The following temperature–composition data were obtained for a mixture of octane (O) and methylbenzene (M) at 1.00 atm, where x is the mole fraction in the liquid and y the mole fraction in the vapour at equilibrium.

θ/°C	110.9	112.0	114.0	115.8	117.3	119.0	121.1	123.0
x_M	0.908	0.795	0.615	0.527	0.408	0.300	0.203	0.097
y_M	0.923	0.836	0.698	0.624	0.527	0.410	0.297	0.164

The boiling points are 110.6 °C and 125.6 °C for M and O, respectively. Plot the temperature–composition diagram for the mixture. What is the composition of the vapour in equilibrium with the liquid of composition (a) $x_M = 0.250$ and (b) $x_O = 0.250$?

68.2 Figure F14.4 shows the experimentally determined phase diagrams for the nearly ideal solution of hexane and heptane. (a) Label the regions of the diagrams to which phases are present. (b) For an equimolar mixture of C_6H_{14} and C_7H_{16}, estimate the vapour pressure at 70 °C when vaporization on reduction of the external pressure just begins. (c) What is the vapour pressure of the solution at 70 °C when just one drop of liquid remains? (d) Estimate from the figures the mole fraction of hexane in the liquid and vapour phases for the conditions of part b. (e) What are the mole fractions for the conditions of part (c)?

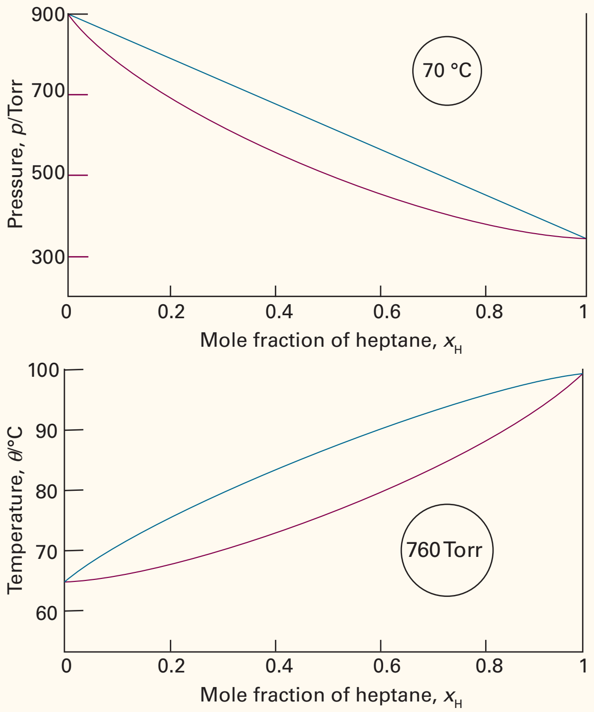

Figure F14.4 The phase diagram for a mixture of hexane and heptane.

68.3 Uranium tetrafluoride and zirconium tetrafluoride melt at 1035 °C and 912 °C respectively. They form a continuous series of solid solutions with a minimum melting temperature of 765 °C and composition $x(ZrF_4) = 0.77$. At 900 °C, the liquid solution of composition $x(ZrF_4) = 0.28$ is in equilibrium with a solid solution of composition $x(ZrF_4) = 0.14$. At 850 °C the two compositions are 0.87 and 0.90, respectively. Sketch the phase diagram for this system and state what is observed when a liquid of composition $x(ZrF_4) = 0.40$ is cooled slowly from 900 °C to 500 °C.

68.4 Hexane and perfluorohexane show partial miscibility below 22.7 °C. The concentration at the upper critical temperature is $x = 0.355$, where x is the mole fraction of C_6F_{14}. At 22.0 °C the two solutions in equilibrium have $x = 0.24$ and $x = 0.48$, respectively, and at 21.5 °C the mole fractions are 0.22 and 0.51. Sketch the phase diagram. Describe the phase changes that occur when perfluorohexane is added to a fixed amount of hexane at (a) 23 °C, (b) 22 °C.

68.5 Methane (melting point 91 K) and tetrafluoromethane (melting point 89 K) do not form solid solutions with each other, and as liquids they are only partially miscible. The upper critical temperature of the liquid mixture is 94 K at $x(CF_4) = 0.43$ and the eutectic temperature is 84 K at $x(CF_4) = 0.88$. At 86 K, the phase in equilibrium with the tetrafluoromethane-rich solution changes from solid methane to a methane-rich liquid. At that temperature, the two liquid solutions that are in mutual equilibrium have the compositions $x(CF_4) = 0.10$ and $x(CF_4) = 0.80$. Sketch the phase diagram.

68.6 Magnesium oxide and nickel oxide withstand high temperatures. However, they do melt when the temperature is high enough and the behaviour of mixtures of the two is of considerable interest to the ceramics industry. Draw the temperature–composition diagram for the system using the data below, where x is the mole fraction of MgO in the solid and y its mole fraction in the liquid.

$\theta/°C$	1960	2200	2400	2600	2800
x	0	0.35	0.60	0.83	1.00
y	0	0.18	0.38	0.65	1.00

State (a) the melting point of a mixture with $x = 0.30$, (b) the composition and proportion of the phases present when a solid of composition $x = 0.30$ is heated to 2200 °C, (c) the temperature at which a liquid of composition $y = 0.70$ will begin to solidify.

Topic 69 Physical transformations

Discussion questions

69.1 Consider the variation of the melting point with pressure observed for water and carbon dioxide. Provide a molecular explanation for differences in behaviour of these two substances.

69.2 Discuss the scope and applicability of the fundamental equation of chemical thermodynamics.

69.3 Compare the dependence of the chemical potential on temperature for a solid, liquid, and gas. How are these dependencies reflected in the phase diagram?

69.4 Interpret the forms of the Clapeyron and Clausius–Clapeyron equations, paying particular attention to the appearance in them of parameters such as the enthalpy of transition and the temperature.

69.5 Why does the chemical potential of a substance depend on the pressure even if the substance is incompressible?

Exercises

69.1(a) The solid and liquid phases of a mixture of water (W) and ethanol (E) are in equilibrium. What are the relationships between the magnitudes of $\mu_W(s)$, $\mu_W(l)$, $\mu_E(s)$, and $\mu_E(l)$?
69.1(b) The liquid and vapour phases of a mixture of benzene (B) and methylbenzene (M) are in equilibrium. What are the relationships between the magnitudes of $\mu_B(l)$, $\mu_B(g)$, $\mu_M(l)$, and $\mu_M(g)$?

69.2(a) A mixture of water and ethanol is prepared with a mole fraction of water of 0.60. If a small change in the mixture composition results in an increase in the chemical potential of water by $0.25\,J\,mol^{-1}$, by how much will the chemical potential of ethanol change?
69.2(b) A mixture of water and ethanol is prepared with a mole fraction of water of 0.40. If a small change in the mixture composition results in an increase in the chemical potential of ethanol by $0.35\,J\,mol^{-1}$, by how much will the chemical potential of water change?

69.3(a) By how much does the chemical potential of pure water change when the temperature of a sample is increased from 20 °C to 25 °C?
69.3(b) By how much does the chemical potential of pure octane change when the temperature of a sample is increased from 20 °C to 25 °C?

69.4(a) By how much does the chemical potential of pure water increase when the pressure on a sample is increased from 1.0 bar to 100 kbar? The mass density of water at 20 °C is $0.997\,g\,cm^{-3}$.
69.4(b) By how much does the chemical potential of pure octane increase when the pressure on a sample is increased from 1.0 bar to 100 kbar? The mass density of octane at 20 °C is $0.703\,g\,cm^{-3}$.

69.5(a) The molar volume of a certain solid is $161.0\,cm^3\,mol^{-1}$ at 1.00 atm and 350.75 K, its melting temperature. The molar volume of the liquid at this temperature and pressure is $163.3\,cm^3\,mol^{-1}$. At 100 atm the melting temperature changes to 351.26 K. Calculate the enthalpy and entropy of fusion of the solid.
69.5(b) The molar volume of a certain solid is $142.0\,cm^3\,mol^{-1}$ at 1.00 atm and 427.15 K, its melting temperature. The molar volume of the liquid at this temperature and pressure is $152.6\,cm^3\,mol^{-1}$. At 1.2 MPa the melting temperature changes to 429.26 K. Calculate the enthalpy and entropy of fusion of the solid.

69.6(a) The vapour pressure of a liquid in the temperature range 200 K to 260 K was found to fit the expression $\ln(p/\text{Torr}) = 19.176 - 1501.8/(T/\text{K})$. Calculate the enthalpy of vaporization of the liquid.

69.6(b) The vapour pressure of a liquid in the temperature range 200 K to 260 K was found to fit the expression $\ln(p/\text{Torr}) = 17.461 - 2100.8/(T/\text{K})$. Calculate the enthalpy of vaporization of the liquid.

69.7(a) When benzene freezes at 5.5 °C (the normal freezing point) its density changes from 0.879 g cm^{-3} to 0.891 g cm^{-3}. Its enthalpy of fusion is 10.59 kJ mol^{-1}. Estimate the freezing point of benzene at 10.0 kbar.

69.7(b) When a certain liquid freezes at −3.65 °C (the normal freezing point) its density changes from 0.790 g cm^{-3} to 0.799 g cm^{-3}. Its enthalpy of fusion is 6.68 kJ mol^{-1}. Estimate the freezing point of the liquid at 100 MPa.

69.8(a) The normal boiling point of carbon tetrachloride is 76.8 °C. Estimate (a) its enthalpy of vaporization and (b) its vapour pressure at 25 °C and 70 °C.

69.8(b) The normal boiling point of hexane is 69.0 °C. Estimate (a) its enthalpy of vaporization and (b) its vapour pressure at 25 °C and 60 °C.

69.9(a) Calculate the melting point of ice under a pressure of 50 bar. Assume that the density of ice under these conditions is approximately 0.92 g cm^{-3} and that of liquid water is 1.00 g cm^{-3}.

69.9(b) Calculate the melting point of ice under a pressure of 10 MPa. Assume that the density of ice under these conditions is approximately 0.915 g cm^{-3} and that of liquid water is 0.998 g cm^{-3}.

Problems

69.1 The temperature dependence of the vapour pressure of solid sulfur dioxide can be approximately represented by the relation $\log(p/\text{Torr}) = 10.5916 - 1871.2/(T/\text{K})$ and that of liquid sulfur dioxide by $\log(p/\text{Torr}) = 8.3186 - 1425.7/(T/\text{K})$. Estimate the temperature and pressure of the triple point of sulfur dioxide.

69.2 The enthalpy of vaporization of a certain liquid is found to be 22.0 kJ mol^{-1} at 380 K, its normal boiling point. The molar volumes of the liquid and the vapour at the boiling point are 120 cm^3 mol^{-1} and 14.5 dm^3 mol^{-1}, respectively. (a) Estimate $\mathrm{d}p/\mathrm{d}T$ from the Clapeyron equation and (b) the percentage error in its value if the Clausius–Clapeyron equation is used instead.

69.3 The enthalpy of fusion of mercury is 2.292 kJ mol^{-1}, and its normal freezing point is 234.3 K with a change in molar volume of +0.517 cm^3 mol^{-1} on melting. At what temperature will the bottom of a column of mercury (density 13.6 g cm^{-3}) of height 10.0 m be expected to freeze?

69.4 The vapour pressure, p, of naphthalene varies with temperature as follows:

T/K	250	270	280	290	300	310	330
p/kPa	0.036	0.514	1.662	4.918	13.43	34.1	182.9

What are (a) the normal boiling point and (b) the enthalpy of vaporization of naphthalene?

69.5 Construct the phase diagram for benzene near its triple point at 36 Torr and 5.50 °C using the following data: $\Delta_{\text{fus}}H = 10.6$ kJ mol^{-1}, $\Delta_{\text{vap}}H = 30.8$ kJ mol^{-1}, $\rho(\text{s}) = 0.891$ g cm^{-3}, $\rho(\text{l}) = 0.879$ g cm^{-3}.

69.6[‡] In an investigation of thermophysical properties of methylbenzene (R.D. Goodwin, *J. Phys. Chem. Ref. Data* **18**, 1565 (1989)), Goodwin presented expressions for two coexistence curves (phase boundaries). The solid–liquid coexistence curve is given by

$$p/\text{bar} = p_3/\text{bar} + 1000 \times (5.60 + 11.727x)x$$

where $x = T/T_3 - 1$ and the triple point pressure and temperature are $p_3 = 0.4362$ μbar and $T_3 = 178.15$ K. The liquid–vapour curve is given by

$$\ln(p/\text{bar}) = -10.418/y + 21.157 - 15.996y + 14.015y^2 - 5.0120y^3 + 4.7224(1-y)^{1.70}$$

where $y = T/T_c = T/(593.95\text{ K})$. (a) Plot the solid–liquid and liquid–vapour phase boundaries. (b) Estimate the standard melting point of methylbenzene. (c) Estimate the standard boiling point of methylbenzene. (d) Compute the standard enthalpy of vaporization of methylbenzene, given that the molar volumes of the liquid and vapour at the normal boiling point are 0.12 dm^3 mol^{-1} and 30.3 dm^3 mol^{-1}, respectively.

69.7 Show that two phases are in thermal equilibrium only if their temperatures are the same.

69.8 Show that two phases are in mechanical equilibrium only if their pressures are equal.

69.9 The change in enthalpy is given by $\mathrm{d}H = C_p\mathrm{d}T + V\mathrm{d}p$. The Clapeyron equation relates $\mathrm{d}p$ and $\mathrm{d}T$ at equilibrium, and so in combination the two equations can be used to find how the enthalpy changes along a phase boundary as the temperature changes and the two phases remain in equilibrium. Show that $\mathrm{d}(\Delta H/T) = \Delta C_p\,\mathrm{d}\ln T$.

69.10 Combine the barometric formula (Problem 51.7) for the dependence of the pressure on altitude with the Clausius–Clapeyron equation, and predict how the boiling temperature of a liquid depends on the altitude and the ambient temperature. Take the mean ambient temperature as 20 °C and predict the boiling temperature of water at 3000 m.

69.11 Figure 69.6 shows a schematic representation of how the chemical potentials of the solid, liquid, and gaseous phases of a substance vary with temperature. All have a negative slope, but it is unlikely that they are truly straight lines as indicated in the illustrations. Derive an expression for the curvatures (specifically, the second derivatives with respect to temperature) of these lines. Is there a restriction on the curvature of these lines? Which state of matter shows the greatest curvature?

69.12[‡] A substance as well known as methane still receives research attention because it is an important component of natural gas, a commonly used fossil fuel. Friend, et al. have published a review of thermophysical properties of methane (*J. Phys. Chem. Ref. Data* **18**, 583 (1989)), which included the following data describing the liquid–vapour phase boundary:

T/K	100	108	110	112	114	120	130	140	150	160	170	190
p/MPa	0.034	0.074	0.088	0.104	0.122	0.192	0.368	0.642	1.041	1.593	2.329	4.521

(a) Plot the liquid–vapour phase boundary. (b) Estimate the standard boiling point of methane. (c) Compute the standard enthalpy of vaporization of methane, given that the molar volumes of the liquid and vapour at the standard boiling point are 3.80 ×10^{-2} and 8.89 dm^3 mol^{-1}, respectively.

[‡] These problems were supplied by Charles Trapp and Carmen Giunta.

Topic 70 Ideal mixtures

Discussion questions

70.1 Describe the molecular basis of Raoult's law.

70.2 What is the difference between an ideal solution and an ideal–dilute solution?

Exercises

70.1(a) An open vessel containing (a) water (vapour pressure 3.2 kPa), (b) benzene (vapour pressure 13.1 kPa) stands in a laboratory measuring 4.0 m × 4.0 m × 3.0 m at 25 °C. What mass of each substance will be found in the air if there is no ventilation?

70.1(b) An open vessel containing mercury (vapour pressure 0.23 Pa) stands in a laboratory measuring 6.0 m × 5.0 m × 3.5 m at 25 °C. What mass of mercury will be found in the air if there is no ventilation?

70.2(a) Consider a container of volume 10.0 $\mathrm{dm^3}$ that is divided into two compartments of equal size. In the left compartment there is nitrogen at 1.5 bar and 25 °C; in the right compartment there is hydrogen at the same temperature and pressure. Calculate the entropy and Gibbs energy of mixing when the partition is removed. Assume that the gases are perfect.

70.2(b) Consider a container of volume 350 $\mathrm{cm^3}$ that is divided into two compartments of equal size. In the left compartment there is argon at 150 kPa and 0 °C; in the right compartment there is neon at the same temperature and pressure. Calculate the entropy and Gibbs energy of mixing when the partition is removed. Assume that the gases are perfect.

70.3(a) Air is approximately 76 per cent N_2, 23 per cent O_2, and 1 per cent Ar by mass. Calculate the entropy, enthalpy, and Gibbs energy of mixing when it is prepared from the pure (and perfect) gases.

70.3(b) Calculate the Gibbs energy, entropy, and enthalpy of mixing when 25 g of hexane is mixed with 25 g of heptane at 298 K; treat the solution as ideal.

70.4(a) What proportions of hexane and heptane should be mixed (a) by mole fraction, (b) by mass in order to achieve the greatest entropy of mixing?

70.4(b) What proportions of benzene and ethylbenzene should be mixed (a) by mole fraction, (b) by mass in order to achieve the greatest entropy of mixing?

70.5(a) At 300 K, the partial vapour pressures of HCl (that is, the partial pressure of the HCl vapour) in liquid $\mathrm{GeCl_4}$ are as follows:

x_{HCl}	0.005	0.012	0.019
$p_{\mathrm{HCl}}/\mathrm{kPa}$	32.0	76.9	121.8

Show that the solution obeys Henry's law in this range of mole fractions, and calculate the Henry's law constant at 300 K.

70.5(b) At 310 K, the partial vapour pressures of a substance B dissolved in a liquid A are as follows:

x_{B}	0.010	0.015	0.020
$p_{\mathrm{B}}/\mathrm{kPa}$	82.0	122.0	166.1

Show that the solution obeys Henry's law in this range of mole fractions, and calculate the Henry's law constant at 310 K.

70.6(a) The vapour pressure of pure liquid A at 300 K is 76.7 kPa and that of pure liquid B is 52.0 kPa. These two compounds form ideal liquid and gaseous mixtures. Consider the equilibrium composition of a mixture in which the mole fraction of A in the vapour is 0.350. Calculate the total pressure of the vapour and the composition of the liquid mixture.

70.6(b) The vapour pressure of pure liquid A at 293 K is 68.8 kPa and that of pure liquid B is 82.1 kPa. These two compounds form ideal liquid and gaseous mixtures. Consider the equilibrium composition of a mixture in which the mole fraction of A in the vapour is 0.612. Calculate the total pressure of the vapour and the composition of the liquid mixture.

70.7(a) Predict the partial vapour pressure of HCl above its solution in liquid germanium tetrachloride of molality 0.15 $\mathrm{mol\,kg^{-1}}$. For data, see Exercise 70.5(a).

70.7(b) Predict the partial vapour pressure of the component B above its solution in A in Exercise 70.5(b) when the molality of B is 0.15 $\mathrm{mol\,kg^{-1}}$.

70.8(a) The vapour pressure of benzene is 53.3 kPa at 60.6 °C, but it fell to 51.5 kPa when 19.0 g of an non-volatile organic compound was dissolved in 500 g of benzene. Calculate the molar mass of the compound.

70.8(b) The vapour pressure of 2-propanol is 50.00 kPa at 338.8 °C, but it fell to 49.62 kPa when 8.69 g of an non-volatile organic compound was dissolved in 250 g of 2-propanol. Calculate the molar mass of the compound.

70.9(a) Use Henry's law and the data in Table 70.1 to calculate the solubility (as a molality) of CO_2 in water at 25 °C when its partial pressure is (a) 0.10 atm, (b) 1.00 atm.

70.9(b) The mole fractions of N_2 and O_2 in air at sea level are approximately 0.78 and 0.21. Calculate the molalities of the solution formed in an open flask of water at 25 °C.

Problems

70.1 The following table gives the mole fraction of methylbenzene (A) in liquid and gaseous mixtures with butanone at equilibrium at 303.15 K and the total pressure p. Take the vapour to be perfect and calculate the partial pressures of the two components. Plot them against their respective mole fractions in the liquid mixture and find the Henry's law constants for the two components.

x_{A}	0	0.0898	0.2476	0.3577	0.5194	0.6036	0.7188	0.8019	0.9105	1
y_{A}	0	0.0410	0.1154	0.1762	0.2772	0.3393	0.4450	0.5435	0.7284	1
p/kPa	36.066	34.121	30.900	28.626	25.239	23.402	20.6984	18.592	15.496	12.295

70.2 For the calculation of the solubility c of a gas in a solvent, it is often convenient to use the expression $c = Kp$, where K is the Henry's law constant. Breathing air at high pressures, such as in scuba diving, results in an increased concentration of dissolved nitrogen. The Henry's law constant for the solubility of nitrogen is $0.18\,\mu g/(g\ H_2O\ atm)$. What mass of nitrogen is dissolved in 100 g of water saturated with air at 4.0 atm and 20 °C? Compare your answer to that for 100 g of water saturated with air at 1.0 atm. (Air is 78.08 mole per cent N_2.) If nitrogen is four times as soluble in fatty tissues as in water, what is the increase in nitrogen concentration in fatty tissue in going from 1 atm to 4 atm?

Topic 71 Colligative properties

Discussion question

71.1 Explain the origin of colligative properties in both thermodynamic and molecular terms.

Exercises

71.1(a) The osmotic pressures of solutions of polystyrene in toluene were measured at 25 °C and the pressure was expressed in terms of the height of the solvent of density $1.004\ g\ cm^{-3}$:

$c/(g\ dm^{-3})$	2.042	6.613	9.521	12.602
h/cm	0.592	1.910	2.750	3.600

Calculate the molar mass of the polymer.

71.1(b) The molar mass of an enzyme was determined by dissolving it in water, measuring the osmotic pressure at 20 °C, and extrapolating the data to zero concentration. The following data were obtained:

$c/(mg\ cm^{-3})$	3.221	4.618	5.112	6.722
h/cm	5.746	8.238	9.119	11.990

Calculate the molar mass of the enzyme.

71.2(a) A sample consists of 30 per cent by mass of a dimer with $M = 30\ kg\ mol^{-1}$ and its monomer. What are the values of the number-average and weight-average molar masses?What is the value of the heterogeneity index?

71.2(b) A sample consists of 25 per cent by mass of a trimer with $M = 22\ kg\ mol^{-1}$ and its monomer. What are the values of the number-average and weight-average molar masses?What is the value of the heterogeneity index?

Problems

71.1‡ Sato, et al. (*J. Polym. Sci., Polym. Phys.* **14**, 619 (1976)) have reported the data in the table below for the osmotic pressures of polychloroprene ($\rho = 1.25\ g\ cm^{-3}$) in toluene ($\rho = 0.858\ g\ cm^{-3}$) at 30 °C. Determine the molar mass of polychloroprene and its second osmotic virial coefficient.

$c/(mg\ cm^{-3})$	1.33	2.10	4.52	7.18	9.87
$\Pi/(N\ m^{-2})$	30	51	132	246	390

71.2 Deduce an expression for the depression of freezing point of an ideal solution and show, subject to a series of approximations that you should specify, that the depression is proportional to the mole fraction of the solute, $\Delta T = K_f x_B$, with $K_f = RT_f^{*}/\Delta_{fus}H$, where T_f^{*} is the freezing temperature of the pure solvent and $\Delta_{fus}H$ its enthalpy of fusion. *Hint*: At the freezing temperature of the solvent, the chemical potential of the liquid solvent is equal to that of the solid solvent.

71.3 Repeat the preceding problem for the elevation of boiling point of a solvent in a solution.

71.4‡ Polymer scientists often report their data in rather strange units. For example, in the determination of molar masses of polymers in solution by osmometry, osmotic pressures are often reported in grams per square centimetre ($g\ cm^{-2}$) and concentrations in grams per cubic centimetre ($g\ cm^{-3}$). (a) With these choices of units, what would be the units of R in the van 't Hoff equation? (b) The data in the table below on the concentration dependence of the osmotic pressure of polyisobutene in chlorobenzene at 25 °C have been adapted from J. Leonard and H. Daoust (*J. Polym. Sci.* **57**, 53 (1962)). From these data, determine the molar mass of polyisobutene by plotting Π/c against c. (c) Theta solvents are solvents for which the second osmotic coefficient is zero; for 'poor' solvents the plot is linear and for good solvents the plot is nonlinear. From your plot, how would you classify chlorobenzene as a solvent for polyisobutene? Rationalize the result in terms of the molecular structure of the polymer and solvent. (d) Determine the second and third osmotic virial coefficients by fitting the curve to the virial form of the osmotic pressure equation. (e) Experimentally, it is often found that the virial expansion can be represented as

$$\Pi/c = RT/M(1 + B'c + gB'^2c'^2 + \cdots)$$

and in good solvents, the parameter g is often about 0.25. With terms beyond the second power ignored, obtain an equation for $(\Pi/c)^{1/2}$ and plot this quantity against c. Determine the second and third virial coefficients from the plot and compare to the values from the first plot. Does this plot confirm the assumed value of g?

$10^{-2}(\Pi/c)/(g\ cm^{-2}/g\ cm^{-3})$	2.6	2.9	3.6	4.3	6.0	12.0
$c/(g\ cm^{-3})$	0.0050	0.010	0.020	0.033	0.057	0.10

$10^{-2}(\Pi/c)/(g\ cm^{-2}/g\ cm^{-3})$	19.0	31.0	38.0	52	63
$c/(g\ cm^{-3})$	0.145	0.195	0.245	0.27	0.29

Topic 72 Real solutions

Discussion questions

72.1 Explain what is meant by a regular solution. Discuss how the magnitude and sign of the parameter ξ captures various features of real solutions.

72.2 Describe the general features of the Debye–Hückel theory of electrolyte solutions. Why is it only a limiting law?

Exercises

72.1(a) The maximum value of the excess enthalpy of mixing of a mixture at 40 °C is 1.8 kJ mol^{-1}. Identify the value of the parameter ξ in the expression that is used to model a regular solution. Can you expect phase separation?

72.1(b) The maximum value of the excess enthalpy of mixing of a mixture at 25 °C is 1.4 kJ mol^{-1}. Identify the value of the parameter ξ in the expression that is used to model a regular solution. Can you expect phase separation?

72.2(a) Substances A and B are both volatile liquids with $p_A^* = 300$ Torr, $p_B^* = 250$ Torr, and $K_B = 200$ Torr (concentration expressed in mole fraction). When $x_A = 0.9$ and $b_B = 2.22$ mol kg^{-1}, then $p_A = 250$ Torr and $p_B = 25$ Torr. Calculate the activities and activity coefficients of A and B. Use the mole fraction, Raoult's law basis system for A and the Henry's law basis system (both mole fractions and molalities) for B.

72.2(b) Given that $p^*(H_2O) = 0.02308$ atm and $p(H_2O) = 0.02239$ atm in a solution in which 0.122 kg of a non-volatile solute ($M = 241$ g mol^{-1}) is dissolved in 0.920 kg water at 293 K, calculate the activity and activity coefficient of water in the solution.

72.3(a) By measuring the equilibrium between liquid and vapour phases of an acetone (A)/methanol (M) solution at 57.2 °C at 1.00 atm, it was found that $x_A = 0.400$ (in liquid) when $y_A = 0.516$ (in vapour). Calculate the activities and activity coefficients of both components in this solution on the Raoult's law basis. The vapour pressures of the pure components at this temperature are: $p_A^* = 105$ kPa and $p_M^* = 73.5$ kPa.

72.3(b) By measuring the equilibrium between liquid and vapour phases of a solution at 30 °C at 1.00 atm, it was found that $x_A = 0.220$ (in liquid) when $y_A = 0.314$ (in vapour). Calculate the activities and activity coefficients of both components in this solution on the Raoult's law basis. The vapour pressures of the pure components at this temperature are: $p_A^* = 73.0$ kPa and $p_B^* = 92.1$ kPa.

72.4(a) The maximum value of the excess enthalpy of mixing of two liquids that form a regular solution at 20 °C is 800 J mol^{-1}. What are the activities of the components at that composition?

72.4(b) The maximum value of the excess enthalpy of mixing of two liquids that form a regular solution at 30 °C is 1.4 kJ mol^{-1}. What are the activities of the components at that composition?

72.5(a) Calculate the ionic strength of a solution that is 0.15 mol kg^{-1} in KCl(aq) and 0.35 mol kg^{-1} in $CuSO_4$(aq).

72.5(b) Calculate the ionic strength of a solution that is 0.080 mol kg^{-1} in $K_3[Fe(CN)_6]$(aq), 0.030 mol kg^{-1} in KCl(aq), and 0.075 mol kg^{-1} in NaBr(aq).

72.6(a) Calculate the masses of (a) $Ca(NO_3)_2$ and, separately, (b) NaCl to add to a 0.250 mol kg^{-1} solution of KNO_3(aq) containing 800 g of solvent to raise its ionic strength to 0.450.

72.6(b) Calculate the masses of (a) KNO_3 and, separately, (b) $Ba(NO_3)_2$ to add to a 0.150 mol kg^{-1} solution of KNO_3(aq) containing 250 g of solvent to raise its ionic strength to 1.00.

72.7(a) Estimate the mean activity coefficient and activity of a solution that is 5.0 mmol kg^{-1} $CaCl_2$(aq) and 4.0 mmol kg^{-1} NaF(aq) at 25 °C.

72.7(b) Estimate the mean activity coefficient and activity of a solution that is 2.5 mmol kg^{-1} NaCl(aq) and 5.5 mmol kg^{-1} $Ca(NO_3)_2$(aq) at 25 °C.

72.8(a) The mean activity coefficients of HBr in three dilute aqueous solutions at 25 °C are 0.930 (at 5.0 mmol kg^{-1}), 0.907 (at 10.0 mmol kg^{-1}), and 0.879 (at 20.0 mmol kg^{-1}). Estimate the value of *B* in the extended Debye–Hückel law.

72.8(b) The mean activity coefficients of KCl in three dilute aqueous solutions at 25 °C are 0.927 (at 5.0 mmol kg^{-1}), 0.902 (at 10.0 mmol kg^{-1}), and 0.816 (at 50.0 mmol kg^{-1}). Estimate the value of B in the extended Debye–Hückel law.

Problems

72.1 The table below lists the vapour pressures of mixtures of iodoethane (I) and ethyl acetate (A) at 50 °C. Find the activity coefficients of both components on (a) the Raoult's law basis, (b) the Henry's law basis with iodoethane as solute.

x_I	0	0.0579	0.1095	0.1918	0.2353	0.3718
p_I/kPa	0	3.73	7.03	11.7	14.05	20.72
p_A/kPa	37.38	35.48	33.64	30.85	29.44	25.05

x_I	0.5478	0.6349	0.8253	0.9093	1.0000
p_I/kPa	28.44	31.88	39.58	43.00	47.12
p_A/kPa	19.23	16.39	8.88	5.09	0

72.2‡ Aminabhavi, et al. examined mixtures of cyclohexane with various long-chain alkanes (*J. Chem. Eng. Data* **41**, 526 (1996)). Among their data are the following measurements of the density of a mixture of cyclohexane and pentadecane as a function of mole fraction of cyclohexane (x_c) at 298.15 K:

x_c	0.6965	0.7988	0.9004
ρ/(g cm^{-3})	0.7661	0.7674	0.7697

Fit a polynomial expression to the data (use mathematical software) and determine the excess volume of mixing and partial molar volumes, $V_J = (\partial V/\partial n_J)_{p,T}$, of the components. Plot your results.

72.3‡ Comelli and Francesconi examined mixtures of propionic acid with various other organic liquids at 313.15 K (*J. Chem. Eng. Data* **41**, 101 (1996)). They report the excess volume of mixing propionic acid with oxane as $V^E = x_1x_2\{a_0 + a_1(x_1 - x_2)\}$, where x_1 is the mole fraction of propionic acid, x_2 that of oxane, $a_0 = -2.4697$ cm^3 mol^{-1}, and $a_1 = 0.0608$ cm^3 mol^{-1}. The density of propionic acid at this temperature is 0.97174 g cm^{-3}; that of oxane is 0.86398 g cm^{-3}. (a) Derive an expression for the partial molar volume $V_J = (\partial V/\partial n_J)_{p,T}$ of each component at this temperature. (b) Compute the partial molar volume for each component in an equimolar mixture.

72.4‡ Francesconi, et al. studied the liquid–vapour equilibria of trichloromethane and 1,2-epoxybutane at several temperatures (*J. Chem. Eng. Data* **41**, 310 (1996)). Among their data are the following measurements of the mole fractions of trichloromethane in the liquid phase (x_T) and the vapour phase (y_T) at 298.15 K as a function of pressure.

p/kPa	23.40	21.75	20.25	18.75	18.15	20.25	22.50	26.30
x	0	0.129	0.228	0.353	0.511	0.700	0.810	1
y	0	0.065	0.145	0.285	0.535	0.805	0.915	1

Compute the activity coefficients of both components on the basis of Raoult's law.

72.5 The mean activity coefficients for aqueous solutions of NaCl at 25 °C are given below. Confirm that they support the Debye–Hückel limiting law and that an improved fit is obtained with the extended law.

b/(mmol kg^{-1})	1.0	2.0	5.0	10.0	20.0
$\gamma_{\pm}$	0.9649	0.9519	0.9275	0.9024	0.8712

72.6 The excess Gibbs energy of a certain binary mixture is equal to $gRTx(1-x)$, where g is a constant and x is the mole fraction of a solute A. Find an expression for the chemical potential of A in the mixture and sketch its dependence on the composition.

72.7 The excess Gibbs energy of mixing of methylcyclohexane (MCH) and tetrahydrofuran (THF) at 303.15 K were found to fit the expression

$$G^{\mathrm{E}} = RTx(1-x)\{0.4857-0.1077(2x-1)+0.0191(2x-1)^2\}$$

where x is the mole fraction of the methylcyclohexane. Does this empirical expression support the view that the solution is regular? If it is not regular over the full range of compositions, is it regular over short regions? Can you adjust the regular model to accommodate the data?

72.8 Use the Gibbs–Duhem equation to show that the chemical potential of a component B in a binary mixture can be obtained if the chemical potential of the second component A is known for all compositions up to the one of interest. Do this by proving that

$$\mu_{\mathrm{B}} = \mu_{\mathrm{B}}^{\star} - \int_{\mu_{\mathrm{A}}^{\star}}^{\mu_{\mathrm{A}}} \frac{x_{\mathrm{A}}}{1-x_{\mathrm{A}}}\,\mathrm{d}\mu_{\mathrm{A}}$$

Go on to formulate a version of this expression for a regular solution in which the activity coefficients are represented by the Margules equations and the parameter ξ.

72.9 A similar expression to that derived in Problem 72.8 applies to the partial molar volume. Use the following data (which are for 298 K) to evaluate the integral graphically to find the partial molar volume of propanone in a propanone/trichloromethane mixture at $x = 0.500$.

x(CHCl$_3$)	0	0.194	0.385	0.559	0.788	0.889	1.000
V_{m}/(cm^3 mol^{-1})	73.99	75.29	76.50	77.55	79.08	79.82	80.67

72.10 The 'osmotic coefficient', ϕ, is defined as $\phi = -(x_{\mathrm{A}}/x_{\mathrm{B}}) \ln a_{\mathrm{A}}$. By writing $r = x_{\mathrm{B}}/x_{\mathrm{A}}$ and using the Gibbs–Duhem equation, show that it is possible to calculate the activity of B from the activities of A over a composition range by using the formula

$$\ln \frac{a_{\mathrm{B}}}{r} = \phi - \phi(0) + \int_0^r \left(\frac{\phi-1}{r}\right)\mathrm{d}r$$

72.11 The addition of a small amount of a salt, such as $(\mathrm{NH_4})_2\mathrm{SO_4}$, to a solution containing a charged protein increases the solubility of the protein in water. This observation is called the *salting-in effect*. However, the addition of large amounts of salt can decrease the solubility of the protein to such an extent that the protein precipitates from solution. This observation is called the *salting-out effect* and is used widely by biochemists to isolate and purify proteins. Consider the equilibrium $\mathrm{PX}_\nu(\mathrm{s}) \rightleftharpoons \mathrm{P}^{\nu+}(\mathrm{aq}) + \nu\,\mathrm{X}^-(\mathrm{aq})$, where $\mathrm{P}^{\nu+}$ is a polycationic protein of charge $+\nu$ and X^- is its counter-ion. Use Le Chatelier's principle and the physical principles behind the Debye–Hückel theory to provide a molecular interpretation for the salting-in and salting-out effects. *Hint*: Le Chatelier's principle should be familiar to you from introductory chemistry.

Integrated activities

F14.1 Plot the vapour pressure data for a mixture of benzene (B) and acetic acid (A) given below and plot the vapour pressure–composition curve for the mixture at 50 °C. Then confirm that Raoult's and Henry's laws are obeyed in the appropriate regions. Deduce the activities and activity coefficients of the components on the Raoult's law basis and then, taking B as the solute, its activity and activity coefficient on a Henry's law basis. Finally, evaluate the excess Gibbs energy of the mixture over the composition range spanned by the data.

x_{A}	0.0160	0.0439	0.0835	0.1138	0.1714
p_{A}/kPa	0.484	0.967	1.535	1.89	2.45
p_{B}/kPa	35.05	34.29	33.28	32.64	30.90

x_{A}	0.2973	0.3696	0.5834	0.6604	0.8437	0.9931
p_{A}/kPa	3.31	3.83	4.84	5.36	6.76	7.29
p_{B}/kPa	28.16	26.08	20.42	18.01	10.0	0.47

F14.2‡ Chen and Lee studied the liquid–vapour equilibria of cyclohexanol with several gases at elevated pressures (J.-T. Chen and M.-J. Lee, *J. Chem. Eng. Data* **41**, 339 (1996)). Among their data are the following measurements of the mole fractions of cyclohexanol in the vapour phase (y) and the liquid phase (x) at 393.15 K as a function of pressure.

p/bar	10.0	20.0	30.0	40.0	60.0	80.0
y_{cyc}	0.0267	0.0149	0.0112	0.00947	0.00835	0.00921
x_{cyc}	0.9741	0.9464	0.9204	0.892	0.836	0.773

Determine the Henry's law constant of $\mathrm{CO_2}$ in cyclohexanol, and compute the activity coefficient of $\mathrm{CO_2}$.

F14.3‡ The following data (x: liquid phase; y: gas phase) have been obtained for the liquid–vapour equilibrium compositions of mixtures of nitrogen and oxygen at 100 kPa.

T/K	77.3	78	80	82	84	86	88	90.2
$x(O_2)$	0	0.10	0.34	0.54	0.70	0.82	0.92	1
$y(O_2)$	0	0.02	0.11	0.22	0.35	0.52	0.73	1
$p^*(O_2)$/Torr	154	171	225	294	377	479	601	760

Plot the data on a temperature–composition diagram and determine the extent to which it fits the predictions for an ideal solution by calculating the activity coefficients of O_2 at each composition.

F14.4 Show that the osmotic pressure of a real solution is given by $\Pi V = -RT\ln a_A$. Go on to show that, provided the concentration of the solution is low, this expression takes the form $\Pi V = \phi RT[\mathrm{B}]$ and hence that the osmotic coefficient, ϕ, (which is defined in Problem 72.10) may be determined from osmometry.

F14.5 Show that the freezing-point depression of a real solution in which the solvent of molar mass M has activity a_A obeys

$$\frac{\mathrm{d}\ln a_A}{\mathrm{d}(\Delta T)} = -\frac{M}{K_f}$$

and use the Gibbs–Duhem equation to show that

$$\frac{\mathrm{d}\ln a_B}{\mathrm{d}(\Delta T)} = -\frac{1}{b_B K_f}$$

where a_B is the solute activity and b_B is its molality. Use the Debye–Hückel limiting law to show that the osmotic coefficient (ϕ, Problem 72.10) is given by $\phi = 1 - \frac{1}{3}A'I$ with $A' = 2.303A$ and $I = b/b^{\ominus}$.

F14.6‡ Diamond is the hardest substance and the best conductor of heat yet characterized. For these reasons, it is used widely in industrial applications that require a strong abrasive. Unfortunately, it is difficult to synthesize diamond from the more readily available allotropes of carbon, such as graphite. To illustrate this point, calculated the pressure required for diamond to become thermodynamically more stable than graphite at 25 °C. The following data apply to 25 °C and 100 kPa. Assume the specific volume, V_s, and κ_T are constant with respect to pressure changes.

	Graphite	Diamond
$\Delta_f G^{\ominus}/(\mathrm{kJ\,mol^{-1}})$	0	+2.8678
$V_s/(\mathrm{cm^3\,g^{-1}})$	0.444	0.284
$\kappa_T/\mathrm{kPa^{-1}}$	3.04×10^{-8}	0.187×10^{-8}

F14.7 Use the expressions relating the Gibbs energy and entropy of a perfect gas to the molecular partition function to show that (a) eqns 64.12b and 60.3 are consistent with eqn 69.11, (b) eqn 64.12b is consistent with eqn 69.12.

F14.8 Use mathematical software, a spreadsheet, or the *Living graphs* (labelled $^{\mathrm{LG}}$) on the website of this book for the following exercises:

(a)$^{\mathrm{LG}}$ Draw graphs of $\Delta_{\mathrm{mix}}G$ against x_A for an ideal solution at different temperatures in the range 298 K to 500 K. For what value of x_A does $\Delta_{\mathrm{mix}}G$ depend on temperature most strongly?

(b) Determine the value of the osmotic virial coefficient B from the data in Exercise 71.1.

(c)$^{\mathrm{LG}}$ Refer to the graph in Fig. 72.3, fix ξ, and vary the temperature. For what value of x_A does the excess enthalpy depend on temperature most strongly?

(d)$^{\mathrm{LG}}$ Refer to the graph in Fig. 72.4, fix ξ at 1.5, and vary the temperature. Is there a range of temperatures over which you observe phase separation?

(e)$^{\mathrm{LG}}$ Plot p_A/p_A^* against x_A with $\xi = 2.5$ by using eqn 70.6 and then eqn 72.17. Above what value of x_A do the values of p_A/p_A^* given by these equations differ by more than 10 per cent?

(f) Consider the plot of log $\gamma_\pm$ against $I^{1/2}$ with $B = 1.50$ and $C = 0$ in the Davies equation as a representation of experimental data for a certain 1,1 electrolyte. Over what range of ionic strengths does the application of the limiting law lead to an error in the value of the activity coefficient of less than 10 per cent of the value predicted by the extended law?

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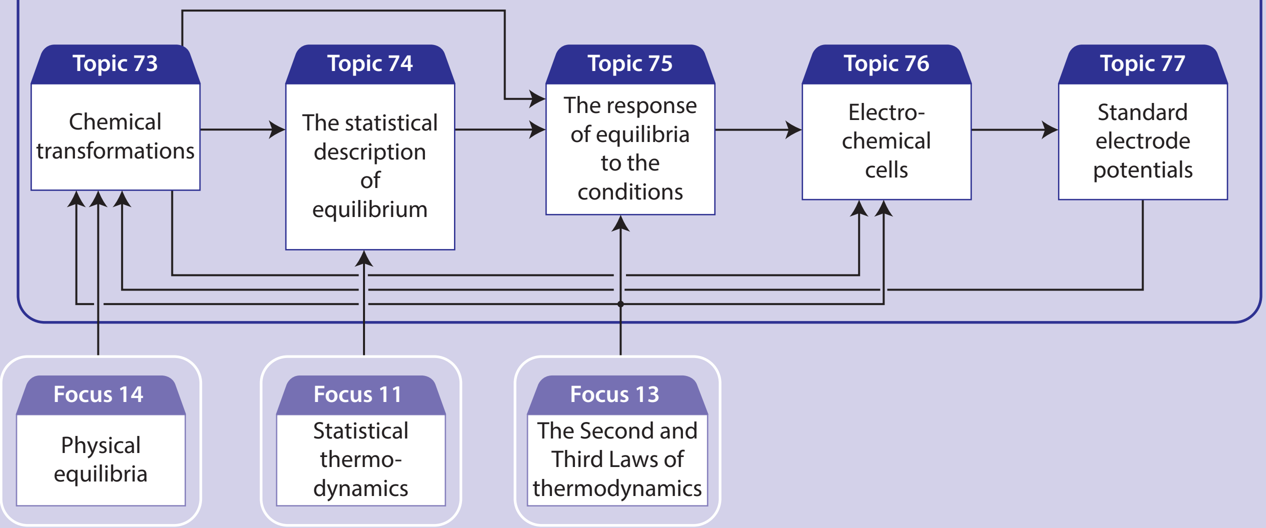
FOCUS 15 ON Chemical equilibria



Of all the applications of thermodynamics to chemistry, probably the most important is its role in the description of chemical equilibrium, including aspects of chemistry that make use of equilibrium concepts, such as electrochemistry.

The concept of chemical potential introduced in *Physical equilibria* plays a central role in the description of chemical equilibrium and the establishment of the connection between the Gibbs energy (introduced in *The Second and Third Laws of thermodynamics*) and the equilibrium constant of a reaction (**Topic 73**). In this context, we can envisage chemical equilibrium as the point of balance between the 'pushing powers', as expressed by their chemical potentials, of the reactants and the products. This important discussion establishes the link between the equilibrium constant and thermodynamic properties that can be measured calorimetrically.

Deeper insight into the significance of the equilibrium constant comes from setting up the relation between it and the molecular partition function introduced in the discussion of the *Statistical thermodynamics* (**Topic 74**). Moreover, because the partition function can be calculated from spectroscopic data, we arrive at a way to predict equilibrium constants by using structural data.

Both thermodynamics and the Boltzmann distribution provide routes to predict and understand how the value of an equilibrium constant depends on the conditions (**Topic 75**), which is invaluable information for maximizing the yield of a reaction.

Many reactions, particularly but not only redox reactions, can be envisaged as occurring by the transfer of electrons. These reactions may often be carried out in an 'electrochemical cell', and hence the electric potential difference between the electrodes of the cell can be used to monitor the progress of the reaction towards equilibrium and to determine the concentrations of electroactive species (**Topic 76**). Moreover, by ascribing different contributions to each electrode (**Topic 77**), data can be compiled that enable the equilibrium constants of a wide variety of reactions to be discussed and used to decide whether one species can reduce another in solution.

What is the impact of this material?

Spontaneous chemical reactions, those heading for equilibrium, are used to generate power. In *Impact* 15.1 we explore biological power, where chemical reactions taking place in biological cells drive the processes that keep organisms alive. In *Impact* 15.2 we explore fuel cells, the technological analogues of biological cells, which generate electrical power to drive the artefacts of civilization.

To read more about the impact of this material, scan the QR code or go to http://bcs.whfreeman.com/webpub/chemistry/qmc2e/impact/qchem_impact15.html.

TOPIC 73

Chemical transformations

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➤ Why do you need to know this material?

This Topic introduces the crucial link between thermodynamic properties and the chemically important concept of the equilibrium constant. Whenever thermodynamic arguments are used in the discussion of equilibria, they are based on the material described here.

➤ What is the key idea?

At constant temperature and pressure, a reaction tends to approach the composition corresponding to minimum Gibbs energy.

➤ What do you need to know already?

You need to know how the Gibbs energy is related to the spontaneous direction of change (Topic 64) and be familiar with the concept of chemical potential and its relation to the activities of species in mixtures (Topics 69, 70, and 72).

Chemical reactions tend to move towards a dynamic equilibrium in which both reactants and products are present but have no further tendency to undergo net change. In some cases, the concentration of products in the equilibrium mixture is so much greater than that of the unchanged reactants that for all practical purposes the reaction is 'complete'. However, in many important cases the equilibrium mixture has significant concentrations of both reactants and products. In this Topic we see how to use thermodynamics to predict the equilibrium composition under any reaction conditions. Because many reactions of ions involve the transfer of electrons, they can be studied (and utilized) by allowing them to take place in an electrochemical cell. Measurements like those described in this Topic provide data that are very useful for discussing the characteristics of electrolyte solutions and of ionic equilibria in solution.

In Topic 64 it is shown that the direction of spontaneous change at constant temperature and pressure is towards lower values of the Gibbs energy, G. The idea is entirely general, and in this Topic we apply it to the discussion of chemical reactions.

73.1 The reaction Gibbs energy

We locate the equilibrium composition of a reaction mixture by calculating the Gibbs energy of the reaction mixture and identifying the composition that corresponds to minimum G.

Consider the reaction $A \rightarrow B$. Even though this reaction looks trivial, there are many examples of it, such as the isomerization of pentane to 2-methylbutane and the conversion of L-alanine to D-alanine. Suppose an infinitesimal amount $d\xi$ of A turns into B, then the change in the amount of A present is $dn_A = -d\xi$ and the change in the amount of B present is $dn_B = +d\xi$. The quantity ξ (xi) is called the **extent of reaction**; it has the dimensions of amount of substance and is reported in moles. When the extent of reaction changes by a measurable amount $\Delta\xi$, the amount of A present changes from $n_{A,0}$ to $n_{A,0} - \Delta\xi$ and the amount of B changes from $n_{B,0}$ to $n_{B,0} + \Delta\xi$. So, if initially 2.0 mol A is present and we wait until $\Delta\xi = +1.5$ mol, then the amount of A remaining will be 0.5 mol.

The **reaction Gibbs energy**, $\Delta_r G$, is defined as the slope of the graph of the Gibbs energy plotted against the extent of reaction at constant temperature and pressure:

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{T,p} \quad \textit{Definition} \quad \text{Reaction Gibbs energy} \quad (73.1)$$

Although Δ normally signifies a *difference* in values, here Δ_r signifies a *derivative*, the slope of G with respect to ξ. However, to see that there is a close relationship with the normal usage, suppose the reaction advances by $d\xi$. The corresponding change in Gibbs energy (at constant temperature and pressure) is

$$dG = \mu_A dn_A + \mu_B dn_B = -\mu_A d\xi + \mu_B d\xi = (\mu_B - \mu_A)d\xi$$

This equation can be reorganized into

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \mu_B - \mu_A$$

That is,

$$\Delta_r G = \mu_B - \mu_A \quad (73.2)$$

We see that $\Delta_r G$ can also be interpreted as the difference between the chemical potentials (the partial molar Gibbs energies) of the reactants and products *at the composition of the reaction mixture*.

Brief illustration 73.1 The reaction Gibbs energy

Suppose that in a certain reaction, the Gibbs energy decreases by 10 J when the reaction advances by 0.10 mol; the reaction Gibbs energy would be

$$\Delta_r G = \frac{-10\,\text{J}}{0.10\,\text{mol}} = -100\,\text{J mol}^{-1}$$

At a later stage in the reaction, the Gibbs energy reduces by 5.0 J for the same advancement; now $\Delta_r G = -50\,\text{J mol}^{-1}$. The magnitude of the slope of the Gibbs energy is decreasing as the reaction approaches equilibrium.

Self-test 73.1 Beyond the equilibrium composition, when there is an excess of products compared to the equilibrium composition, two states of a system differ by 10 J for a difference in advancement of 0.10 mol. What is the reaction Gibbs energy now?

Answer: $+100\,\text{J mol}^{-1}$

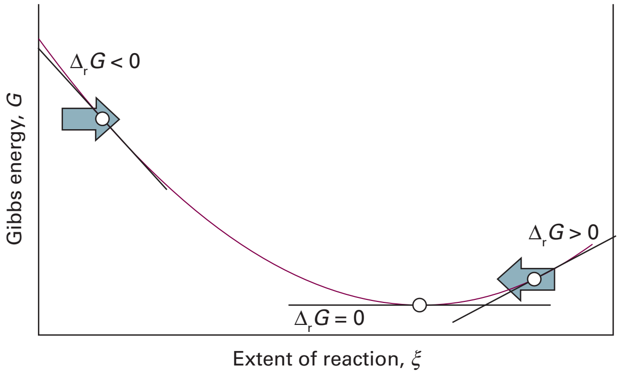


Figure 73.1 As the reaction advances (represented by motion from left to right along the horizontal axis) the slope of the Gibbs energy changes. Equilibrium corresponds to zero slope, at the foot of the valley.

Because chemical potential varies with composition, the slope of the plot of Gibbs energy against extent of reaction changes as the reaction proceeds. Moreover, because the reaction runs in the direction of decreasing G (that is, down the slope of G plotted against ξ), we see from eqn 73.2 that the reaction $A \rightarrow B$ is spontaneous when $\mu_A > \mu_B$, whereas the reverse reaction is spontaneous when $\mu_B > \mu_A$. The slope is zero, and the reaction is spontaneous in neither direction, when

$$\Delta_r G = 0 \quad (73.3)$$

This condition occurs when $\mu_B = \mu_A$ (Fig. 73.1). It follows that if we can find the composition of the reaction mixture that ensures $\mu_B = \mu_A$, then we can identify the composition of the reaction mixture at equilibrium.

We can express the spontaneity of a reaction at constant temperature and pressure in terms of the reaction Gibbs energy:

- If $\Delta_r G < 0$, the forward reaction is spontaneous.
- If $\Delta_r G > 0$, the reverse reaction is spontaneous.
- If $\Delta_r G = 0$, the reaction is at equilibrium.

73.2 The thermodynamic description of equilibrium

With the background established, we are ready to see how to apply thermodynamics to the description of chemical equilibrium.

(a) Perfect gas equilibria

When A and B are perfect gases we can use $\mu = \mu^\ominus + RT\ln(p/p^\ominus)$ (see *Justification* 70.1 of Topic 70) to write

$$\Delta_r G = \mu_B - \mu_A = \mu_B^{\ominus} + RT\ln(p_B/p^{\ominus}) - (\mu_A^{\ominus} + RT\ln(p_A/p^{\ominus}))$$
$$= \Delta_r G^{\ominus} + RT\ln\frac{p_B}{p_A} \qquad (73.4)$$

where $\Delta_r G^{\ominus} = \mu_B^{\ominus} - \mu_A^{\ominus}$. If we denote the ratio of partial pressures by Q, we obtain

$$\Delta_r G = \Delta_r G^{\ominus} + RT\ln Q \qquad Q = \frac{p_B}{p_A} \qquad (73.5)$$

The ratio Q is an example of a **reaction quotient**. It ranges from 0 when $p_B = 0$ (corresponding to pure A) to infinity when $p_A = 0$ (corresponding to pure B). The **standard reaction Gibbs energy**, $\Delta_r G^{\ominus}$, is defined (like the standard reaction enthalpy) as the difference in the standard molar Gibbs energies of the reactants and products. For our reaction

$$\Delta_r G^{\ominus} = G_{B,m}^{\ominus} - G_{A,m}^{\ominus} \qquad (73.6a)$$

In Topic 65 it is shown that the difference in standard molar Gibbs energies of the products and reactants is equal to the difference in their standard Gibbs energies of formation, so in practice we calculate $\Delta_r G^{\ominus}$ from

$$\Delta_r G^{\ominus} = \Delta_f G^{\ominus}(B) - \Delta_f G^{\ominus}(A) \qquad (73.6b)$$

At equilibrium, $\Delta_r G = 0$. The ratio of partial pressures at equilibrium is denoted K, and eqn 73.5 becomes

$$0 = \Delta_r G^{\ominus} + RT\ln K$$

This expression rearranges to

$$RT\ln K = -\Delta_r G^{\ominus} \qquad (73.7)$$

This relation is a special case of one of the most important equations in chemical thermodynamics: it is the link between tables of thermodynamic data, such as those in the *Resource section*, and the chemically important **equilibrium constant**, K.

Brief illustration 73.2 The equilibrium constant 1

The standard Gibbs energies of formation of gas-phase species A and B are −8.20 kJ mol^{-1} and −12.50 kJ mol^{-1}, respectively (at 298 K). The standard reaction Gibbs energy for the reaction $A(g) \rightarrow B(g)$ in the gas phase is therefore

$$\Delta_r G^{\ominus} = (-12.50\ \text{kJ mol}^{-1}) - (-8.20\ \text{kJ mol}^{-1}) = -4.30\ \text{kJ mol}^{-1}$$

It follows from eqn 73.7 that

$$\ln K = -\frac{-4.30\times10^3\,\text{J mol}^{-1}}{(8.3145\ \text{J K}^{-1}\text{mol}^{-1})\times(298\ \text{K})} = +1.73\ldots$$

It follows that $K = e^{1.73} = 5.7$, so the partial pressure of B is 5.7 times that of A at equilibrium.

Self-test 73.2 In a similar reaction, the standard Gibbs energies of formation of A and B are −16.0 kJ mol^{-1} and −9.7 kJ mol^{-1}, respectively, at 298 K. Calculate K.

Answer: 0.079

We see from eqn 73.7 (and in Self-test 73.2) that when $\Delta_r G^{\ominus} > 0$, the equilibrium constant $K < 1$. Therefore, at equilibrium the partial pressure of A exceeds that of B, which means that the reactant A is favoured in the equilibrium. When $\Delta_r G^{\ominus} < 0$, the equilibrium constant $K > 1$ (as in *Brief illustration* 73.2), so at equilibrium the partial pressure of B exceeds that of A. Now the product B is favoured in the equilibrium.

In molecular terms, the minimum in the Gibbs energy, which corresponds to $\Delta_r G = 0$, stems from the Gibbs energy of mixing of the two gases. Hence, an important contribution to the position of chemical equilibrium is the mixing of the products with the reactants as the products are formed.

To appreciate the role of mixing, consider a hypothetical reaction in which A molecules at 1 bar change into B molecules also at 1 bar without mingling together. The Gibbs energy of the system changes from $G^{\ominus}(A)$ to $G^{\ominus}(B)$ in proportion to the amount of B that had been formed, and the slope of the plot of G against the extent of reaction is a constant and equal to $\Delta_r G^{\ominus}$ at all stages of the reaction (Fig. 73.2). There is no intermediate minimum in the graph. However, in fact the newly produced B molecules do mix with the surviving A molecules. The contribution of a mixing process to the change in Gibbs energy is

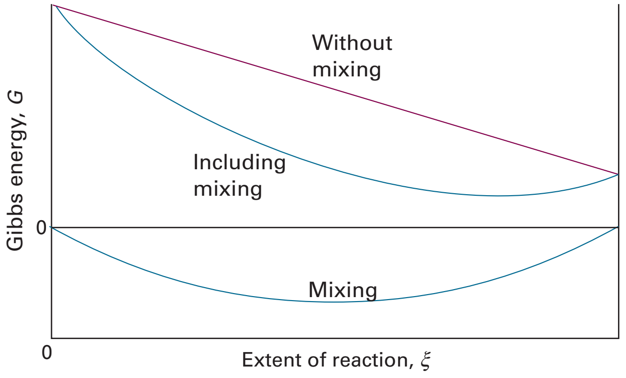


Figure 73.2 If the mixing of reactants and products is ignored, then the Gibbs energy changes linearly from its initial value (pure reactants) to its final value (pure products) and the slope of the line is $\Delta_r G^{\ominus}$. However, as products are produced, there is a further contribution to the Gibbs energy arising from their mixing (lowest curve). The sum of the two contributions (middle curve) has a minimum. That minimum corresponds to the equilibrium composition of the system.

given by eqn 70.1 of Topic 70 ($\Delta_{\text{mix}}G = nRT(x_A \ln x_A + x_B \ln x_B)$). This expression makes a U-shaped contribution to the total change in Gibbs energy. As can be seen from Fig. 73.2, there is now an intermediate minimum in the Gibbs energy, and its position corresponds to the equilibrium composition of the reaction mixture.

(b) The general case of a reaction

We can easily extend the argument that led to eqn 73.7 to a general reaction. First, we need to generalize the concept of extent of reaction.

In Topic 57 it is shown that a chemical reaction, such as 2 A + B → 3 C + D, can be expressed in the form

$$0 = \sum_J \nu_J J \qquad (73.8)$$

where J denotes the substances and the ν_J are the corresponding stoichiometric numbers in the chemical equation. In our example, these numbers have the values $\nu_A = -2$, $\nu_B = -1$, $\nu_C = +3$, and $\nu_D = +1$; a stoichiometric number is positive for products and negative for reactants. We now define ξ so that if it changes by $d\xi$, then the change in the amount of any species J is $\nu_J d\xi$.

Brief illustration 73.3 The advancement of a reaction

In the notation of eqn 73.8, the stoichiometric numbers in the equation $N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$ are $\nu_{N_2} = -1$, $\nu_{H_2} = -3$, and $\nu_{NH_3} = +2$. Therefore, if initially 10 mol N_2 is present, then when the extent of reaction changes from $\xi = 0$ to $\xi = 1$ mol, implying that $\Delta\xi = +1$ mol, the amount of N_2 changes from 10 mol to 9 mol. All the N_2 has been consumed when $\xi = 10$ mol. When $\Delta\xi = +1$ mol, the amount of H_2 changes by $-3 \times (1\text{ mol}) = -3$ mol and the amount of NH_3 changes by $+2 \times (1\text{ mol}) = +2$ mol.

Self-test 73.3 Consider the reaction $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g)$. By how much do the amounts of the substances change when $\Delta\xi = +1$ mol?

Answer: H_2: −2 mol; O_2: −1 mol; H_2O: +2 mol

In the following *Justification*, we show that the Gibbs energy of reaction can always be written

$$\Delta_r G = \Delta_r G^{\ominus} + RT \ln Q \qquad \text{Reaction Gibbs energy} \qquad (73.9)$$

with the standard reaction Gibbs energy calculated from

$$\Delta_r G^{\ominus} = \sum_{\text{Products}} \nu \Delta_f G^{\ominus} - \sum_{\text{Reactants}} \nu \Delta_f G^{\ominus} \qquad \textit{Practical implementation} \qquad \text{Reaction Gibbs energy} \qquad (73.10a)$$

or, more formally,

$$\Delta_r G^{\ominus} = \sum_J \nu_J \Delta_f G^{\ominus}(J) \qquad (73.10b)$$

The **reaction quotient**, Q, has the form

$$Q = \frac{\text{activities of products}}{\text{activities of reactants}} \qquad \textit{Definition} \qquad \text{Reaction quotient} \qquad (73.11a)$$

with each species raised to the power given by its stoichiometric coefficient. More formally, to write the general expression for Q we introduce the symbol Π to denote the product of what follows it (just as Σ denotes the sum), and define Q as

$$Q = \prod_J a_J^{\nu_J} \qquad (73.11b)$$

Because reactants have negative stoichiometric numbers, they automatically appear as the denominator when the product is written out explicitly. Recall from Table 72.1 that, for pure solids and liquids, the activity is 1 under ordinary laboratory conditions, so such substances make no contribution to Q even though they may appear in the chemical equation.

Brief illustration 73.4 The reaction quotient

Consider the reaction 2 A + 3 B → C + 2 D, in which case $\nu_A = -2$, $\nu_B = -3$, $\nu_C = +1$, and $\nu_D = +2$. The reaction quotient is then

$$Q = a_A^{-2} a_B^{-3} a_C^{1} a_D^{2} = \frac{a_C a_D^2}{a_A^2 a_B^3}$$

Self-test 73.4 Write Q for the reaction A + 2 B → 2 C.

Answer: $Q = a_C^2 / a_A a_B^2$

Justification 73.1 The dependence of the reaction Gibbs energy on the reaction quotient

Consider a reaction with stoichiometric numbers ν_J. When the reaction advances by $d\xi$, the amounts of reactants and products change by $dn_J = \nu_J d\xi$. The resulting infinitesimal change in the Gibbs energy at constant temperature and pressure is

$$dG = \sum_J \mu_J dn_J = \sum_J \mu_J \nu_J d\xi = \left(\sum_J \mu_J \nu_J\right) d\xi$$

It follows that

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \sum_J \nu_J \mu_J$$

To make further progress, we note that the chemical potential of a species J is related to its activity by eqn 72.8 ($\mu_J = \mu_J^{\ominus} + RT \times \ln a_J$; see also Table 72.1). When this expression is substituted into the preceding equation we obtain

$$\begin{aligned}\Delta_r G &= \sum_J \nu_J(\mu_J^{\ominus} + RT\ln a_J) = \overbrace{\sum_J \nu_J \mu_J^{\ominus}}^{\Delta_r G^{\ominus}} + RT\sum_J \nu_J \ln a_J \\ &= \Delta_r G^{\ominus} + RT\sum_J \ln a_J^{\nu_J} = \Delta_r G^{\ominus} + RT\ln \overbrace{\prod_J a_J^{\nu_J}}^{Q} \\ &= \Delta_r G^{\ominus} + RT\ln Q\end{aligned}$$

with Q given by eqn 73.11b. We have used the relations

$$a\ln x = \ln x^a \qquad \overbrace{\sum_i \ln x_i}^{\ln a + \ln b + \ldots} = \overbrace{\ln\left(\prod_i x_i\right)}^{\ln ab\ldots}$$

Now we conclude the argument based on eqn 73.9. At equilibrium, the slope of G is zero: $\Delta_r G = 0$. The activities then have their equilibrium values and we can write

$$K = Q_{\text{equilibrium}} = \left(\prod_J a_J^{\nu_J}\right)_{\text{equilibrium}} \qquad \textit{Definition} \qquad \text{Equilibrium constant} \qquad (73.12)$$

This expression has the same form as for Q, eqn 73.11, but is evaluated using *equilibrium* activities. From now on, we shall not write the 'equilibrium' subscript explicitly, and will rely on the context to make it clear that for K we use equilibrium values and for Q we use the values at the specified stage of the reaction.

An equilibrium constant K expressed in terms of activities is called a **thermodynamic equilibrium constant**. Note that, because activities are dimensionless numbers, the thermodynamic equilibrium constant is also dimensionless. In elementary applications, the activities that occur in eqn 73.12 are often replaced by the numerical values of molalities (that is, by replacing a_J by $b_J/b^{\ominus}$, where $b^{\ominus} = 1\ \text{mol kg}^{-1}$), molar concentrations (that is, as $[J]/c^{\ominus}$, where $c^{\ominus} = 1\ \text{mol dm}^{-3}$), or partial pressures (that is, by $p_J/p^{\ominus}$, where $p^{\ominus} = 1$ bar). In each case, the resulting expressions are only approximations. The approximation is particularly severe for electrolyte solutions, for in them activity coefficients differ from 1 even in very dilute solutions (Topic 72).

Brief illustration 73.5 The equilibrium constant 2

The equilibrium constant for the heterogeneous equilibrium $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ is

$$K = a_{CaCO_3(s)}^{-1} a_{CaO(s)} a_{CO_2(g)} = \frac{\overbrace{a_{CaO(s)}}^{1} a_{CO_2(g)}}{\underbrace{a_{CaCO_3(s)}}_{1}} = a_{CO_2(g)} \approx p_{CO_2}/p^{\ominus}$$

where the activities of CaO(s) and $CaCO_3$(s) are set to 1 because each substance appears in the reaction as a separate, pure phase. The approximation depends on being able to treat carbon dioxide as a perfect gas. We can conclude that in this case the equilibrium constant is the numerical value of the decomposition vapour pressure of calcium carbonate.

Self-test 73.5 Write the expression for the equilibrium constant of the reaction $2\ H_2(g) + O_2(g) \rightleftharpoons 2\ H_2O(l)$.

Answer: $K = 1/a_{H_2}^2 a_{O_2} \approx p^{\ominus 3}/p_{H_2}^2 p_{O_2}$

(c) Calculating equilibrium constants from thermodynamic data

If we set $\Delta_r G = 0$ in eqn 73.9 and replace Q by K, then we immediately obtain

$$RT\ln K = -\Delta_r G^{\ominus} \qquad K \text{ from thermodynamic data} \qquad (73.13)$$

as in eqn 73.7 for perfect-gas equilibria. This is an exact and highly important thermodynamic relation, for it enables us to predict the equilibrium constant of any reaction from tables of thermodynamic data, and hence to predict the equilibrium composition of the reaction mixture.

Example 73.1 Calculating an equilibrium constant

Calculate the equilibrium constant for the ammonia synthesis reaction, $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$, at 298 K and show how K is related to the partial pressures of the species at equilibrium when the overall pressure is low enough for the gases to be treated as perfect.

Method Calculate the standard reaction Gibbs energy from eqn 73.10 and convert it to the value of the equilibrium constant by using eqn 73.13. The expression for the equilibrium constant is obtained from eqn 73.12, and, because the gases are taken to be perfect, replace each activity by the ratio $p/p^{\ominus}$, where p is a partial pressure.

Answer The standard Gibbs energy of the reaction is

$$\begin{aligned}\Delta_r G^{\ominus} &= 2\Delta_f G^{\ominus}(NH_3,g) - \{\Delta_f G^{\ominus}(N_2,g) + 3\Delta_f G^{\ominus}(N_2,g)\} \\ &= 2\Delta_f G^{\ominus}(NH_3,g) = 2\times(-16.5\ \text{kJ mol}^{-1})\end{aligned}$$

Then,

$$\ln K = -\frac{2\times(-16.5\times10^3\,\mathrm{J\,mol^{-1}})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})} = \frac{2\times16.5\times10^3}{8.3145\times298} = 13.3\ldots$$

Hence, $K = 6.1\times10^5$. This result is thermodynamically exact. The thermodynamic equilibrium constant for the reaction is

$$K = \frac{a_{\mathrm{NH_3}}^2}{a_{\mathrm{N_2}}a_{\mathrm{H_2}}^3}$$

and this ratio has exactly the value we have just calculated. At low overall pressures, the activities can be replaced by the ratios $p/p^{\ominus}$, where p is a partial pressure, and an approximate form of the equilibrium constant is

$$K \approx \frac{(p_{\mathrm{NH_3}}/p^{\ominus})^2}{(p_{\mathrm{N_2}}/p^{\ominus})(p_{\mathrm{H_2}}/p^{\ominus})^3} = \frac{p_{\mathrm{NH_3}}^2\,p^{\ominus 2}}{p_{\mathrm{N_2}}\,p_{\mathrm{H_2}}^3}$$

Self-test 73.6 Evaluate the equilibrium constant for $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ at 298 K.

Answer: $K = 0.15$

We can also express the thermodynamic equilibrium constant in terms of the mole fractions, x_J, or molalities, b_J, of the species. To do so, we need to know the activity coefficients, and then use $a_J = \gamma_J x_J$ or $a_J = \gamma_J b_J/b^{\ominus}$ (recalling that the activity coefficients depend on the choice). For example, in the latter case, for an equilibrium of the form $A + B \rightleftharpoons C + D$, where all four species are solutes, we write

$$K = \frac{a_C a_D}{a_A a_B} = \frac{\gamma_C\gamma_D}{\gamma_A\gamma_B}\times\frac{b_C b_D}{b_A b_B} = K_\gamma K_b \qquad (73.14)$$

The activity coefficients must be evaluated at the equilibrium composition of the mixture (for instance, by using one of the Debye–Hückel expressions, Topic 72), which may involve a complicated calculation, because the activity coefficients are known only if the equilibrium composition is already known. In elementary applications, and to begin the iterative calculation of the concentrations in a real example, the assumption is often made that the activity coefficients are all so close to unity that $K_\gamma = 1$. Then we obtain the result widely used in elementary chemistry that $K \approx K_b$, and equilibria are discussed in terms of molalities (or molar concentrations) themselves.

(d) Equilibria in biological systems

For biological systems it is appropriate to adopt the biological standard state (as indicated by the superscript $^{\oplus}$), in which $a_{\mathrm{H^+}} = 10^{-7}$ and $\mathrm{pH} = -\log a_{\mathrm{H^+}} = 7$. It follows from eqn 73.9 that the relation between the thermodynamic and biological standard Gibbs energies of reaction for a reaction of the form

$$A + \nu H^+(aq) \rightarrow P \qquad (73.15a)$$

is

$$\Delta_r G^{\oplus} = \Delta_r G^{\ominus} + 7\nu RT \ln 10 \qquad (73.15b)$$

Note that there is no difference between the two standard values if hydrogen ions are not involved in the reaction ($\nu = 0$).

Brief illustration 73.6 The biological equilibrium constant

Consider the reaction

$$\mathrm{NADH(aq)} + \mathrm{H^+(aq)} \rightarrow \mathrm{NAD^+(aq)} + \mathrm{H_2(g)}$$

at 37 °C, for which $\Delta_r G^{\ominus} = -21.8\,\mathrm{kJ\,mol^{-1}}$; NADH is the reduced form of nicotinamide adenine dinucleotide and NAD^+ is its oxidized form; the molecules play an important role in the later stages of the respiratory process. It follows that because $\nu = 1$ and $7\ln 10 = 16.1$,

$$\Delta_r G^{\oplus} = -21.8\,\mathrm{kJ\,mol^{-1}} + 16.1\times(8.3145\times10^{-3}\,\mathrm{kJ\,K^{-1}mol^{-1}}) \times(310\,\mathrm{K}) = +19.7\,\mathrm{kJ\,mol^{-1}}$$

Note that the biological standard value is opposite in sign (in this example) to the thermodynamic standard value: the much lower concentration of hydronium ions (by seven orders of magnitude) at pH = 7 in place of pH = 0 has resulted in the reverse reaction becoming spontaneous under these biologically standard conditions (with all other species at unit activity).

Self-test 73.7 For a particular reaction of the form $A \rightarrow B + 2\,H^+$ in aqueous solution, it was found that $\Delta_r G^{\ominus} = +20\,\mathrm{kJ\,mol^{-1}}$ at 28 °C. Estimate the value of $\Delta_r G^{\oplus}$.

Answer: $-61\,\mathrm{kJ\,mol^{-1}}$

73.3 Exergonic and endergonic reactions

A reaction for which $\Delta_r G < 0$ is called **exergonic** (from the Greek words for 'work producing'). The name signifies that, because the process is spontaneous, it can be used to drive another process, such as another reaction, or used to do non-expansion work. A simple mechanical analogy is a pair of weights joined by a string (Fig. 73.3): the lighter of the pair of weights will be pulled up as the heavier weight falls down. Although the lighter weight has a natural tendency to move downward, its coupling to the heavier weight results in it being raised. In biological cells, the oxidations of carbohydrates act as the heavy weights

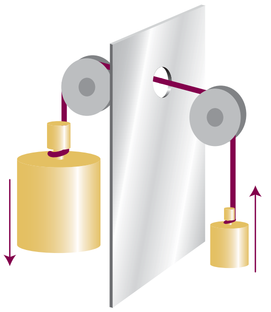


Figure 73.3 If two weights are coupled as shown here, then the heavier weight will move the lighter weight in its non-spontaneous direction: overall, the process is still spontaneous. The weights are the analogues of two chemical reactions: a reaction with a large negative ΔG can force another reaction with a positive or smaller negative ΔG to run in its non-spontaneous direction.

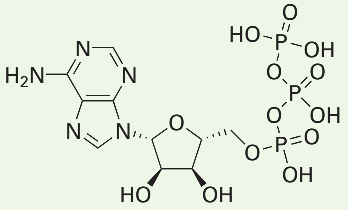
that drive other reactions forward and result in the formation of proteins from amino acids, muscle contraction, and brain activity. A reaction for which $\Delta_r G > 0$ is called **endergonic** (signifying 'work consuming'). The reaction can be made to occur only by doing work on it, such as electrolysing water to reverse its spontaneous formation reaction.

Brief illustration 73.7 Exergonic reactions

In biological cells, the energy released by the oxidation of foods is stored in adenosine triphosphate (ATP, **1**). The essence of the action of ATP is its ability to lose its terminal phosphate group by hydrolysis and to form adenosine diphosphate (ADP):

$$\mathrm{ATP(aq)} + \mathrm{H_2O(l)} \rightarrow \mathrm{ADP(aq)} + \mathrm{P_i^-(aq)} + \mathrm{H_3O^+(aq)}$$

where $\mathrm{P_i^-}$ denotes an inorganic phosphate group, such as $\mathrm{H_2PO_4^-}$. The biological standard values for ATP hydrolysis at 37 °C (310 K, blood temperature) are $\Delta_r G^{\ominus} = -31\ \mathrm{kJ\ mol^{-1}}$, $\Delta_r H^{\ominus} = -20\ \mathrm{kJ\ mol^{-1}}$, and $\Delta_r S^{\ominus} = +34\ \mathrm{J\ K^{-1}\ mol^{-1}}$. The hydrolysis is therefore exergonic ($\Delta_r G < 0$) under these conditions and $31\ \mathrm{kJ\ mol^{-1}}$ is available for driving other reactions, such as the strongly endergonic biosynthesis of proteins from amino acids. Moreover, because the reaction entropy is large, the reaction Gibbs energy is sensitive to temperature.



1 ATP

Self-test 73.8 At blood temperature, $\Delta_r G^{\ominus} = -147\ \mathrm{kJ\ mol^{-1}}$ for the oxidation of glucose by $\mathrm{NAD^+}$ to pyruvate ions. This oxidation is coupled to the conversion of two ADP molecules to two ATP molecules. What is the value of $\Delta_r G^{\ominus}$ for the overall reaction? Is the overall reaction spontaneous?

Answer: $-85\ \mathrm{kJ\ mol^{-1}}$; yes

In view of its exergonicity, as described in the preceding *Brief illustration*, the ADP–phosphate bond has been called a 'high-energy phosphate bond'. The name is intended to signify a high tendency to undergo reaction, and should not be confused with 'strong' bond. In fact, even in the biological sense it is not of very 'high energy'. The action of ATP depends on it being intermediate in activity. Thus ATP acts as a phosphate donor to a number of acceptors (for example, glucose), but is recharged by more powerful phosphate donors in a number of biochemical processes.

Checklist of concepts

☐ 1. The **extent of reaction** is defined such that, when it changes by $d\xi$, the amount of J present in a reaction mixture changes by $\nu_J d\xi$.

☐ 2. The **reaction Gibbs energy**, $\Delta_r G$, is the slope of the graph of the Gibbs energy plotted against the extent of reaction at constant temperature and pressure.

☐ 3. If $\Delta_r G < 0$, the forward reaction is spontaneous; if $\Delta_r G > 0$, the reverse reaction is spontaneous; if $\Delta_r G = 0$, the reaction is at equilibrium.

☐ 4. A natural measure of the composition of a reaction measure is the **reaction quotient**, Q.

☐ 5. The (thermodynamic) **equilibrium constant**, K, of a reaction is the value of Q at equilibrium.

☐ 6. The **standard reaction Gibbs energy**, $\Delta_r G^{\ominus}$, is the difference in the standard molar Gibbs energies of the reactants and products.

☐ 7. A reaction for which $\Delta_r G < 0$ is **exergonic**; a reaction for which $\Delta_r G > 0$ is **endergonic**.

Checklist of equations

Property	Equation	Comment	Equation number
Reaction Gibbs energy	$\Delta_\mathrm{r}G=(\partial G/\partial \xi)_{T,p}$	Definition	73.1
Chemical reaction	$0=\sum_\mathrm{J} \nu_\mathrm{J}\mathrm{J}$	Formal structure	73.8
Reaction Gibbs energy	$\Delta_\mathrm{r}G=\Delta_\mathrm{r}G^{\ominus}+RT\ln Q$	General stage of reaction	73.9
Standard reaction Gibbs energy	$\Delta_\mathrm{r}G^{\ominus}=\sum_\mathrm{J} \nu_\mathrm{J}\Delta_\mathrm{f}G^{\ominus}(\mathrm{J})$	Practical implementation	73.10a
Reaction quotient	$Q=\prod_\mathrm{J} a_\mathrm{J}^{\nu_\mathrm{J}}$	Definition	73.10b
Equilibrium constant	$K=Q_\mathrm{equilibrium}=\left(\prod_\mathrm{J} a_\mathrm{J}^{\nu_\mathrm{J}}\right)_\mathrm{equilibrium}$	Definition	73.12
Thermodynamic connection	$RT\ln K=-\Delta_\mathrm{r}G^{\ominus}$		73.13
Biological standard value	$\Delta_\mathrm{r}G^{\oplus}=\Delta_\mathrm{r}G^{\ominus}+7\nu RT\ln 10$	$\mathrm{A}+\nu\,\mathrm{H}^+(\mathrm{aq})\rightarrow\mathrm{P}$	73.15b

TOPIC 74

The statistical description of equilibrium

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➤ Why do you need to know this material?

The equilibrium constant provides an important link between thermodynamic and chemically significant quantities; this Topic shows how to extend that link to relate the equilibrium constant to structural and spectroscopic data.

➤ What is the key idea?

The equilibrium constant can be expressed in terms of the molecular partition function.

➤ What do you need to know already?

You need to know the significance of the molecular partition function and how to calculate it from structural data (Topic 52). You also need to know how the molecular partition function is related to the Gibbs energy of a substance (Topic 64) and how the thermodynamic equilibrium constant is related to the standard reaction Gibbs energy (Topic 73).

The Gibbs energy of a gas of independent molecules is given by eqn 64.12b of Topic 64 ($G=G(0)-nRT\ln q/N$, with $N=nN_A$). The equilibrium constant K of a reaction is related to the standard Gibbs energy of reaction by eqn 73.13 of Topic 73 ($\Delta_r G^{\ominus}=-RT\ln K$). It follows that we should be able to combine these two equations to calculate the equilibrium constant. We shall consider gas-phase reactions in which the equilibrium constant is expressed in terms of the partial pressures of the reactants and products.

74.1 The relation between *K* and the partition function

To find an expression for the standard reaction Gibbs energy in terms of partition functions we need expressions for the standard molar Gibbs energies, $G^{\ominus}/n$, of each species J:

$$\overbrace{G_m^{\ominus}(\mathrm{J})}^{G^{\ominus}/n}=\overbrace{G_m^{\ominus}(\mathrm{J},0)}^{G^{\ominus}(0)/n}-RT\ln\frac{\overbrace{q^{\ominus}}^{q^{\ominus}/N}}{nN_A} \qquad (74.1)$$

It will prove convenient in this Topic to define the **molar partition function** as $q_m=q/n$; its units are mol^{-1}. In particular, we shall need the value of the molar partition function when $p=p^{\ominus}$ (where $p^{\ominus}=1$ bar): we denote the resulting **standard molar partition function** $q_m^{\ominus}$. For a species J it follows that

$$G_m^{\ominus}(\mathrm{J})=G_m^{\ominus}(\mathrm{J},0)-RT\ln\frac{q_m^{\ominus}(\mathrm{J})}{N_A} \qquad \text{Standard molar Gibbs energy} \qquad (74.2)$$

The molar partition function has the form given by eqn 52.6 of Topic 52, which we repeat here:

$$\begin{aligned}q_m&=\frac{q^{T}q^{R}q^{V}q^{E}}{n}\\&=q^{R}q^{V}q^{E}\frac{V/n}{\Lambda^3}=q^{R}q^{V}q^{E}\frac{V_m}{\Lambda^3}\end{aligned} \qquad \text{Molar partition function} \qquad (74.3)$$

with $\Lambda=h/(2\pi mkT)^{1/2}$ (eqn 52.7b). Because only the translational component depends on the pressure, $q_{\rm m}^{\ominus}$ is found by evaluating the partition function with $V_{\rm m}$ replaced by $V_{\rm m}^{\ominus}$, where $V_{\rm m}^{\ominus}=RT/p^{\ominus}$.

By combining expressions like eqn 74.2 (as shown in the following *Justification*), the equilibrium constant for the reaction $a\,{\rm A}+b\,{\rm B}\rightarrow c\,{\rm C}+d\,{\rm D}$ is given by the expression

$$K=\frac{\{q_{\rm m}^{\ominus}({\rm C})/N_{\rm A}\}^{c}\{q_{\rm m}^{\ominus}({\rm D})/N_{\rm A}\}^{d}}{\{q_{\rm m}^{\ominus}({\rm A})/N_{\rm A}\}^{a}\{q_{\rm m}^{\ominus}({\rm B})/N_{\rm A}\}^{b}}{\rm e}^{-\Delta_{\rm r}E_0/RT} \qquad \text{K in terms of q} \tag{74.4a}$$

where $\Delta_{\rm r}E_0$ is the difference in molar energies of the ground states of the products and reactants (this term is defined more precisely in the *Justification*), and is calculated from the bond dissociation energies of the species (Fig. 74.1). More formally and generally, in terms of the stoichiometric numbers, we write this relation as

$$K=\left\{\prod_{\rm J}\left(\frac{q_{\rm m}^{\ominus}({\rm J})}{N_{\rm A}}\right)^{\nu_{\rm J}}\right\}{\rm e}^{-\Delta_{\rm r}E_0/RT} \tag{74.4b}$$

Although these expressions might look formidable, their form resembles those given for K in Topic 73 $(K=\prod_{\rm J} a_{\rm J}^{\nu_{\rm J}})$ with $a_{\rm J}$ replaced by $q_{\rm m}^{\ominus}({\rm J})/N_{\rm A}$ and an additional exponential factor.

Justification 74.1 The equilibrium constant in terms of the partition function 1

The standard molar reaction Gibbs energy for the reaction is

$$\begin{aligned}\Delta_{\rm r}G^{\ominus}&=\sum_{\rm J}\nu_{\rm J}G_{\rm m}^{\ominus}({\rm J})\\&=\sum_{\rm J}\nu_{\rm J}\left\{G_{\rm m}^{\ominus}({\rm J},0)-RT\ln\frac{q_{\rm m}^{\ominus}({\rm J})}{N_{\rm A}}\right\}\\&=\sum_{\rm J}\nu_{\rm J}G_{\rm m}^{\ominus}({\rm J},0)-RT\sum_{\rm J}\nu_{\rm J}\ln\frac{q_{\rm m}^{\ominus}({\rm J})}{N_{\rm A}}\end{aligned}$$

Because $G_{\rm m}^{\ominus}({\rm J},0)=U_{\rm m}({\rm J},0)$ and at $T=0$ only the ground state of a species is accessible, $G_{\rm m}^{\ominus}({\rm J},0)=E_{\rm m}({\rm J})$, the molar ground-state energy of J. The first term on the right is therefore

$$\sum_{\rm J}\nu_{\rm J}G_{\rm m}^{\ominus}({\rm J},0)=\sum_{\rm J}\nu_{\rm J}E_{\rm m}({\rm J})=\Delta_{\rm r}E_0$$

The second term on the right is

$$RT\sum_{\rm J}\nu_{\rm J}\ln\frac{q_{\rm m}^{\ominus}({\rm J})}{N_{\rm A}}=RT\overbrace{\sum_{\rm J}\ln\left(\frac{q_{\rm m}^{\ominus}({\rm J})}{N_{\rm A}}\right)^{\nu_{\rm J}}}^{\ln a+\ln b+\dots}=RT\ln\overbrace{\prod_{\rm J}\left(\frac{q_{\rm m}^{\ominus}({\rm J})}{N_{\rm A}}\right)^{\nu_{\rm J}}}^{\ln ab\dots}$$

Now we can write

$$\begin{aligned}\Delta_{\rm r}G^{\ominus}&=\Delta_{\rm r}E_0-RT\ln\prod_{\rm J}\left(\frac{q_{\rm m}^{\ominus}({\rm J})}{N_{\rm A}}\right)^{\nu_{\rm J}}\\&=-RT\left\{-\frac{\Delta_{\rm r}E_0}{RT}+\ln\prod_{\rm J}\left(\frac{q_{\rm m}^{\ominus}({\rm J})}{N_{\rm A}}\right)^{\nu_{\rm J}}\right\}\end{aligned}$$

At this stage we can pick out an expression for K by comparing this equation with $\Delta_{\rm r}G^{\ominus}=-RT\ln K$, which gives

$$\ln K=-\frac{\Delta_{\rm r}E_0}{RT}+\ln\prod_{\rm J}\left(\frac{q_{\rm m}^{\ominus}({\rm J})}{N_{\rm A}}\right)^{\nu_{\rm J}}$$

This expression is easily rearranged into eqn 74.4 by forming the exponential of both sides.

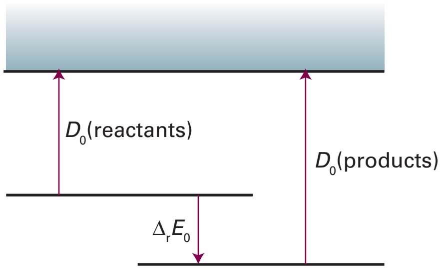

Figure 74.1 The definition of $\Delta_{\rm r}E_0$ for the calculation of equilibrium constants.

We shall illustrate the application of eqn 74.4 to an equilibrium in which a diatomic molecule X_2 dissociates into its atoms in the gas phase, with all gases treated as perfect:

$${\rm X}_2({\rm g})\rightleftharpoons 2\,{\rm X}({\rm g}) \qquad K=\frac{(p_{\rm X}/p^{\ominus})^2}{p_{{\rm X}_2}/p^{\ominus}}=\frac{p_{\rm X}^2}{p_{{\rm X}_2}p^{\ominus}}$$

According to eqn 74.4,

$$K=\frac{\{q_{\rm m}^{\ominus}({\rm X})/N_{\rm A}\}^2}{q_{\rm m}^{\ominus}({\rm X}_2)/N_{\rm A}}{\rm e}^{-\Delta_{\rm r}E_0/RT}=\frac{q_{\rm m}^{\ominus}({\rm X})^2}{q_{\rm m}^{\ominus}({\rm X}_2)N_{\rm A}}{\rm e}^{-\Delta_{\rm r}E_0/RT} \tag{74.5a}$$

with

$$\Delta_{\rm r}E_0=2E_{\rm m}({\rm X})-E_{\rm m}({\rm X}_2)=D_0({\rm X{-}X}) \tag{74.5b}$$

where D_0(X–X) is the (molar) dissociation energy of the X–X bond. The standard molar partition functions of the atoms X are

$$q_{\rm m}^{\ominus}({\rm X})=g_{\rm e}({\rm X})\frac{V_{\rm m}^{\ominus}}{\Lambda({\rm X})^3}=\frac{g_{\rm e}({\rm X})RT}{p^{\ominus}\Lambda({\rm X})^3}$$

where $g_e(X)$ is the degeneracy of the electronic ground state of X. The diatomic molecule X_2 also has rotational and vibrational degrees of freedom, so its standard molar partition function is

$$q_m^{\ominus}(X_2)=g_e(X_2)q^R(X_2)q^V(X_2)\frac{V_m^{\ominus}}{\Lambda(X_2)^3}$$
$$=\frac{g_e(X_2)q^R(X_2)q^V(X_2)RT}{p^{\ominus}\Lambda(X_2)^3}$$

where $g_e(X_2)$ is the degeneracy of the electronic ground state of X_2. It follows from eqn 74.5 that the equilibrium constant is

$$K=\frac{kT}{p^{\ominus}}\left(\frac{g_e(X)^2}{g_e(X_2)}\right)\left(\frac{1}{q^V(X_2)q^R(X_2)}\right)\times\left(\frac{\Lambda(X_2)}{\Lambda(X)^2}\right)^3 e^{-D_0(X-X)/RT} \qquad (74.6)$$

(We have used $R/N_A=k$.) All the quantities in this expression can be calculated from spectroscopic data. Expressions for the Λs, the thermal wavelengths of the species, are given in eqn 52.7b of Topic 52 ($\Lambda=h/(2\pi mkT)^{1/2}$) and depend on the masses of the species and the temperature; the expressions for the rotational and vibrational partition functions are also available in Topic 52 as eqns 52.13–52.15 ($q^R=kT/\sigma hc\tilde{B}$ for linear molecules and $q^V=1/(1-e^{-\beta hc\tilde{\nu}})$) and depend on the rotational constant and vibrational wavenumber of the molecule.

Example 74.1 Calculating an equilibrium constant

Calculation is sometimes the only way to arrive at the value of an equilibrium constant, for experimental values are often not available. Evaluate the equilibrium constant for the dissociation $Na_2(g)\rightarrow 2\,Na(g)$ at 1000 K from the following data: $\tilde{B}=0.1547\ \mathrm{cm^{-1}}$, $\tilde{\nu}=159.2\ \mathrm{cm^{-1}}$, $D_0=70.4\ \mathrm{kJ\ mol^{-1}}$. The Na atoms have doublet ground terms.

Method The partition functions required are specified in eqn 74.6. They are evaluated by using the expressions in Topic 52 quoted above. For a homonuclear diatomic molecule, $\sigma=2$. In the evaluation of $kT/p^{\ominus}$ use $p^{\ominus}=10^5$ Pa and $1\ \mathrm{Pa\ m^3}=1$ J.

Answer The partition functions and other quantities required are as follows:

$\Lambda(Na_2)=8.14\ \mathrm{pm}$	$\Lambda(Na)=11.5\ \mathrm{pm}$	
$q^R(Na_2)=2246$	$q^V(Na_2)=4.885$	
$g(Na)=2$	$g(Na_2)=1$	$D_0/RT=8.47\ldots$

Then, from eqn 74.6,

$$K=\frac{(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})\times(1000\ \mathrm{K})}{10^5}\times2^2$$
$$\times\frac{1}{2246\times4.885}\times\left(\frac{8.14\times10^{-12}\ \mathrm{m}}{(11.5\times10^{-12}\ \mathrm{m})^2}\right)^3\times e^{-8.47\ldots}$$
$$=2.47$$

We have used $1\ \mathrm{J}=1\ \mathrm{kg\,m^2\,s^{-2}}$ and $1\ \mathrm{Pa}=1\ \mathrm{kg\,m^{-1}\,s^{-1}}$.

Self-test 74.1 Evaluate K at 1500 K.

Answer: 52

74.2 Contributions to the equilibrium constant

We are now in a position to appreciate the physical basis of equilibrium constants. To see what is involved, consider a simple $R\rightleftharpoons P$ gas-phase equilibrium (R for reactants, P for products).

Figure 74.2 shows two sets of energy levels; one set of states belongs to R, and the other belongs to P. The populations of the states are given by the Boltzmann distribution, and are independent of whether any given state happens to belong to R or to P. We can therefore imagine a single Boltzmann distribution spreading, without distinction, over the two sets of states. If the spacings of R and P are similar (as in Fig. 74.2), and P lies above R, the diagram indicates that R will dominate in the equilibrium mixture. However, if P has a high density of states (a large number of states in a given energy range, as in Fig. 74.3), then even though its zero-point energy lies above that of R, the species P might still dominate at equilibrium.

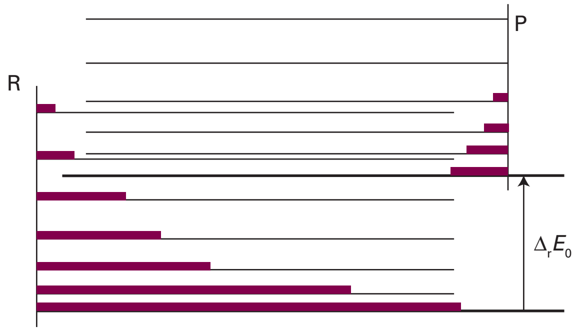

Figure 74.2 The array of R(eactants) and P(roducts) energy levels. At equilibrium all are accessible (to differing extents, depending on the temperature), and the equilibrium composition of the system reflects the overall Boltzmann distribution of populations. As Δ_rE_0 increases, R becomes dominant.

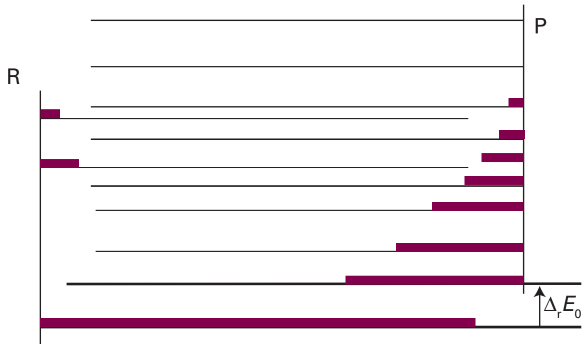

Figure 74.3 It is important to take into account the densities of states of the molecules. Even though P might lie above R in energy (that is, $\Delta_r E_0$ is positive), P might have so many states that its total population dominates in the mixture. In classical thermodynamic terms, we have to take entropies into account as well as enthalpies when considering equilibria.

It is quite easy to show (see the *Justification* below) that the ratio of numbers of R and P molecules at equilibrium is given by

$$\frac{N_P}{N_R} = \frac{q_P}{q_R} e^{-\Delta_r E_0/RT} \qquad (74.7a)$$

and therefore that the equilibrium constant for the reaction is

$$K = \frac{q_P}{q_R} e^{-\Delta_r E_0/RT} \qquad (74.7b)$$

just as would be obtained from eqn 74.4. For an R ⇌ P equilibrium, the V factors in the partition functions cancel, so the appearance of q in place of $q^{\ominus}$ has no effect. In the case of a more general reaction, the conversion from q to $q^{\ominus}$ comes about at the stage of converting the pressures that occur in K to numbers of molecules.

Justification 74.2 The equilibrium constant in terms of the partition function 2

The population in a state i of the composite (R,P) system is

$$n_i = \frac{N e^{-\beta\varepsilon_i}}{q}$$

where N is the total number of molecules and q is the partition function for the composite system. The total number of R molecules is the sum of these populations taken over the states belonging to R; these states we label r with energies ε_r. The total number of P molecules is the sum over the states belonging to P; these states we label P with energies ε'_p (the prime is explained in a moment):

$$N_R = \sum_r n_r = \frac{N}{q}\sum_r e^{-\beta\varepsilon_r} \qquad N_P = \sum_p n_p = \frac{N}{q}\sum_p e^{-\beta\varepsilon'_p}$$

The sum over the states of R is its partition function, q_R, so

$$N_R = \frac{N q_R}{q}$$

The sum over the states of P is also a partition function, but the energies are measured from the ground state of the combined system, which is the ground state of R. However, because $\varepsilon'_p = \varepsilon_p + \Delta\varepsilon_0$ where $\Delta\varepsilon_0$ is the separation of zero-point energies,

$$N_P = \frac{N}{q}\sum_p e^{-\beta(\varepsilon_p+\Delta\varepsilon_0)} = \frac{N}{q}\left(\sum_p e^{-\beta\varepsilon_p}\right)e^{-\beta\Delta\varepsilon_0} = \frac{Nq_P}{q}e^{-\Delta E_0/RT}$$

The switch from $\Delta\varepsilon_0/k$ to $\Delta_r E_0/R$ in the last step is the conversion of molecular energies to molar energies: $E_0 = N_A\varepsilon$ and $R = N_A k$.

The equilibrium constant of the R ⇌ P reaction is proportional to the ratio of the numbers of the two types of molecule. Therefore,

$$K = \frac{N_P}{N_R} = \frac{q_P}{q_R} e^{-\Delta_r E_0/RT}$$

as in eqn 74.7b.

The content of eqn 74.7 can be seen most clearly by exaggerating the molecular features that contribute to it. We shall suppose that R has only a single accessible level, which implies that $q_R = 1$. We also suppose that P has a large number of evenly, closely spaced levels (Fig. 74.4). The partition function of P is then $q_P = kT/\varepsilon$ (see Topic 52). In this model system, the equilibrium constant is

$$K = \frac{kT}{\varepsilon} e^{-\Delta_r E_0/RT} \qquad (74.8)$$

When $\Delta_r E_0$ is very large, the exponential term dominates and $K \ll 1$, which implies that very little P is present at equilibrium.

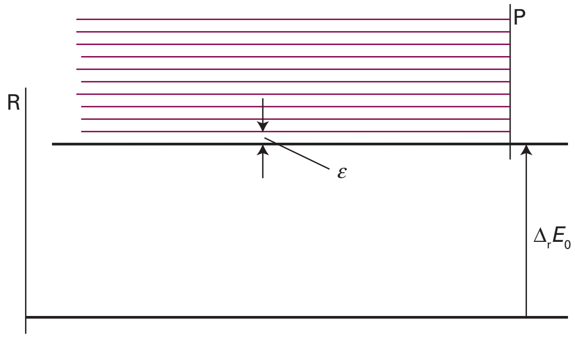

Figure 74.4 The model used in the text for exploring the effects of energy separations and densities of states on equilibria. The products P can dominate provided $\Delta_r E_0$ is not too large and P has an appreciable density of states.

When $\Delta_r E_0$ is small but still positive, K can exceed 1 because the factor kT/ε may be large enough to overcome the small size of the exponential term. The size of K then reflects the predominance of P at equilibrium on account of its high density of states.

Brief illustration 74.1 Interpretation of the equilibrium constant

Suppose P has an array of energy levels separated by 1.00 cm^{-1} beginning 1000 cm^{-1} above the single state of R. The equilibrium constant of the system at 25 °C is calculated, with wavenumbers converted to energies, by writing

$$\begin{aligned}\frac{kT}{\varepsilon} &= \frac{kT}{hc\tilde{\nu}}\\ &= \frac{(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})\times(298\ \mathrm{K})}{(6.626\times10^{-34}\ \mathrm{J\ s})\times(2.998\times10^{10}\ \mathrm{cm\ s^{-1}})\times(1.00\ \mathrm{cm^{-1}})}\\ &= 207\end{aligned}$$

$$\begin{aligned}\frac{\Delta_r E_0}{RT} = \frac{\Delta_r\varepsilon_0}{kT} &= \frac{hc\Delta_r\tilde{\nu}_0}{kT}\\ &= \frac{(6.626\times10^{-34}\ \mathrm{J\ s})\times(2.998\times10^{10}\ \mathrm{cm\,s^{-1}})\times(1000\ \mathrm{cm^{-1}})}{(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})\times(298\ \mathrm{K})}\\ &= 4.82\ldots\end{aligned}$$

Therefore,

$$K = 207\times e^{-4.82\ldots} = 1.7$$

and products are more abundant than reactants, despite lying at a higher energy.

Self-test 74.2 For the same separation of ground states, what separation of energy levels of P (expressed as a wavenumber) would correspond to $K=1$?

Answer: 1.66 cm^{-1}

The model also shows why the Gibbs energy, G, and not just the enthalpy, determines the position of equilibrium. It shows that the density of states (and hence the entropy) of each species as well as their relative energies controls the distribution of populations and hence the value of the equilibrium constant. This competition is mirrored in eqn 73.13 of Topic 73 ($\Delta_r G^{\ominus} = -RT\ln K$), as can be seen most clearly by using $\Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$ and writing it in the form

$$K = e^{-\Delta_r H^{\ominus}/RT} e^{\Delta_r S^{\ominus}/R} \qquad (74.9)$$

Note that a positive reaction enthalpy results in a lowering of the equilibrium constant (that is, an endothermic reaction can be expected to have an equilibrium composition that favours the reactants). However, if there is positive reaction entropy, then the equilibrium composition may favour products, despite the endothermic character of the reaction.

Checklist of concepts

☐ **1.** The equilibrium constant can be expressed in terms of the standard molar partition functions of the reactants and products.

☐ **2.** The density of states (and hence the entropy) of each species as well as their relative energies controls the distribution of populations and hence the value of the equilibrium constant.

Checklist of equations

Property	Equation	Comment	Equation number
Standard molar Gibbs energy	$G_m^{\ominus}(\mathrm{J}) = G_m^{\ominus}(\mathrm{J},0) - RT\ln(q_m^{\ominus}(\mathrm{J})/N_A)$	Independent molecules, $q_m = q/n$	74.2
Equilibrium constant	$K = \left\{\prod_{\mathrm{J}}(q_m^{\ominus}(\mathrm{J})/N_A)^{\nu_{\mathrm{J}}}\right\} e^{-\Delta_r E_0/RT}$	Independent molecules	74.4b

TOPIC 75

The response of equilibria to the conditions

Contents

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➤ Why do you need to know this material?

Chemists and chemical engineers often need to know whether the yield of a reaction that reaches equilibrium can be improved by changing the conditions, such as the temperature or the pressure. The thermodynamic arguments presented here let us make predictions about these questions.

➤ What is the key idea?

A system at equilibrium, when subjected to a disturbance, responds in a way that tends to minimize the effect of the disturbance.

➤ What do you need to know already?

This material develops the discussion of the thermodynamic description of chemical equilibrium (Topic 73). It uses a result (the Gibbs–Helmholtz equation) derived in Topic 66. Some of the explanation draws on the discussion of the statistical basis of the equilibrium constant (Topic 74), but only qualitatively.

Equilibria respond to changes in pressure, temperature, and concentrations of reactants and products. The equilibrium constant for a reaction is not affected by the presence of a catalyst or an enzyme (a biological catalyst). Catalysts increase the rate at which equilibrium is attained but do not affect its position. However, it is important to note that in industry reactions rarely reach equilibrium, partly on account of the rates at which reactants mix.

75.1 The response of equilibria to pressure

The thermodynamic equilibrium constant depends on the value of $\Delta_r G^{\ominus}$, which is defined at a single, standard pressure (Topic 65). The value of $\Delta_r G^{\ominus}$, and hence of *K*, is therefore independent of the pressure at which the equilibrium is actually established. Formally we may express this independence as

$$\left(\frac{\partial K}{\partial p}\right)_T = 0 \qquad K \text{ independent of } p \qquad (75.1)$$

The conclusion that *K* is independent of pressure does not necessarily mean that the equilibrium composition is independent of the pressure, and its effect depends on how the pressure is changed. The pressure within a reaction vessel can be increased by injecting an inert gas into it. However, so long as the gases are perfect, this addition of gas leaves all the partial pressures of the reacting gases unchanged: the partial pressure of a perfect gas is the pressure it would exert if it were alone in the container, so the presence of another gas has no effect. It follows that pressurization by the addition of an inert gas has no effect on the equilibrium composition of the system (provided the gases are perfect). Alternatively, the pressure of the system may be increased by confining the gases to a smaller volume (that is, by compression). Now the individual partial pressures are changed but their ratio (as it appears in the equilibrium constant) remains the same. Consider, for instance, the perfect gas equilibrium A $\rightleftharpoons$ 2 B, for which the equilibrium constant is

$$K=\frac{(p_B/p^\ominus)^2}{p_A/p^\ominus}=\frac{p_B^2}{p_A p^\ominus}$$

The right-hand side of this expression remains constant only if an increase in p_A cancels an increase in the *square* of p_B. This relatively steep increase of p_A compared to p_B will occur if the equilibrium composition shifts in favour of A at the expense of B. Then the number of A molecules will increase as the volume of the container is decreased and its partial pressure will rise more rapidly than can be ascribed to a simple change in volume alone (Fig. 75.1).

The increase in the number of A molecules and the corresponding decrease in the number of B molecules in the equilibrium A $\rightleftharpoons$ 2 B is a special case of a principle proposed by the French chemist Henri Le Chatelier. **Le Chatelier's principle** states that:

> A system at equilibrium, when subjected to a disturbance, responds in a way that tends to minimize the effect of the disturbance.

The principle implies that if a system at equilibrium is compressed, then the reaction will adjust so as to minimize the increase in pressure. This it can do by reducing the number of particles in the gas phase, which implies a shift A ← 2 B.

To treat the effect of compression quantitatively, we suppose that there is an amount n of A present initially (and no B). At equilibrium the amount of A is $(1-\alpha)n$ and the amount of B is $2\alpha n$, where α is the extent of dissociation of A into 2B. It follows that the mole fractions present at equilibrium are

$$x_A=\frac{(1-\alpha)n}{(1-\alpha)n+2\alpha n}=\frac{1-\alpha}{1+\alpha}\qquad x_B=\frac{2\alpha}{1+\alpha}$$

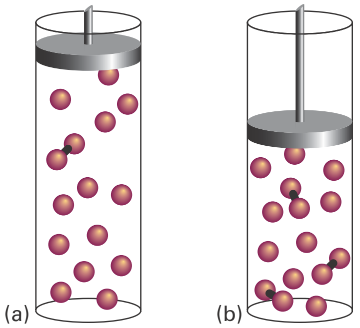

Figure 75.1 When a reaction at equilibrium is compressed (from *a* to *b*), the reaction responds by reducing the number of molecules in the gas phase (in this case by producing the dimers represented by the linked spheres).

The equilibrium constant for the reaction is

$$K=\frac{p_B^2}{p_A p^\ominus}=\frac{x_B^2 p^2}{x_A p p^\ominus}=\frac{4\alpha^2}{1-\alpha^2}\frac{p}{p^\ominus}$$

which rearranges to

$$\alpha=\left(\frac{1}{1+4p/Kp^\ominus}\right)^{1/2} \tag{75.2}$$

This formula shows that, even though K is independent of pressure, the amounts of A and B do depend on pressure (Fig. 75.2). It also shows that, as p is increased, α decreases, in accord with Le Chatelier's principle.

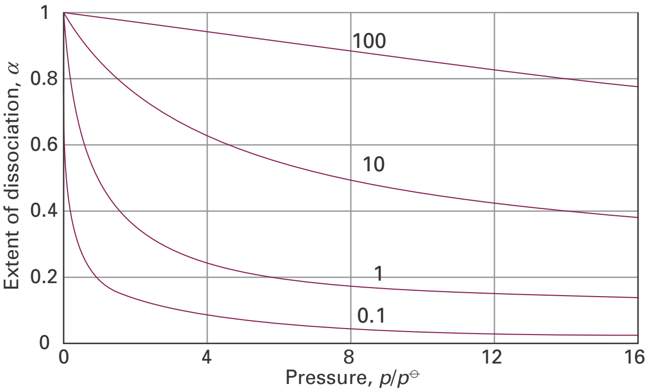

Figure 75.2 The pressure dependence of the degree of dissociation, α, at equilibrium for an A(g) $\rightleftharpoons$ 2 B(g) reaction for different values of the equilibrium constant K. The value $\alpha=0$ corresponds to pure A, $\alpha=1$ to pure B.

Brief illustration 75.1 The effect of compression

To predict the effect of compression on the composition of the ammonia synthesis at equilibrium, $N_2(g)+3\,H_2(g)\rightarrow 2\,NH_3(g)$, we note that the number of gas molecules decreases (from 4 to 2). So, Le Chatelier's principle predicts that compression will favour the product. The equilibrium constant, treating all gases as perfect, is

$$K=\frac{(p_{NH_3}/p^\ominus)^2}{(p_{N_2}/p^\ominus)(p_{H_2}/p^\ominus)^3}=\frac{p_{NH_3}^2 p^{\ominus 2}}{p_{N_2}p_{H_2}^3}=\frac{x_{NH_3}^2 p^2 p^{\ominus 2}}{x_{N_2}x_{H_2}^3 p^4}=\frac{K_x p^{\ominus 2}}{p^2}$$

where K_x is the part of the equilibrium constant expression that contains the equilibrium mole fractions of reactants and products (note that unlike K itself, K_x is not an equilibrium constant). Therefore, doubling the pressure must increase K_x by a factor of 4 to preserve the value of K.

Self-test 75.1 Predict the effect of a compression that results in a tenfold pressure increase on the equilibrium composition of the reaction $3\,N_2(g)+H_2(g)\rightarrow 2\,N_3H(g)$.

Answer: 100-fold increase in K_x

75.2 The response of equilibria to temperature

Le Chatelier's principle predicts that a system at equilibrium will tend to shift in the endothermic direction if the temperature is raised, for then energy is absorbed as heat and the rise in temperature is opposed. Conversely, an equilibrium can be expected to shift in the exothermic direction if the temperature is lowered, for then energy is released as heat and the reduction in temperature is opposed. These conclusions can be summarized as follows:

Exothermic reactions ($\Delta_r H^\ominus < 0$): increased temperature favours the reactants.

Endothermic reactions ($\Delta_r H^\ominus > 0$): increased temperature favours the products.

We shall now justify these remarks and see how to express the changes quantitatively.

(a) The van 't Hoff equation

The **van 't Hoff equation**, which is derived in the following *Justification*, is an expression for the slope of a plot of the equilibrium constant (specifically, ln K) as a function of temperature. It may be expressed in either of two ways:

$$\text{(a)}\ \frac{\mathrm{d}\ln K}{\mathrm{d}T}=\frac{\Delta_r H^\ominus}{RT^2} \qquad \text{(b)}\ \frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)}=-\frac{\Delta_r H^\ominus}{R} \qquad (75.3)$$

van 't Hoff equation

Justification 75.1 The van 't Hoff equation

We start with eqn 73.13 of Topic 73 ($-RT\ln K=\Delta_r G^\ominus$) in the form

$$\ln K=-\frac{\Delta_r G^\ominus}{RT}$$

Differentiation of ln K with respect to temperature then gives

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T}=-\frac{1}{R}\frac{\mathrm{d}(\Delta_r G^\ominus/T)}{\mathrm{d}T}$$

The differentials are complete because K and $\Delta_r G^\ominus$ depend only on temperature, not on pressure. To develop this equation we use the Gibbs–Helmholtz equation (eqn 66.9 of Topic 66, $\mathrm{d}(\Delta G/T)/\mathrm{d}T=-\Delta H/T^2$) in the form

$$\frac{\mathrm{d}\left(\Delta_r G^\ominus/T\right)}{\mathrm{d}T}=-\frac{\Delta_r H^\ominus}{T^2}$$

where $\Delta_r H^\ominus$ is the standard reaction enthalpy at the temperature T. Combining the two equations gives the van 't Hoff equation, eqn 75.3a. The second form of the equation is obtained by noting that

$$\frac{\mathrm{d}(1/T)}{\mathrm{d}T}=-\frac{1}{T^2},\quad \text{so}\quad \mathrm{d}T=-T^2\mathrm{d}(1/T)$$

It follows that eqn 75.3a can be rewritten as

$$-\frac{\mathrm{d}\ln K}{T^2\mathrm{d}(1/T)}=\frac{\Delta_r H^\ominus}{RT^2}$$

which simplifies into eqn 75.3b.

Equation 75.3a shows that d ln $K/\mathrm{d}T<0$ (and therefore that $\mathrm{d}K/\mathrm{d}T<0$) for an exothermic reaction ($\Delta_r H^\ominus<0$). A negative slope means that ln K, and therefore K itself, decreases as the temperature rises. Therefore, as asserted above, in the case of an exothermic reaction the equilibrium shifts away from products. The opposite occurs in the case of endothermic reactions.

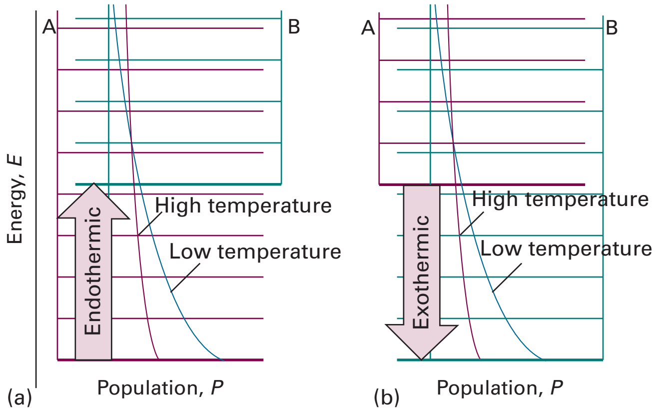

Figure 75.3 The effect of temperature on a chemical equilibrium can be interpreted in terms of the change in the Boltzmann distribution with temperature and the effect of that change in the population of the species. (a) In an endothermic reaction, the population of B increases at the expense of A as the temperature is raised. (b) In an exothermic reaction, the opposite happens.

Some insight into the thermodynamic basis of this behaviour comes from the expression $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$ written in the form $-\Delta_r G^\ominus/T = -\Delta_r H^\ominus/T + \Delta_r S^\ominus$. When the reaction is exothermic, $-\Delta_r H^\ominus/T$ corresponds to a positive change of entropy of the surroundings and favours the formation of products. When the temperature is raised, $-\Delta_r H^\ominus/T$ decreases and the increasing entropy of the surroundings has a less important role. As a result, the equilibrium lies less to the right. When the reaction is endothermic, the principal factor is the increasing entropy of the reaction system. The importance of the unfavourable change of entropy of the surroundings is reduced if the temperature is raised (because then $\Delta_r H^\ominus/T$ is smaller), and the reaction is able to shift towards products.

From a molecular perspective, consider the typical arrangement of energy levels for an endothermic reaction, as shown in Fig. 75.3a. When the temperature is increased, the Boltzmann distribution adjusts and the populations change as shown. The change corresponds to an increased population of the higher energy states at the expense of the population of the lower energy states. We see that the states that arise from the B molecules become more populated at the expense of the A molecules. Therefore, the total population of B states increases, and B becomes more abundant in the equilibrium mixture. Conversely, if the reaction is exothermic (Fig. 75.3b), then an increase in temperature increases the population of the A states (which start at higher energy) at the expense of the B states, so the reactants become more abundant.

Example 75.1 Measuring a reaction enthalpy

The data below show the temperature variation of the equilibrium constant of the reaction $Ag_2CO_3(s) \rightleftharpoons Ag_2O(s) + CO_2(g)$. Calculate the standard reaction enthalpy of the decomposition.

T/K	350	400	450	500
K	3.98×10^{-4}	1.41×10^{-2}	1.86×10^{-1}	1.48

Method It follows from eqn 75.3b that, provided the reaction enthalpy can be assumed to be independent of temperature, a plot of $-\ln K$ against $1/T$ should be a straight line of slope $\Delta_r H^\ominus/R$.

Answer We draw up the following table:

T/K	350	400	450	500
$(10^3\ \mathrm{K})/T$	2.86	2.50	2.22	2.00
$-\ln K$	7.83	4.26	1.68	−0.39

These points are plotted in Fig. 75.4. The slope of the graph is $+9.6\times10^3$, so

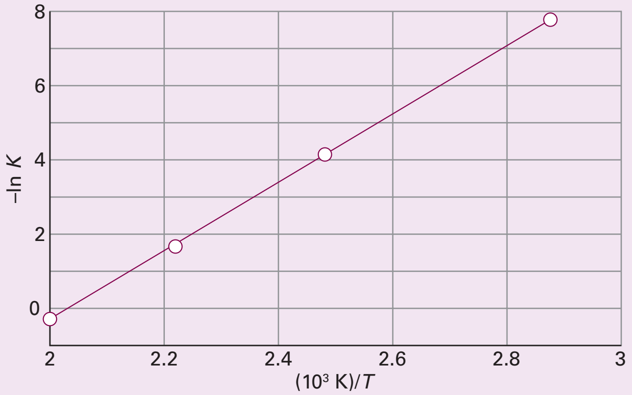

Figure 75.4 When $-\ln K$ is plotted against $1/T$, a straight line is expected with slope equal to $\Delta_r H^\ominus/R$ if the standard reaction enthalpy does not vary appreciably with temperature. This is a non-calorimetric method for the measurement of reaction enthalpies. The data points are from Example 75.1.

$$\Delta_r H^\ominus = (+9.6\times10^3\,\mathrm{K})\times R = +80\,\mathrm{kJ\,mol^{-1}}$$

The temperature dependence of the equilibrium constant provides a non-calorimetric method of determining $\Delta_r H^\ominus$. A drawback is that the reaction enthalpy is actually temperature-dependent, so the plot is not expected to be perfectly linear. However, the temperature dependence is weak in many cases, so the plot is reasonably straight. In practice, the method is not very accurate, but it is often the only method available.

Self-test 75.2 The equilibrium constant of the reaction $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$ is 4.0×10^{24} at 300 K, 2.5×10^{10} at 500 K, and 3.0×10^4 at 700 K. Estimate the reaction enthalpy at 500 K.

Answer: −200 kJ mol⁻¹

(b) The value of *K* at different temperatures

To find the value of the equilibrium constant at a temperature T_2 in terms of its value K_1 at another temperature T_1, we integrate eqn 75.3b between these two temperatures:

$$\ln K_2 - \ln K_1 = -\frac{1}{R}\int_{1/T_1}^{1/T_2} \Delta_r H^\ominus \,\mathrm{d}(1/T) \qquad (75.4)$$

If we need to consider the temperature dependence of $\Delta_r H^\ominus$, we can use Kirchhoff's law (Topic 57). However, if we suppose that $\Delta_r H^\ominus$ varies only slightly with temperature over the temperature range of interest, we may take it outside the integral. It follows that

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (75.5)$$

Brief illustration 75.2 The temperature dependence of *K*

To estimate the equilibrium constant for the synthesis of ammonia at 500 K from its value at 298 K (6.1×10^5 for the reaction $N_2(g)+3\,H_2(g)\rightarrow 2\,NH_3(g)$) we use the standard reaction enthalpy, which can be obtained from Table 57.4 in the *Resource section* by using $\Delta_r H^\ominus = 2\Delta_f H^\ominus(NH_3,g)$, and assume that its value is constant over the range of temperatures. Then, with $\Delta_r H^\ominus = -92.2$ kJ mol^{-1}, from eqn 75.5 we find

$$\begin{aligned}\ln K_2 &= \ln(6.1\times10^5) - \frac{(-92.2\times10^3\,\mathrm{J\,mol^{-1}})}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\left(\frac{1}{500\,\mathrm{K}}-\frac{1}{298\,\mathrm{K}}\right)\\ &= -1.71\ldots\end{aligned}$$

It follows that $K_2 = 0.18$, a lower value than at 298 K, as expected for this exothermic reaction.

Self-test 75.3 The equilibrium constant for $N_2O_4(g)\rightleftharpoons 2\,NO_2(g)$ was calculated in Self-test 73.6 Estimate its value at 100 °C.

Answer: 15

Knowledge of the temperature dependence of the equilibrium constant for a reaction can be useful in the design of laboratory and industrial processes. For example, synthetic chemists can improve the yield of a reaction by changing the temperature of the reaction mixture. Also, reduction of a metal oxide with carbon or carbon monoxide results in the extraction of the metal when the process is carried out at a temperature for which $K \gg 1$.

Checklist of concepts

☐ 1. The thermodynamic equilibrium constant is independent of pressure.

☐ 2. **Le Chatelier's principle** states that a system at equilibrium, when subjected to a disturbance, responds in a way that tends to minimize the effect of the disturbance.

☐ 3. Even though *K* is independent of pressure, the composition of the equilibrium mixture may depend on pressure.

☐ 4. For exothermic reactions ($\Delta_r H^\ominus < 0$) an increase in temperature favours the reactants; for endothermic reactions ($\Delta_r H^\ominus > 0$) an increase in temperature favours the products.

☐ 5. The **van 't Hoff equation** (see below) is an expression for the dependence of the equilibrium constant on the temperature.

Checklist of equations

Property	Equation	Comment	Equation number
Variation of *K* with pressure	$(\partial K/\partial p)_T = 0$		75.1
Variation of *K* with temperature	$\mathrm{d}(\ln K)/\mathrm{d}T = \Delta_r H^\ominus/RT^2$	van 't Hoff equation	75.3
	$\mathrm{d}(\ln K)/\mathrm{d}(1/T) = -(\Delta_r H^\ominus/R)$		
	$\ln K_2 - \ln K_1 = -(\Delta_r H^\ominus/R)(1/T_2 - 1/T_1)$	$\Delta_r H^\ominus$ independent of temperature	75.5

TOPIC 76

Electrochemical cells

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➤ Why do you need to know this material?

Electrochemistry is already of considerable technological importance, as it underlies the operation of batteries and the industrial production and refinement of some metals. Concepts arising in electrochemistry are also used to assess the viability of redox reactions, and its arguments are central to many discussions of inorganic chemistry. Electrochemistry also provides sensitive techniques for the measurement of thermodynamic properties.

➤ What is the key idea?

The electrical work that a cell reaction can produce is equal to the reaction Gibbs energy.

➤ What do you need to know already?

You need to know the connection between Gibbs energy and non-expansion work (Topic 64), how the reaction Gibbs energy is defined in terms of the advancement of the reaction, and how its value is related to the reaction quotient (Topic 73).

Thermodynamic arguments about equilibrium, with certain changes of technical detail, can be used to describe the properties of reactions taking place in electrochemical cells. The ability to make very precise measurements of currents and potential differences (‘voltages’) means that electrochemical methods can be used to determine thermodynamic properties of reactions that may be inaccessible by other methods.

An **electrochemical cell** consists of two **electrodes**, or metallic conductors, in contact with an **electrolyte**, an ionic conductor (which may be a solution, a liquid, or a solid). An electrode and its electrolyte comprise an **electrode compartment**. The two electrodes may share the same compartment. The various kinds of electrode are summarized in Table 76.1. Any ‘inert metal’ shown as part of the specification is present to act as a source or sink of electrons, but takes no part in the reaction other than perhaps acting as a catalyst for it. If the electrolytes are different, the two compartments may be joined by a **salt**

Table 76.1 Varieties of electrode

Electrode type	Designation	Redox couple	Half-reaction
Metal/metal ion	$M(s)\vert M^+(aq)$	M^+/M	$M^+(aq)+e^- \rightarrow M(s)$
Gas	$Pt(s)\vert X_2(g)\vert X^+(aq)$	X^+/X_2	$X^+(aq)+e^- \rightarrow \frac{1}{2}X_2(g)$
	$Pt(s)\vert X_2(g)\vert X^-(aq)$	X_2/X^-	$\frac{1}{2}X_2(g)+e^- \rightarrow X^-(aq)$
Metal/insoluble salt	$M(s)\vert MX(s)\vert X^-(aq)$	$MX/M,X^-$	$MX(s)+e^- \rightarrow M(s)+X^-(aq)$
Redox	$Pt(s)\vert M^+(aq),M^{2+}(aq)$	M^{2+}/M^+	$M^{2+}(aq)+e^- \rightarrow M^+(aq)$

bridge, which is a tube containing a concentrated electrolyte solution (almost always potassium chloride in agar jelly) that completes the electrical circuit and enables the cell to function. A **galvanic cell** (also called a 'voltaic cell') is an electrochemical cell that produces electricity as a result of the spontaneous reaction occurring inside it. An **electrolytic cell** is an electrochemical cell in which a non-spontaneous reaction is driven by an external source of current.

76.1 Half-reactions and electrodes

It will be familiar from introductory chemistry that **oxidation** is the removal of electrons from a species, **reduction** is the addition of electrons to a species, and a **redox reaction** is a reaction in which there is a transfer of electrons from one species to another. The electron transfer may be accompanied by other events, such as atom or ion transfer, but the net effect is electron transfer and hence a change in oxidation number of an element. The **reducing agent** (or 'reductant') is the electron donor; the **oxidizing agent** (or 'oxidant') is the electron acceptor.

It should also be familiar that any redox reaction may be expressed as the difference of two reduction **half-reactions**, which are conceptual reactions showing the gain of electrons. Even reactions that are not redox reactions may often be expressed as the difference of two reduction half-reactions. The reduced and oxidized species in a half-reaction form a **redox couple**. In general we write a couple as Ox/Red and the corresponding reduction half-reaction as

$$\mathrm{Ox} + \nu\mathrm{e}^- \rightarrow \mathrm{Red} \qquad (76.1)$$

General reduction half-reaction

Brief illustration 76.1 Half-reactions

The dissolution of silver chloride in water $\mathrm{AgCl(s)} \rightarrow \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)}$, which is not a redox reaction, can be written as the difference of the following two reduction half-reactions:

$$\mathrm{AgCl(s)} + \mathrm{e}^- \rightarrow \mathrm{Ag(s)} + \mathrm{Cl^-(aq)}$$

$$\mathrm{Ag^+(aq)} + \mathrm{e}^- \rightarrow \mathrm{Ag(s)}$$

$$\text{Difference:}\quad \mathrm{AgCl(s)} - \mathrm{Ag^+(aq)} \rightarrow \mathrm{Cl^-(aq)}$$

$$\text{Rearrange:}\quad \mathrm{AgCl(s)} \rightarrow \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)}$$

The redox couples are AgCl/Ag, $\mathrm{Cl^-}$ and $\mathrm{Ag^+}$/Ag, respectively.

Self-test 76.1 Express the formation of H_2O from H_2 and O_2 in acidic solution (a redox reaction) as the difference of two reduction half-reactions.

Answer: $4\,\mathrm{H^+(aq)} + 4\,\mathrm{e}^- \rightarrow 2\,\mathrm{H_2(g)}$, $\mathrm{O_2(g)} + 4\,\mathrm{H^+(aq)} + 4\,\mathrm{e}^- \rightarrow 2\,\mathrm{H_2O(l)}$

We shall often find it useful to express the composition of an electrode compartment in terms of the reaction quotient, Q, for the half-reaction. This quotient is defined like the reaction quotient for the overall reaction (Topic 73), but the electrons are ignored.

Brief illustration 76.2 The reaction quotient of a half-reaction

The reaction quotient for the reduction of O_2 to H_2O in acid solution, $\mathrm{O_2(g)} + 4\,\mathrm{H^+(aq)} + 4\,\mathrm{e}^- \rightarrow 2\,\mathrm{H_2O(l)}$, is

$$Q = \frac{a_{\mathrm{H_2O}}^2}{a_{\mathrm{O_2}}a_{\mathrm{H^+}}^4} = \frac{1}{(p_{\mathrm{O_2}}/p^{\ominus})a_{\mathrm{H^+}}^4} = \frac{p^{\ominus}}{p_{\mathrm{O_2}}a_{\mathrm{H^+}}^4}$$

The approximations used in the second step are that the activity of water is 1 (because the solution is dilute) and the oxygen behaves as a perfect gas, so $a_{\mathrm{O_2}} \approx p_{\mathrm{O_2}}/p^{\ominus}$.

Self-test 76.2 Write the half-reaction and the reaction quotient for a chlorine gas electrode.

Answer: $\mathrm{Cl_2(g)} + 2\,\mathrm{e}^- \rightarrow 2\,\mathrm{Cl^-(aq)}$, $Q = a_{\mathrm{Cl^-}}^2 p^{\ominus}/p_{\mathrm{Cl_2}}$

The reduction and oxidation processes responsible for the overall reaction in a cell are separated in space: oxidation takes place at one electrode and reduction takes place at the other. As the reaction proceeds, the electrons released in the oxidation $\mathrm{Red_1} \rightarrow \mathrm{Ox_1} + \nu\,\mathrm{e}^-$ at one electrode travel through the external circuit and re-enter the cell through the other electrode. There they bring about reduction $\mathrm{Ox_2} + \nu\,\mathrm{e}^- \rightarrow \mathrm{Red_2}$. The electrode at which oxidation occurs is called the **anode**; the electrode at which reduction occurs is called the **cathode**. In a galvanic cell, the cathode has a higher potential than the anode: the species undergoing reduction, $\mathrm{Ox_2}$, withdraws electrons from its electrode (the cathode, Fig. 76.1), so leaving a relative positive charge on it (corresponding to a high potential). At the anode, oxidation results in the transfer of electrons to the electrode, so giving it a relative negative charge (corresponding to a low potential).

76.2 Varieties of cells

The simplest type of cell has a single electrolyte common to both electrodes (as in Fig. 76.1). In some cases it is necessary to immerse the electrodes in different electrolytes, as in the 'Daniell cell' in which the redox couple at one electrode is $\mathrm{Cu^{2+}}$/Cu and at the other is $\mathrm{Zn^{2+}}$/Zn (Fig. 76.2). In an **electrolyte concentration cell**, the electrode compartments are identical except for the concentrations of the electrolytes. In an **electrode concentration cell** the electrodes themselves have

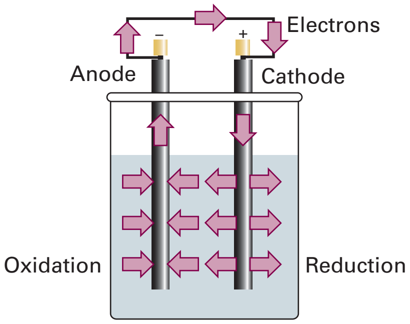

Figure 76.1 When a spontaneous reaction takes place in a galvanic cell, electrons are deposited in one electrode (the site of oxidation, the anode) and collected from another (the site of reduction, the cathode), and so there is a net flow of current which can be used to do work. Note that the + sign of the cathode can be interpreted as indicating the electrode at which electrons enter the cell, and the − sign of the anode is where the electrons leave the cell.

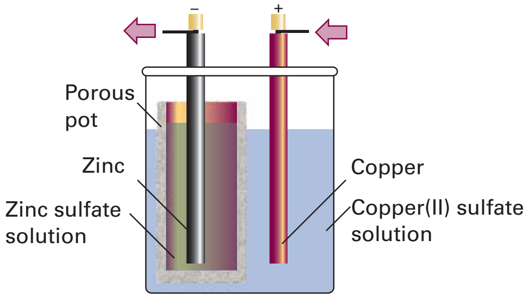

Figure 76.2 One version of the Daniell cell. The copper electrode is the cathode and the zinc electrode is the anode. Electrons leave the cell from the zinc electrode and enter it again through the copper electrode.

different concentrations, either because they are gas electrodes operating at different pressures or because they are amalgams (solutions in mercury) with different concentrations.

In a cell with two different electrolyte solutions in contact, as in the Daniell cell, there is an additional source of potential difference across the interface of the two electrolytes. This potential is called the **liquid junction potential**, E_{lj}. Another example of a junction potential is that between different concentrations of hydrochloric acid. At the junction, the mobile H^+ ions diffuse into the more dilute solution. The bulkier Cl^- ions follow, but initially do so more slowly, which results in a potential difference at the junction. The potential then settles down to a value such that, after that brief initial period, the ions diffuse at the same rates. Electrolyte concentration cells always have a liquid junction; electrode concentration cells do not.

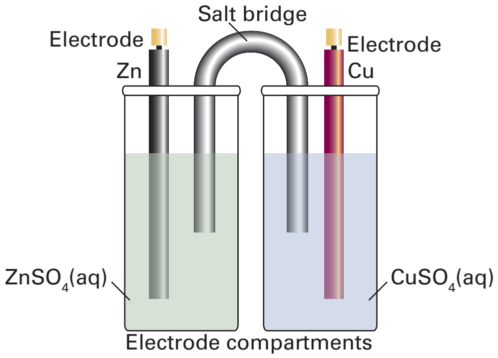

Figure 76.3 The salt bridge, essentially an inverted U-tube full of concentrated salt solution in a jelly, has two opposing liquid junction potentials which almost cancel.

The contribution of the liquid junction to the potential can be reduced (to about 1 to 2 mV) by joining the electrolyte compartments through a salt bridge (Fig. 76.3). The reason for the success of the salt bridge is that the liquid junction potentials at either end are largely independent of the concentrations of the two dilute solutions, and so nearly cancel.

The following conventions are used to denote cells:

- Phase boundaries are denoted by a vertical bar: |
- A liquid junction is denoted by a dotted vertical line: ⋮
- An interface for which it is assumed that the junction potential has been eliminated is denoted by a double vertical line: ||

When it is necessary to specify the 'left' and 'right' electrodes, the electrode on the left of the cell diagram (not necessarily in physical space) is denoted L and that on the right is denoted R. These letters may be used to denote the molalities, b (as b_{L} or b_{R}), and pressures, p (as p_{L} or p_{R}), of the electroactive species in each compartment of the cell.

Brief illustration 76.3 Cell notation

The cell in Fig. 76.4 is denoted

$$\mathrm{Pt(s)}|\mathrm{H_2}(\mathrm{g},p_{\mathrm{L}})|\mathrm{HCl(aq)}|\mathrm{AgCl(s)}|\mathrm{Ag(s)}$$

The cell in Fig. 76.2 is denoted

$$\mathrm{Zn(s)}|\mathrm{ZnSO_4}(\mathrm{aq},b_{\mathrm{L}})\vdots\mathrm{CuSO_4}(\mathrm{aq},b_{\mathrm{R}})|\mathrm{Cu(s)}$$

An example of an electrolyte concentration cell in which the liquid junction potential is assumed to be eliminated, as it is Fig. 76.3 but with compartments that differ only in concentration of the electroactive species, is denoted

$$\mathrm{Zn(s)}|\mathrm{ZnSO_4}(\mathrm{aq},b_{\mathrm{L}})||\mathrm{ZnSO_4}(\mathrm{aq},b_{\mathrm{R}})|\mathrm{Zn(s)}$$

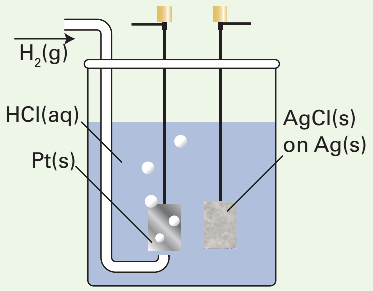

Figure 76.4 A cell with a common electrolyte: a hydrogen electrode on the left and a silver/silver chloride electrode on the right.

Self-test 76.3 Write the specification of a cell in which both electrodes are hydrogen electrodes and each compartment is hydrochloric acid; there is a salt bridge.

Answer: $Pt(s)|H_2(g,p_L)|\ HCl(aq,b_L)||HCl(aq,b_R)|H_2(g,p_R)|Pt(s)$

76.3 The cell potential

The current produced by a galvanic cell arises from the spontaneous chemical reaction taking place inside it. The **cell reaction** is the reaction in the cell written on the assumption that the right-hand electrode is the cathode, and hence that the spontaneous reaction is one in which reduction is taking place in the right-hand compartment. In Topic 77 we see how to predict if the right-hand electrode is in fact the cathode; if it is, then the cell reaction is spontaneous as written. If the left-hand electrode turns out to be the cathode, then the reverse of the corresponding cell reaction is spontaneous.

To write the cell reaction corresponding to a cell diagram, we first write the right-hand half-reaction as a reduction (because we have assumed that to be the spontaneous direction of the cell reaction). Then we subtract from it the left-hand reduction half-reaction (for, by implication, that electrode is the site of oxidation).

Brief illustration 76.4 The cell reaction

In the cell $Zn(s)|ZnSO_4(aq)||CuSO_4(aq)|Cu(s)$ the two electrodes and their reduction half-reactions are

$$\text{Right-hand electrode: } Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$$
$$\text{Left-hand electrode: } Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$$

Hence, the overall cell reaction is the difference:

$$Cu^{2+}(aq) - Zn^{2+}(aq) \rightarrow Cu(s) - Zn(s)$$

rearranged into

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$

Self-test 76.4 Construct the cell reaction for the cell $Pt(s)$, $H_2(g)|HCl(aq)|AgCl(s)|Ag(s)$.

Answer: $2\,AgCl(s) + H_2(g) \rightarrow 2\,Ag(s) + 2\,HCl(aq)$, as $2\,H^+(aq) + 2\,Cl^-(aq)$

(a) The cell potential and the reaction Gibbs energy

A cell in which the overall cell reaction has not reached chemical equilibrium can do electrical work as the reaction drives electrons through an external circuit. The work that a given transfer of electrons can accomplish depends on the potential difference between the two electrodes. When this potential difference is large, a given number of electrons travelling between the electrodes can do a lot of electrical work. When the potential difference is small, the same number of electrons can do only a little work. A cell in which the overall reaction is at equilibrium can do no work, and then its potential difference is zero.

According to the discussion in Topic 64, the maximum non-expansion work, which in the current context is electrical work, that a system (the cell) can do is given by eqn 64.17b ($w_{e,max} = \Delta G$), with ΔG identified (as we shall show) with the Gibbs energy of the cell reaction, $\Delta_r G$. It follows that to draw thermodynamic conclusions from measurements of the work a cell can do, we must ensure that the cell is operating reversibly, for only then is it producing maximum work. Moreover, as shown in Topic 73, the reaction Gibbs energy is actually a property relating to a specified composition of the reaction mixture (through eqn 73.9, $\Delta_r G = \Delta_r G^{\ominus} + RT \ln Q$). Therefore, to make use of $\Delta_r G$ we must ensure that the cell is operating reversibly at a specific, constant composition. Both these conditions are achieved by measuring the potential difference generated by the cell when it is balanced by an exactly opposing source of potential so that the cell reaction occurs reversibly, the composition is constant, and no current flows: in effect, the cell reaction is poised for change, but not actually changing. The resulting potential difference is called the **cell potential**, E_{cell}. The cell potential was formerly and is still widely called the *electromotive force* (emf). That name, however, has fallen out of favour with the IUPAC because the cell potential is not a force.

As we show in the following *Justification*, the relation between the reaction Gibbs energy and the cell potential is

$$-\nu F E_{cell} = \Delta_r G \qquad (76.2)$$

Reversible conditions Cell potential and Gibbs energy

where F is Faraday's constant, $F = eN_A$, and ν is the stoichiometric coefficient of the electrons in the two matching (electron-balanced) half-reactions into which the cell reaction can be divided. This equation is the key connection between electrical measurements on the one hand and thermodynamic properties on the other. It is the basis of all that follows.

Justification 76.1 The relation between the cell potential and the reaction Gibbs energy

The variation of Gibbs energy with the advancement, ξ, of a reaction is treated in Topic 73, where the reaction Gibbs energy is defined as $\Delta_r G = (\partial G/\partial \xi)_{T,p}$. We consider the change in G when the cell reaction advances by an infinitesimal amount $d\xi$ at some composition, the temperature and pressure being constant. It follows that

$$dG = \left(\frac{\partial G}{\partial \xi}\right)_{T,p} d\xi = \Delta_r G d\xi$$

Because $dw_e = dG$, the maximum non-expansion (electrical) work that the reaction can do as it advances by $d\xi$ at constant temperature and pressure is therefore

$$dw_e = \Delta_r G d\xi$$

This work is infinitesimal, and the composition of the system is virtually constant when it occurs.

Suppose that the reaction advances by $d\xi$; then $\nu d\xi$ electrons must travel from the anode to the cathode. The total charge transported between the electrodes when this change occurs is $-\nu e N_A d\xi$ (because $\nu d\xi$ is the amount of electrons and the charge per mole of electrons is $-eN_A$). Hence, the total charge transported is $-\nu F d\xi$, because $eN_A = F$. The work done when an infinitesimal charge $-\nu F d\xi$ travels from the anode to the cathode is equal to the product of the charge and the potential difference E_{cell}:

$$dw_e = -\nu F E_{cell} d\xi$$

When this relation is equated to the one above ($dw_e = \Delta_r G d\xi$), the advancement $d\xi$ cancels, and we obtain eqn 76.2.

It follows from eqn 76.2 that, by knowing the reaction Gibbs energy at a specified composition, we can state the cell potential at that composition. Note that a negative reaction Gibbs energy, corresponding to a spontaneous cell reaction, corresponds to a positive cell potential. Another way of looking at the content of eqn 76.2 is that it shows that the driving power of a cell is proportional to the slope of the Gibbs energy with respect to the extent of reaction. It is plausible that a reaction that is far from equilibrium (when the slope is steep) has a strong tendency to drive electrons through an external circuit (Fig. 76.5). When the slope is close to zero (when the cell reaction is close to equilibrium), the cell potential is small.

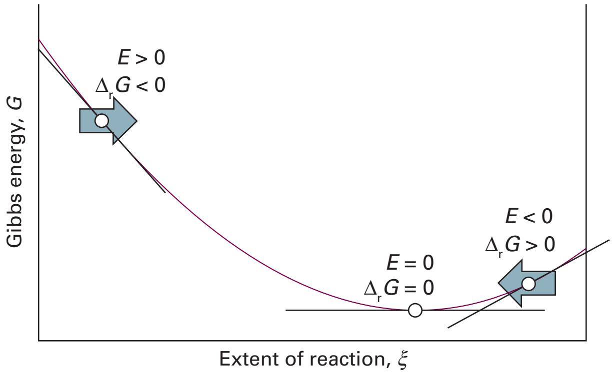

Figure 76.5 A spontaneous reaction occurs in the direction of decreasing Gibbs energy. The spontaneous direction of change can be expressed in terms of the cell potential, E_{cell}. The reaction is spontaneous as written (from left to right on the illustration) when $E_{cell} > 0$. The reverse reaction is spontaneous when $E_{cell} < 0$. When the cell reaction is at equilibrium, the cell potential is zero.

Brief illustration 76.5 The cell potential

Equation 76.2 provides an electrical method for measuring a reaction Gibbs energy at any composition of the reaction mixture: we simply measure the cell potential and convert it to $\Delta_r G$. Conversely, if we know the value of $\Delta_r G$ at a particular composition, then we can predict the cell potential. For example, if $\Delta_r G = -100$ kJ mol^{-1} (taking 100 to be 1×10^2) and $\nu = 1$, then

$$E_{cell} = -\frac{\Delta_r G}{\nu F} = -\frac{(-1\times10^5 \,\mathrm{J\,mol^{-1}})}{1\times(9.6485\times10^4\,\mathrm{C\,mol^{-1}})} = 1\,\mathrm{V}$$

We have used 1 J = 1 C V.

Self-test 76.5 What is the reaction Gibbs energy of a typical cell that produces 1.5 V and involves the transfer of two electrons in each reaction event?

Answer: -290 kJ mol^{-1}

An important feature of cell potentials is that they are unchanged if the chemical equation for the cell reaction or a half-reaction is multiplied by a numerical factor. A numerical factor increases the value of the standard Gibbs energy for the reaction. However, it also increases the number of electrons transferred by the same factor, and by eqn 76.2 the value of E_{cell} remains unchanged. A practical consequence is that a cell potential is independent of the physical size of the cell. In other words, cell potential is an intensive property.

(b) The Nernst equation

We can go on to relate the cell potential to the activities of the participants in the cell reaction. We know that the reaction

Gibbs energy is related to the composition of the reaction mixture by eqn 73.9 of Topic 73 ($\Delta_r G=\Delta_r G^{\ominus}+RT\ln Q$); it follows, on division of both sides by $-\nu F$, that

$$\frac{\Delta_r G}{-\nu F}=\frac{\Delta_r G^{\ominus}}{-\nu F}+\frac{RT}{-\nu F}\ln Q=-\frac{\Delta_r G^{\ominus}}{\nu F}-\frac{RT}{\nu F}\ln Q$$

The term on the far left (in blue) is E_{cell}; the first term on the right is written

$$E^{\ominus}_{\text{cell}}=-\frac{\Delta_r G^{\ominus}}{\nu F} \qquad \textit{Definition} \qquad \text{Standard cell potential} \qquad (76.3)$$

and is called the **standard cell potential**. That is, the standard cell potential is the standard reaction Gibbs energy expressed as a potential (in volts). It follows that

$$E_{\text{cell}}=E^{\ominus}_{\text{cell}}-\frac{RT}{\nu F}\ln Q \qquad \text{Nernst equation} \qquad (76.4)$$

This equation for the cell potential in terms of the composition is called the **Nernst equation**; the dependence on composition that it predicts is summarized in Fig. 76.6.

We see from eqn 76.4 that the standard cell potential can be interpreted as the cell potential when all the reactants and products in the cell reaction are in their standard states, for then all activities are 1, so $Q=1$ and $\ln Q=0$. However, the fact that the standard cell potential is merely a disguised form of the standard reaction Gibbs energy (eqn 76.3) should always be kept in mind and underlies all its applications.

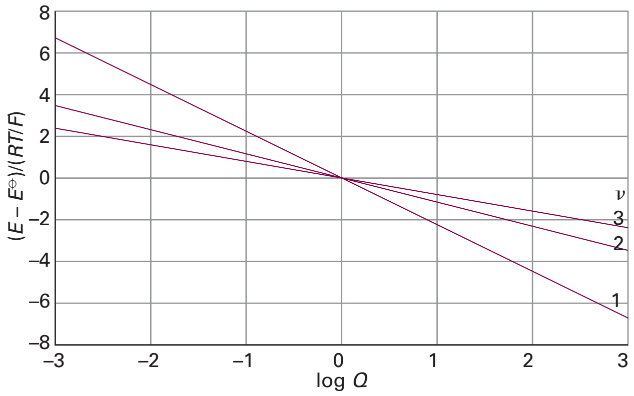

Figure 76.6 The variation of cell potential with the value of the reaction quotient for the cell reaction for different values of ν (the number of electrons transferred). At 298 K, $RT/F=25.69$ mV, so the vertical scale refers to multiples of this value.

Brief illustration 76.6 The Nernst equation

Because $RT/F=25.7$ mV at 25 °C, a practical form of the Nernst equation at that temperature is

$$E_{\text{cell}}=E^{\ominus}_{\text{cell}}-\frac{25.7\,\text{mV}}{\nu}\ln Q$$

It then follows that for a reaction in which $\nu=1$, if Q is increased by a factor of 10, then the cell potential decreases by (25.7 mV) ln 10 = 59.2 mV.

Self-test 76.6 What is the cell potential at 25 °C when $E^{\ominus}_{\text{cell}}=+1.20$ V and $Q=0.10$ in a cell for which $\nu=2$?

Answer: +1.23 V

(c) Cells at equilibrium

A special case of the Nernst equation has great importance in electrochemistry and provides a link to other parts of chemistry. Suppose the reaction has reached equilibrium; then $Q=K$, where K is the equilibrium constant of the cell reaction. However, a chemical reaction at equilibrium cannot do work, and hence it generates zero potential difference between the electrodes of a galvanic cell. Therefore, setting $E_{\text{cell}}=0$ and $Q=K$ in the Nernst equation gives

$$\ln K=\frac{\nu F E^{\ominus}_{\text{cell}}}{RT} \qquad \text{Equilibrium constant} \qquad (76.5)$$

This very important equation lets us predict equilibrium constants from measured standard cell potentials.

Brief illustration 76.7 The equilibrium constant

Because the standard potential of the Daniell cell is +1.10 V, the equilibrium constant at 298 K for the cell reaction $Cu^{2+}(aq)+Zn(s)\rightarrow Cu(s)+Zn^{2+}(aq)$, for which $\nu=2$, is obtained from

$$\ln K=\frac{2\times(+1.10\,\text{V})}{25.7\times10^{-3}\,\text{V}}=85.6\ldots$$

and is $K=1.5\times10^{37}$. We conclude that the displacement of copper by zinc goes virtually to completion. Note that a cell potential of about 1 V is easily measurable but corresponds to an equilibrium constant that would be impossible to measure by direct chemical analysis.

Self-test 76.7 Evaluate the equilibrium constant for a cell reaction for which $E^{\ominus}_{\text{cell}}=-0.22$ V at 25 °C and $\nu=2$.

Answer: 3.7×10^{-8}

Checklist of concepts

☐ 1. **Oxidation** is the removal of electrons from a species; **reduction** is the addition of electrons to a species.

☐ 2. A redox reaction (and some other reactions) may be expressed as the difference of two reduction **half-reactions**, which are conceptual reactions showing the gain of electrons.

☐ 3. An **electrochemical cell** consists of two **electrodes**, or metallic conductors, in contact with an **electrolyte**, an ionic conductor.

☐ 4. A **galvanic cell** is an electrochemical cell that produces electricity as a result of the spontaneous reaction occurring inside it.

☐ 5. An **electrolytic cell** is an electrochemical cell in which a non-spontaneous reaction is driven by an external source of current.

☐ 6. The electrode at which oxidation occurs is called the **anode**; the electrode at which reduction occurs is called the **cathode**.

☐ 7. In an **electrolyte concentration cell**, the electrode compartments are identical except for the concentrations of the electrolytes.

☐ 8. A **salt bridge** reduces the contribution of the liquid junction to the potential.

☐ 9. The **cell reaction** is the reaction in the cell written on the assumption that the right-hand electrode is the cathode.

☐ 10. The **standard cell potential** is the standard reaction Gibbs energy expressed as a potential.

Checklist of equations

Property	Equation	Comment	Equation number
Half-reaction	$\mathrm{Ox} + \nu\,\mathrm{e}^- \rightarrow \mathrm{Red}$	e^- is stateless	76.1
Cell potential	$-\nu F E_{\mathrm{cell}} = \Delta_{\mathrm{r}} G$	Constant temperature and pressure, reversible	76.2
Standard cell potential	$E^{\ominus}_{\mathrm{cell}} = -\Delta_{\mathrm{r}} G^{\ominus}/\nu F$	Definition	76.3
Nernst equation	$E_{\mathrm{cell}} = E^{\ominus}_{\mathrm{cell}} - (RT/\nu F)\ln Q$		76.4
Equilibrium constant	$\ln K = \nu F E^{\ominus}_{\mathrm{cell}}/RT$		76.5

TOPIC 77

Standard electrode potentials

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➤ Why do you need to know this material?

The tabulation of individual electrode potentials allows the calculation of several chemically important quantities, including cell potentials, activity coefficients, and equilibrium constants. It is also a route to the determination of the values of thermodynamic properties of ions in solution.

➤ What is the key idea?

The cell potential can be expressed as the difference between the two electrode potentials that form the cell.

➤ What do you need to know already?

You need to know the notation and construction of galvanic cells and how the cell potential is related to the reaction Gibbs energy (Topic 76). The material draws on the discussion of activity coefficients and the Debye–Hückel limiting law (Topic 72).

The structure and thermodynamic properties of galvanic cells are described in Topic 76, where it is shown that each one is a combination of two electrodes. Instead of listing the cell potential of every conceivable cell, it turns out to be sensible and economical, as well as having other advantages, to consider that each individual electrode makes a certain contribution.

77.1 The conventions

Each electrode is considered to make a characteristic contribution to the overall cell potential, the difference of the two contributions being the cell potential:

$$\mathrm{Red_L,Ox_L}\,||\,\mathrm{Red_R,Ox_R} \qquad E_{\mathrm{cell}} = E_\mathrm{R} - E_\mathrm{L} \qquad \text{Electrode potentials} \qquad (77.1)$$

Here E_R is the potential of the right-hand electrode (of the cell as written) and E_L is that of the left-hand electrode. It is conventional to label each contribution by the redox couple, as in $E(\mathrm{Ox,Red})$.

Although it is not possible to measure the contribution of a single electrode, we can define the potential of one of the electrodes as zero and then assign values to others on that basis. The specially selected electrode is the **standard hydrogen electrode** (SHE):

$$\begin{array}{l}\mathrm{Pt(s)|H_2(g)|H^+(aq)}\\ E^{\ominus}(\mathrm{H^+,H_2})=0\end{array} \qquad \textit{Convention} \qquad \text{Standard hydrogen electrode} \qquad (77.2)$$

Table 77.1* Standard potentials at 298 K

Couple	$E^\ominus/\text{V}$
$\text{Ce}^{4+}(\text{aq})+\text{e}^-\rightarrow\text{Ce}^{3+}(\text{aq})$	+1.61
$\text{Cu}^{2+}(\text{aq})+2\,\text{e}^-\rightarrow\text{Cu(s)}$	+0.34
$\text{H}^+(\text{aq})+\text{e}^-\rightarrow\tfrac{1}{2}\text{H}_2(\text{g})$	0
$\text{AgCl(s)}+\text{e}^-\rightarrow\text{Ag(s)}+\text{Cl}^-(\text{aq})$	+0.22
$\text{Zn}^{2+}(\text{aq})+2\,\text{e}^-\rightarrow\text{Zn(s)}$	−0.76
$\text{Na}^+(\text{aq})+\text{e}^-\rightarrow\text{Na(s)}$	−2.71

* More values are given in the *Resource section*.

at all temperatures. To achieve the standard conditions, the activity of the hydrogen ions must be 1 (that is, pH=0) and the pressure of the hydrogen gas must be 1 bar. The **standard potential**, $E^\ominus(\text{Ox,Red})$, of another couple is then assigned by constructing a cell in which it is the right-hand electrode and the standard hydrogen electrode is the left-hand electrode. Table 77.1 lists the standard potentials of a number of electrodes at 298 K.

(a) The determination of standard electrode potentials

The procedure for measuring a standard potential can be illustrated by considering a specific case, the silver chloride electrode. The measurement is made on the 'Harned cell':

$$\text{Pt(s)}|\text{H}_2(\text{g},p)|\text{HCl}(\text{aq},b)|\text{AgCl(s)}|\text{Ag(s)}$$
$$\tfrac{1}{2}\text{H}_2(\text{g})+\text{AgCl(s)}\rightarrow\text{HCl(aq)}+\text{Ag(s)}$$

We show in the following *Justification* that

$$g(b)=E^\ominus(\text{Ag,AgCl,Cl}^-)+Cb^{1/2},$$
$$\text{with } g(b)=E_\text{cell}+\frac{2RT}{F}\ln b \qquad (77.3)$$

Therefore, if $g(b)$ is evaluated at a range of molalities, plotted against $b^{1/2}$, and extrapolated to $b=0$, then the intercept at $b^{1/2}=0$ is the value of $E^\ominus(\text{Ag, AgCl, Cl}^-)$.

Justification 77.1 The determination of the standard cell potential

The Nernst equation for the Harned cell is

$$E_\text{cell}=\overbrace{E^\ominus_\text{cell}}^{E^\ominus(\text{Ag,AgCl,Cl}^-)-\overbrace{E^\ominus(\text{H}^+,\text{H}_2)}^{0}}-\frac{RT}{F}\ln\frac{a_{\text{H}^+}a_{\text{Cl}^-}}{a_{\text{H}_2}^{1/2}}$$
$$=E^\ominus(\text{Ag,AgCl,Cl}^-)-\frac{RT}{F}\ln\frac{a_{\text{H}^+}a_{\text{Cl}^-}}{a_{\text{H}_2}^{1/2}}$$

We shall suppose that the pressure of hydrogen (treated as a perfect gas) is 1 bar, so set $a_{\text{H}_2}=1$:

$$E_\text{cell}=E^\ominus(\text{Ag,AgCl,Cl}^-)-\frac{RT}{F}\ln a_{\text{H}^+}a_{\text{Cl}^-}$$

As shown in Topic 72, the activities can be expressed in terms of the molality b of HCl(aq) through $a_{\text{H}^+}=\gamma_\pm b/b^\ominus$ and $a_{\text{Cl}^-}=\gamma_\pm b/b^\ominus$, so

$$E_\text{cell}=E^\ominus(\text{Ag,AgCl,Cl}^-)-\frac{RT}{F}\ln\gamma_\pm^2 b^2$$
$$=E^\ominus(\text{Ag,AgCl,Cl}^-)-\frac{RT}{F}\ln\gamma_\pm^2-\frac{RT}{F}\ln b^2$$

where for simplicity we have replaced $b/b^\ominus$ by b. This expression rearranges to

$$\overbrace{E_\text{cell}+\frac{2RT}{F}\ln b}^{g(b)}=E^\ominus(\text{Ag,AgCl,Cl}^-)-\frac{2RT}{F}\ln\gamma_\pm$$

The function $g(b)$ can be determined by measuring the cell potential for each molality b and forming $E_\text{cell}+2(RT/F)\ln b$ in each case.

From the Debye–Hückel limiting law for an electrolyte consisting of singly charged M⁺ and X⁻ ions (eqn 72.26 of Topic 72, $\log\gamma_\pm=-AI^{1/2}$, with $I=b/b^\ominus$), we can infer that $\ln\gamma_\pm\propto -b^{1/2}$. Therefore, with all the constants of proportionality absorbed into a single symbol C, the last equation becomes

$$g(b)=E^\ominus(\text{Ag,AgCl,Cl}^-)+Cb^{1/2}$$

as in eqn 77.3. In precise work, the $b^{1/2}$ term is brought to the left, and a higher-order correction term from the extended Debye–Hückel law (Topic 72) is used on the right.

Example 77.1 Determining a standard electrode potential

The potential of the cell $\text{Pt(s)}|\text{H}_2(\text{g},p^\ominus)|\text{HCl}(\text{aq},b)|\text{AgCl(s)}|\text{Ag(s)}$ at 25 °C has the following values:

$b/(10^{-3}\,b^\ominus)$	3.215	5.619	9.138	25.63
E_cell/V	0.520 53	0.492 57	0.468 60	0.418 24

Determine the standard potential of the silver/silver chloride electrode.

Method As outlined in the text, we draw up a table of values of $g(b)=E_\text{cell}+(2RT/F)\ln b$, using $2RT/F=0.051\,39$ V. The extrapolated intercept on the vertical axis at $b=0$ is the value of $E^\ominus(\text{Ag, AgCl, Cl}^-)$. Although the graph gives an indication of the intercept, use linear regression to preserve the precision of the data.

Answer The data give the following table:

$b/(10^{-3}\,b^\ominus)$	3.215	5.619	9.138	25.63
$\{b/(10^{-3}\,b^\ominus)\}^{1/2}$	1.793	2.370	3.023	5.063
E_{cell}/V	0.520 53	0.492 57	0.468 60	0.418 24
$g(b)/\text{V}$	0.2256	0.2263	0.2273	0.2299

The data are plotted in Fig. 77.1; as can be seen (and is in fact verified by a linear regression analysis), they extrapolate to $E^\ominus(\text{Ag, AgCl, Cl}^-) = +0.2232\,\text{V}$.

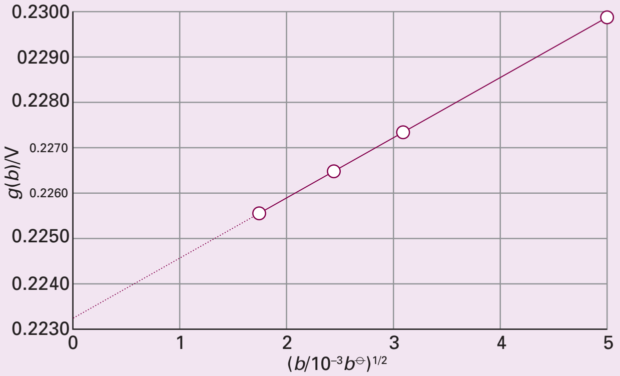

Figure 77.1 The plot and the extrapolation used in Example 77.1 for the experimental measurement of a standard electrode potential. The intercept at $b^{1/2}=0$ is $E^\ominus(\text{Ag, AgCl, Cl}^-)$.

Self-test 77.1 The data below are for the cell $\text{Pt(s)}|\text{H}_2(\text{g},p^\ominus)|\text{HBr(aq},b)|\text{AgBr(s)}|\text{Ag(s)}$ at 25 °C. Determine the standard potential of the cell.

$b/(10^{-4}\,b^\ominus)$	4.042	8.444	37.19
E_{cell}/V	0.473 81	0.436 36	0.361 73

Answer: +0.071 V

(b) Combining electrode potentials

The standard potentials in Table 77.1 may be combined to give values for couples that are not listed there. However, to do so, we must take into account the fact that different couples may correspond to the transfer of different numbers of electrons. The procedure is illustrated in the following example.

Example 77.2 Evaluating a standard potential from two others

Given that the standard potentials of the Cu^{2+}/Cu and Cu^{+}/Cu couples are +0.340 V and +0.522 V, respectively, evaluate $E^\ominus(\text{Cu}^{2+}, \text{Cu}^{+})$.

Method First, we note that reaction Gibbs energies may be added (as in a Hess's law analysis of reaction enthalpies, Topic 57). Therefore, we should convert the $E^\ominus$ values to $\Delta_r G^\ominus$ values by using the relation $\Delta_r G^\ominus = -\nu F E^\ominus$ developed in Topic 76 (which applies to electrode potentials as well as to the overall cell potential), add them appropriately, and then convert the overall $\Delta_r G^\ominus$ to the required $E^\ominus$ by using the same relation again. This roundabout procedure is necessary because, as we shall see, although the factor F cancels, the factor ν in general does not.

Answer The electrode reactions are as follows:

(a) $\text{Cu}^{2+}(\text{aq}) + 2\,\text{e}^- \rightarrow \text{Cu(s)}$

$E^\ominus(\text{Cu}^{2+},\text{Cu}) = +0.340\ \text{V},$

so $\Delta_r G^\ominus = -2(0.340\ \text{V})F$

(b) $\text{Cu}^{+}(\text{aq}) + \text{e}^- \rightarrow \text{Cu(s)}$

$E^\ominus(\text{Cu}^{+},\text{Cu}) = +0.522\ \text{V},$

so $\Delta_r G^\ominus = -(0.522\,\text{V})F$

The required reaction is

(c) $\text{Cu}^{2+}(\text{aq}) + \text{e}^- \rightarrow \text{Cu}^{+}(\text{aq})$

$E^\ominus(\text{Cu}^{2+},\text{Cu}^{+}) = -\Delta_r G^\ominus/F$

Because (c) = (a) − (b), the standard Gibbs energy of reaction (c) is

$$\Delta_r G^\ominus = \Delta_r G^\ominus(\text{a}) - \Delta_r G^\ominus(\text{b}) = -(0.158\,\text{V}) \times F$$

Therefore, $E^\ominus(\text{Cu}^{2+},\text{Cu}^{+}) = +0.158\,\text{V}$.

Self-test 77.2 Calculate the standard potential of the Fe^{3+}/Fe couple from the values for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and Fe^{2+}/Fe couples.

Answer: −0.037 V

The generalization of the calculation in Example 77.2, since (a) = (b) + (c), is

$$\nu_a E^\ominus(\text{a}) = \nu_b E^\ominus(\text{b}) + \nu_c E^\ominus(\text{c}) \qquad (77.4)$$

Combination of standard potentials

A note on good practice Whenever combining standard potentials to obtain the standard potential of a third couple, always work via the Gibbs energies because they are additive, whereas, in general, standard potentials are not.

77.2 Applications of standard potentials

Cell potentials are a convenient source of data on equilibrium constants and the Gibbs energies, enthalpies, and entropies of reactions. In practice the standard values of these quantities are the ones normally determined.

(a) The electrochemical series

In Topic 76 it is shown that a cell reaction is spontaneous under standard conditions (and therefore in the sense $K>1$, as explained in that Topic) if $E^{\ominus}_{\text{cell}}>0$ (corresponding to $\Delta_r G^{\ominus}<0$). We have seen that, for two redox couples Ox_1/Red_1 and Ox_2/Red_2, the cell potential is given by eqn 77.1; for their standard values

$$\text{Red}_L,\text{Ox}_L \| \text{Red}_R,\text{Ox}_R \qquad E^{\ominus}_{\text{cell}}=E^{\ominus}_R-E^{\ominus}_L \tag{77.5a}$$

It follows that the cell reaction $(\text{Ox}+\nu\,\text{e}^-\rightarrow\text{Red})_R-(\text{Ox}+\nu\,\text{e}^-\rightarrow\text{Red})_L$, which is

$$\text{Red}_L+\text{Ox}_R\rightarrow\text{Ox}_L+\text{Red}_R \tag{77.5b}$$

is spontaneous as written (in the sense $K>1$) if $E^{\ominus}_R>E^{\ominus}_L$. Because in the cell reaction Red_L reduces Ox_R, we can conclude that

> Red_L has a thermodynamic tendency to reduce Ox_R if $E^{\ominus}_L<E^{\ominus}_R$.

More briefly: low reduces high.

Table 77.2 shows a part of the **electrochemical series**, the metallic elements (and hydrogen) arranged in the order of their reducing power as measured by their standard potentials in aqueous solution. A metal low in the series (with a lower standard potential) can reduce the ions of metals with higher standard potentials. This conclusion is qualitative. The quantitative value of K for the reaction is obtained by doing the calculations described in Topic 76. It should always be remembered that even for reactions that are thermodynamically favourable there may be kinetic factors that result in very slow rates of reaction.

Table 77.2 The electrochemical series of the metals*

Least strongly reducing
Gold
Platinum
Silver
Mercury
Copper
(Hydrogen)
Lead
Tin
Nickel
Iron
Zinc
Chromium
Aluminium
Magnesium
Sodium
Calcium
Potassium
Most strongly reducing

* The complete series can be inferred from Table 77.1 in the *Resource section*.

Brief illustration 77.1 The electrochemical series

Because $E^{\ominus}(\text{Zn}^{2+},\text{Zn})=-0.76\,\text{V}<E^{\ominus}(\text{Cu}^{2+},\text{Cu})=+0.34\,\text{V}$, zinc has a thermodynamic tendency to reduce Cu^{2+} ions in aqueous solution. More qualitatively: to determine whether zinc can displace magnesium from aqueous solutions, we note that zinc lies above magnesium in the electrochemical series, so zinc cannot reduce magnesium ions in aqueous solution.

Self-test 77.3 Can zinc displace hydrogen from acid? Can copper?

Answer: Yes; no

(b) The determination of activity coefficients

Once the standard potential of an electrode in a cell is known, perhaps by calculation from tables of standard electrode potentials or by direct measurement, it can be used to determine mean activity coefficients. The procedure involves measuring the cell potential for a known molality, b, of electroactive species, using the Nernst equation to find the value of the activity, a, that corresponds to the observed cell potential, and then determining the activity coefficient from an expression of the form $\gamma=a/(b/b^{\ominus})$. For instance, if we write the Nernst equation for the Harned cell in the form

$$g(b)-E^{\ominus}(\text{Ag},\text{AgCl},\text{Cl}^-)=-\frac{2RT}{F}\ln\gamma_{\pm} \tag{77.6}$$

then all we need do is measure $g(b)=E_{\text{cell}}+(2RT/F)\ln b$ (with b interpreted as $b/b^{\ominus}$) for a given value of b.

Brief illustration 77.2 The activity coefficient

From the data in Example 77.1 we know that $E^{\ominus}(\text{Ag, AgCl, Cl}^-)=+0.2232\,\text{V}$ and that when $b=9.138\,\text{mmol\,kg}^{-1}$, $E_{\text{cell}}=0.468\,60\,\text{V}$, corresponding to $g(b)=0.2273\,\text{V}$. Therefore, with $RT/F=25.693\,\text{mV}$,

$$\ln\gamma_{\pm}=-\frac{0.2273\,\text{V}-0.2232\,\text{V}}{2\times(25.693\times10^{-3}\,\text{V})}=-0.0798\ldots$$

That is, $\gamma_{\pm}=0.9233$.

Self-test 77.4 Use data from Example 77.1 to determine $\gamma_{\pm}$ when $b=25.63\,\text{mmol\,kg}^{-1}$.

Answer: 0.8778

(c) The determination of equilibrium constants

The principal use for standard potentials is to calculate the standard potential of a cell formed from any two electrodes. To do so, we subtract the standard potential of the left-hand electrode from the standard potential of the right-hand electrode, $E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{R}} - E^{\ominus}_{\text{L}}$. Because $\Delta G^{\ominus} = -\nu F E^{\ominus}_{\text{cell}}$, it then follows that if the result gives $E^{\ominus}_{\text{cell}} > 0$, then the corresponding cell reaction has $K > 1$. To calculate the numerical value of K we use eqn 76.5 of Topic 76 ($\ln K = \nu F E^{\ominus}_{\text{cell}}/RT$).

Brief illustration 77.3 Equilibrium constants

A disproportionation is a reaction in which a species is both oxidized and reduced. To study the disproportionation $2\,\text{Cu}^+(\text{aq}) \rightarrow \text{Cu(s)} + \text{Cu}^{2+}(\text{aq})$ we combine the following electrodes:

Right-hand electrode: $\text{Cu(s)}|\text{Cu}^+(\text{aq})$

$$\text{Cu}^+(\text{aq}) + \text{e}^- \rightarrow \text{Cu(aq)} \quad E^{\ominus}_{\text{R}} = +0.52\,\text{V}$$

Left-hand electrode: $\text{Pt(s)}|\text{Cu}^{2+}(\text{aq}),\text{Cu}^+(\text{aq})$

$$\text{Cu}^{2+}(\text{aq}) + \text{e}^- \rightarrow \text{Cu}^+(\text{s}) \quad E^{\ominus}_{\text{L}} = +0.16\,\text{V}$$

where the standard potentials are measured at 298 K. The standard cell potential is therefore

$$E^{\ominus}_{\text{cell}} = +0.52\,\text{V} - 0.16\,\text{V} = +0.36\,\text{V}$$

We can now calculate the equilibrium constant of the cell reaction. Because $\nu = 1$ and $RT/F = 25.693\,\text{V}$,

$$\ln K = \frac{0.36\,\text{V}}{25.693 \times 10^{-3}\,\text{V}} = 14.0\ldots$$

Hence, $K = 1.2 \times 10^6$.

Self-test 77.5 Calculate the solubility constant (the equilibrium constant for the reaction $\text{Hg}_2\text{Cl}_2(\text{s}) \rightleftharpoons \text{Hg}_2^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$) at 298.15.

Answer: 2.6×10^{-18}

(d) The determination of thermodynamic functions

The standard cell potential is related to the standard reaction Gibbs energy through eqn 76.3 of Topic 76 ($\Delta_{\text{r}} G^{\ominus} = -\nu F E^{\ominus}_{\text{cell}}$). Therefore, by measuring $E^{\ominus}_{\text{cell}}$ or by constructing its value from standard electrode potentials we can obtain this important thermodynamic quantity. Its value can then be used to calculate the Gibbs energy of formation of ions by using the convention explained in Topic 65.

The temperature coefficient of the standard cell potential, $\text{d}E^{\ominus}_{\text{cell}}/\text{d}T$, gives the standard entropy of the cell reaction. This conclusion follows from the thermodynamic relation $(\partial G/\partial T)_p = -S$ (Topic 66) and eqn 76.3 of Topic 76 ($\Delta_{\text{r}} G^{\ominus} = -\nu F E^{\ominus}_{\text{cell}}$), which combine to give

$$\frac{\text{d}E^{\ominus}_{\text{cell}}}{\text{d}T} = \frac{\Delta_{\text{r}} S^{\ominus}}{\nu F} \qquad \text{Temperature coefficient of the cell potential} \qquad (77.7)$$

The derivative is complete because $E^{\ominus}_{\text{cell}}$, like $\Delta_{\text{r}} G^{\ominus}$, is independent of the pressure. Hence we have an electrochemical technique for obtaining standard reaction entropies and through them the entropies of ions in solution.

Finally, we can combine the results obtained so far and use them to obtain the standard reaction enthalpy by writing $\Delta G = \Delta H - T\Delta S$ in the form $\Delta H = \Delta G + T\Delta S$:

$$\Delta_{\text{r}} H^{\ominus} = -\nu F \left(E^{\ominus}_{\text{cell}} - T \frac{\text{d}E^{\ominus}_{\text{cell}}}{\text{d}T} \right) \qquad \text{Standard reaction enthalpy} \qquad (77.8)$$

This expression provides a non-calorimetric method for measuring $\Delta_{\text{r}} H^{\ominus}$ and, through the convention $\Delta_{\text{f}} H^{\ominus}(\text{H}^+, \text{aq}) = 0$, the standard enthalpies of formation of ions in solution (Topic 57).

Example 77.3 Using the temperature coefficient of the cell potential

The standard potential of the cell $\text{Pt(s)}|\text{H}_2(\text{g})|\text{HBr(aq)}|\text{AgBr(s)}|\text{Ag(s)}$ was measured over a range of temperatures, and the data were fitted to the following polynomial:

$$E^{\ominus}_{\text{cell}}/\text{V} = 0.07131 - 4.99 \times 10^{-4}(T/\text{K} - 298) - 3.45 \times 10^{-6}(T/\text{K} - 298)^2$$

Evaluate the standard reaction Gibbs energy, enthalpy, and entropy at 298 K of the reaction $\text{AgBr(s)} + \frac{1}{2}\,\text{H}_2(\text{g}) \rightarrow \text{Ag(s)} + \text{HBr(aq)}$.

Method The standard Gibbs energy of reaction is obtained by using $\Delta_{\text{r}} G^{\ominus} = -\nu F E^{\ominus}$ after evaluating $E^{\ominus}$ at 298 K, and by using $1\,\text{V C} = 1\,\text{J}$. The standard entropy of reaction is obtained by using eqn 77.7, which involves differentiating the polynomial with respect to T and then setting $T = 298\,\text{K}$. The reaction enthalpy is obtained by combining the values of the standard Gibbs energy and entropy.

Answer At $T = 298\,\text{K}$, $E^{\ominus}_{\text{cell}} = +0.07131\,\text{V}$, so

$$\begin{aligned}\Delta_{\text{r}} G^{\ominus} &= -\nu F E^{\ominus}_{\text{cell}} = -(1) \times (9.6485 \times 10^4\,\text{C mol}^{-1}) \times (+0.07131\,\text{V}) \\ &= -6.880 \times 10^3\,\text{V C mol}^{-1} = -6.880\,\text{kJ mol}^{-1}\end{aligned}$$

The temperature coefficient of the standard cell potential is

$$\frac{dE^{\ominus}_{\text{cell}}}{dT} = -4.99\times10^{-4}\,\text{V K}^{-1} - 2(3.45\times10^{-6})(T/\text{K}-298)\,\text{V K}^{-1}$$

At $T=298\,\text{K}$ this expression evaluates to

$$\frac{dE^{\ominus}_{\text{cell}}}{dT} = -4.99\times10^{-4}\,\text{V K}^{-1}$$

So, from eqn 77.7, the reaction entropy is

$$\begin{aligned}\Delta_r S^{\ominus} &= 1\times(9.6485\times10^{4}\,\text{C mol}^{-1})\times(-4.99\times10^{-4}\,\text{V K}^{-1})\\ &= -48.1\,\text{J K}^{-1}\,\text{mol}^{-1}\end{aligned}$$

It then follows that

$$\begin{aligned}\Delta_r H^{\ominus} &= \Delta_r G^{\ominus} + T\Delta_r S^{\ominus}\\ &= -6.880\,\text{kJ mol}^{-1} + (298\,\text{K})\times(-0.0481\,\text{kJ K}^{-1}\,\text{mol}^{-1})\\ &= -21.2\,\text{kJ mol}^{-1}\end{aligned}$$

One difficulty with this procedure lies in the accurate measurement of small temperature coefficients of the cell potential. Nevertheless, it is another example of the striking ability of thermodynamics to relate the apparently unrelated, in this case to relate electrical measurements to thermal properties.

Self-test 77.6 Predict the standard potential of the Harned cell at 303 K from tables of thermodynamic data.

Answer: +0.2222 V

Checklist of concepts

☐ **1.** Each electrode is considered to make a characteristic contribution to the overall cell potential, the difference of the two contributions being the cell potential.

☐ **2.** Tables of standard electrode potentials are compiled on the basis that the **standard hydrogen electrode** has zero potential at all temperatures.

☐ **3.** In the **electrochemical series**, the metallic elements (and hydrogen) are arranged in the order of their reducing power as measured by their standard potentials in aqueous solution.

☐ **4.** A metal low in the electrochemical series (with a lower standard potential) can reduce the ions of metals with higher standard potentials.

☐ **5.** The temperature coefficient of the standard cell potential, $dE^{\ominus}_{\text{cell}}/dT$, gives the standard entropy of the cell reaction.

☐ **6.** Standard potentials can be used to determine activity coefficients, equilibrium constants, and thermodynamic functions.

Checklist of equations

Property	Equation	Comment	Equation number
Cell potential	$E_{\text{cell}}=E_R-E_L$	Definition	77.1
Standard hydrogen electrode	$E^{\ominus}(H^+,H_2)=0$	Convention, at all temperatures	77.2
Combinations of standard electrode potentials	$\nu_a E^{\ominus}(a)=\nu_b E^{\ominus}(b)+\nu_c E^{\ominus}(c)$		77.4
Temperature coefficient of cell potential	$dE^{\ominus}_{\text{cell}}/dT=\Delta_r S^{\ominus}/\nu F$		77.7
Standard reaction enthalpy	$\Delta_r H^{\ominus}=-\nu F(E^{\ominus}_{\text{cell}}-T dE^{\ominus}_{\text{cell}}/dT)$		77.8

Focus 15 on Chemical equilibria

Topic 73 Chemical transformations

Discussion questions

73.1 Explain how the mixing of reactants and products affects the position of chemical equilibrium.

73.2 Explain how a reaction that is not spontaneous may be driven forward by coupling to a spontaneous reaction.

73.3 Suggest how the thermodynamic equilibrium constant may respond differently to changes in pressure and temperature from the equilibrium constant expressed in terms of partial pressures.

Exercises

73.1(a) Write the expressions for the equilibrium constants of the following reactions in terms of (i) activities and (ii) where appropriate, the ratios $p/p^{\ominus}$ and the products γb:
(a) $CO(g)+Cl_2(g) \rightleftharpoons COCl(g)+Cl(g)$
(b) $2\,SO_2(g)+O_2(g) \rightleftharpoons 2\,SO_3(g)$
(c) $Fe(s)+PbSO_4(aq) \rightleftharpoons FeSO_4(aq)+Pb(s)$
(d) $Hg_2Cl_2(s)+H_2(g) \rightleftharpoons 2\,HCl(aq)+2\,Hg(l)$
(e) $2\,CuCl(aq) \rightleftharpoons Cu(s)+CuCl_2(aq)$

73.1(b) Write the expressions for the equilibrium constants of the following reactions in terms of (i) activities and (ii) where appropriate, the ratios $p/p^{\ominus}$ and the products γb:
(a) $H_2(g)+Br_2(g) \rightleftharpoons 2\,HBr(g)$
(b) $2\,O_3(g) \rightleftharpoons 3\,O_2(g)$
(c) $2\,H_2(g)+O_2(g) \rightleftharpoons 2\,H_2O(l)$
(d) $H_2(g)+O_2(g) \rightleftharpoons H_2O_2(aq)$
(e) $H_2(g)+I_2(g) \rightleftharpoons 2\,HI(aq)$

73.2(a) Identify the stoichiometric numbers in the reaction $Hg_2Cl_2(s)+H_2(g) \rightarrow 2\,HCl(aq)+2\,Hg(l)$.

73.2(b) Identify the stoichiometric numbers in the reaction $CH_4(g)+2\,O_2(g) \rightarrow CO_2(g)+2\,H_2O(l)$.

73.3(a) The standard reaction Gibbs energy of the isomerization of borneol ($C_{10}H_{17}OH$) to isoborneol in the gas phase at 503 K is $+9.4\,kJ\,mol^{-1}$. Calculate the reaction Gibbs energy in a mixture consisting of 0.15 mol of borneol molecules and 0.30 mol of isoborneol molecules when the total pressure is 600 Torr. Under these conditions, is the isomerization of borneol spontaneous?

73.3(b) The standard reaction Gibbs energy of the isomerization of *cis*-2-butene to *trans*-2-butene in the gas phase at 298 K is $-2.9\,kJ\,mol^{-1}$. Calculate the reaction Gibbs energy in a mixture consisting of 0.25 mol of *cis*-2-butene molecules and 0.95 mol of *trans*-2-butene molecules when the total pressure is 600 Torr. Under these conditions, is the isomerization of *cis*-2-butene spontaneous?

73.4(a) The equilibrium pressure of O_2 over solid silver and silver oxide, Ag_2O, at 298 K is 11.85 Pa. Calculate the standard Gibbs energy of formation of $Ag_2O(s)$ at 298 K.

73.4(b) The equilibrium pressure of H_2 over solid uranium and uranium hydride, UH_3, at 500 K is 139 Pa. Calculate the standard Gibbs energy of formation of $UH_3(s)$ at 500 K.

73.5(a) For $CaF_2(s) \rightleftharpoons Ca^{2+}(aq)+2\,F^{-}(aq)$, $K=3.9\times10^{-11}$ at 25 °C and the standard Gibbs energy of formation of $CaF_2(s)$ is $-1167\,kJ\,mol^{-1}$. Calculate the standard Gibbs energy of formation of $CaF_2(aq)$.

73.5(b) For $PbI_2(s) \rightleftharpoons Pb^{2+}(aq)+2\,I^{-}(aq)$, $K=1.4\times10^{-8}$ at 25 °C and the standard Gibbs energy of formation of $PbI_2(s)$ is $-173.64\,kJ\,mol^{-1}$. Calculate the standard Gibbs energy of formation of $PbI_2(aq)$.

73.6(a) In the gas-phase reaction $2\,A+B \rightleftharpoons 3\,C+2\,D$, it was found that when 1.00 mol A, 2.00 mol B, and 1.00 mol D were mixed and allowed to come to equilibrium at 25 °C, the resulting mixture contained 0.90 mol C at a total pressure of 1.00 bar. Calculate (a) the mole fractions of each species at equilibrium, (b) K_x, (c) K, and (d) $\Delta_r G^{\ominus}$.

73.6(b) In the gas-phase reaction $A+B \rightleftharpoons C+2\,D$, it was found that when 2.00 mol A, 1.00 mol B, and 3.00 mol D were mixed and allowed to come to equilibrium at 25 °C, the resulting mixture contained 0.79 mol C at a total pressure of 1.00 bar. Calculate (a) the mole fractions of each species at equilibrium, (b) K_x, (c) K, and (d) $\Delta_r G^{\ominus}$.

73.7(a) The hydrolysis of ATP is written as $ATP^{4-}(aq)+H_2O(l) \rightarrow ADP^{3-}(aq)+HPO_4^{2-}(aq)+H_3O^{+}(aq)$. For this reaction the standard reaction Gibbs energy is $+10\,kJ\,mol^{-1}$ at 298 K. What is the biological standard state value?

73.7(b) The overall reaction for the glycolysis reaction is $C_6H_{12}O_6(aq)+2\,NAD^{+}(aq)+2\,ADP^{3-}(aq)+2\,HPO_4^{2-}(aq)+2\,H_2O(l) \rightarrow 2\,CH_3COCO_2^{-}(aq)+2\,NADH(aq)+2\,ATP^{4-}(aq)+2\,H_3O^{+}(aq)$. For this reaction, the standard reaction Gibbs energy is $-80.6\,kJ\,mol^{-1}$ at 298 K. What is the biological standard state value?

Problems

73.1 The equilibrium constant for the reaction, $I_2(s)+Br_2(g) \rightleftharpoons 2\,IBr(g)$ is 0.164 at 25 °C. (a) Calculate $\Delta_r G^{\ominus}$ for this reaction. (b) Bromine gas is introduced into a container with excess solid iodine. The pressure and temperature are held at 0.164 atm and 25 °C. Find the partial pressure of IBr(g) at equilibrium. Assume that all the bromine is in the liquid form and that the vapour pressure of iodine is negligible. (c) In fact, solid iodine has a measurable vapour pressure at 25 °C. In this case, how would the calculation have to be modified?

73.2 The standard Gibbs energy of formation of $NH_3(g)$ is $-16.5\,kJ\,mol^{-1}$ at 298 K. What is the reaction Gibbs energy when the partial pressures of the

N_2, H_2, and NH_3 (treated as perfect gases) are 3.0 bar, 1.0 bar, and 4.0 bar, respectively? What is the spontaneous direction of the reaction in this case?

73.3 The degree of dissociation, α, is defined as the fraction of reactant that has decomposed; if the initial amount of reactant is n and the amount at equilibrium is n_{eq}, then $\alpha = (n - n_{eq})/n$. The standard Gibbs energy of reaction for the decomposition $H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$ is $+118.08\,kJ\,mol^{-1}$ at 2300 K. What is the degree of dissociation of H_2O at 2300 K and 1.00 bar? *Hints*: The equilibrium constant is obtained from the standard Gibbs energy of reaction by using eqn 73.13, so the task is to relate the degree of dissociation, α, to K and then to find its numerical value. Proceed by expressing the equilibrium compositions in terms of α. For example, if an amount n H_2O is present initially, then an amount αn H_2O reacts to reach equilibrium and an amount $(1-\alpha)n$ $H_2O(g)$ is present at equilibrium. Then, solve for α in terms of K. Because the standard Gibbs energy of reaction is large and positive, we can anticipate that K will be small and hence that $\alpha \ll 1$, which opens the way to making approximations to obtain its numerical value.

73.4 Calculate the equilibrium constant of the reaction $CO(g) + H_2(g) \rightleftharpoons H_2CO(g)$ given that for the production of liquid formaldehyde $\Delta_r G^{\ominus} = +28.95\,kJ\,mol^{-1}$ at 298 K and that the vapour pressure of formaldehyde is 1500 Torr at that temperature.

73.5 A sealed container was filled with 0.300 mol $H_2(g)$, 0.400 mol $I_2(g)$, and 0.200 mol HI(g) at 870 K and total pressure 1.00 bar. Calculate the amounts of the components in the mixture at equilibrium given that $K = 870$ for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$.

73.6[‡] In a study of $Cl_2O(g)$ by photoelectron ionization (R.P. Thorn, et al. *J. Phys. Chem.* **100**, 14178 (1996)), the authors report $\Delta_f H^{\ominus}(Cl_2O) = +77.2\,kJ\,mol^{-1}$. They combined this measurement with literature data on the reaction $Cl_2O(g) + H_2O(g) \rightarrow 2\,HOCl(g)$, for which $K = 8.2 \times 10^{-2}$ and $\Delta_r S^{\ominus} = +16.38\,J\,K^{-1}\,mol^{-1}$, and with readily available thermodynamic data on water vapour to report a value for $\Delta_f H^{\ominus}(HOCl)$. Calculate that value. All quantities refer to 298 K.

73.7[‡] The 1980s saw reports of $\Delta_f H^{\ominus}(SiH_2)$ ranging from 243 to 289 kJ mol^{-1}. For example, the lower value was cited in the review article by R. Walsh (*Acc. Chem. Res.* **14**, 246 (1981)); Walsh later leant towards the upper end of the range (H.M. Frey, et al. *J. Chem. Soc., Chem. Commun.* 1189 (1986)). The higher value was reported by S.-K. Shin and J.L. Beauchamp (*J. Phys. Chem.* **90**, 1507 (1986)). If the standard enthalpy of formation is uncertain by this amount, by what factor is the equilibrium constant for the formation of SiH_2 from its elements uncertain at (a) 298 K, (b) 700 K?

73.8 Express the equilibrium constant of a gas-phase reaction $A + 3\,B \rightleftharpoons 2\,C$ in terms of the equilibrium value of the extent of reaction, ξ, given that initially A and B were present in stoichiometric proportions. Find an expression for ξ as a function of the total pressure, p, of the reaction mixture and sketch a graph of the expression obtained.

73.9 The equilibrium constant K calculated from thermodynamic data refers to activities. For gas-phase reactions, that means partial pressures (and explicitly, $p_J/p^{\ominus}$). However, in practical applications we might wish to discuss gas-phase reactions in terms of molar concentrations. The equilibrium constant is then denoted K_c, and for the equilibrium $a\,A(g) + b\,B(g) \rightleftharpoons c\,C(g) + d\,D(g)$, we write

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

with, as usual, the molar concentration [J] interpreted as $[J]/c^{\ominus}$ with $c^{\ominus} = 1\,mol\,dm^{-3}$. Show that

$$K = K_c \times \left(\frac{T}{T^{\ominus}}\right)^{\Delta\nu_{gas}} \qquad T^{\ominus} = \frac{p^{\ominus}}{Rc^{\ominus}}$$

where $\Delta\nu_{gas} = c + d - (a + b)$. Evaluate $T^{\ominus}$.

73.10 The protein myoglobin (Mb) stores O_2 in muscle and the protein haemoglobin (Hb) transports O_2 in blood; haemoglobin is composed of four myoglobin-like molecules. Here we explore the chemical equilibria associated with binding of O_2 in these proteins. (a) First, consider the equilibrium between Mb and O_2:

$$Mb(aq) + O_2(g) \rightleftharpoons MbO_2(aq) \qquad K = \frac{[MbO_2]}{[Mb]p}$$

where p is the numerical value of the partial pressure (in Torr) of O_2 gas. Show that the *fractional saturation*, s, the fraction of Mb molecules that are oxygenated, is

$$s = \frac{Kp}{1 + Kp}$$

and plot the dependence of s on p for $K = 5$ Torr. (b) Now consider the equilibria between Hb and O_2:

$$\begin{aligned}
&Hb(aq) + O_2(g) \rightleftharpoons HbO_2(aq) && K_1 = \frac{[HbO_2]}{[Hb]p}\\
&HbO_2(aq) + O_2(g) \rightleftharpoons Hb(O_2)_2(aq) && K_2 = \frac{[Hb(O_2)_2]}{[HbO_2]p}\\
&Hb(O_2)_2(aq) + O_2(g) \rightleftharpoons Hb(O_2)_3(aq) && K_3 = \frac{[Hb(O_2)_3]}{[Hb(O_2)_2]p}\\
&Hb(O_2)_3(aq) + O_2(g) \rightleftharpoons Hb(O_2)_4(aq) && K_4 = \frac{[Hb(O_2)_4]}{[Hb(O_2)_3]p}
\end{aligned}$$

Show that

$$s = \frac{[O_2]_{bound}}{4[Hb]_{total}} = \frac{AK_1p}{4B}$$

with

$$\begin{aligned}
A &= 1 + 2K_2p + 3K_2K_3p^2 + 4K_2K_3K_4p^3\\
B &= 1 + K_1p + K_1K_2p^2 + K_1K_2K_3p^3 + K_1K_2K_3K_4p^3
\end{aligned}$$

and plot the dependence of s on p (in torr) for $K_1 = 0.01$, $K_2 = 0.02$, $K_3 = 0.04$, and $K_4 = 0.08$. *Hints*: To develop an expression for s, proceed as follows: (i) express $[Hb(O_2)_2]$ in terms of $[HbO_2]$ by using K_2, then express $[HbO_2]$ in terms of [Hb] by using K_1, and likewise for all the other concentrations of $Hb(O_2)_3$ and $Hb(O_2)_4$. (ii) Show that

$$\begin{aligned}
[O_2]_{bound} &= [HbO_2] + 2[Hb(O_2)_2] + 3[Hb(O_2)_3] + 4[Hb(O_2)_4]\\
&= AK_1p[Hb]\\
[Hb]_{total} &= B[Hb]
\end{aligned}$$

(iii) Use the fact that each Hb molecule has four sites at which O_2 can attach. (c) The binding of O_2 to haemoglobin is an example of *cooperative binding*, in which the binding of a ligand (in this case O_2) to a biopolymer (in this case Hb) becomes more favourable thermodynamically (that is, the equilibrium constant increases) as the number of bound ligands increases up to the maximum number of binding sites. Which features of the plot from part (b) can be ascribed to cooperative binding of O_2 to Hb?

[‡] These problems were supplied by Charles Trapp and Carmen Giunta.

73.11 The curves you were asked to plot in Problem 73.10 may also be modelled mathematically by the equation

$$\log\left(\frac{s}{1-s}\right)=\nu_{\mathrm{H}}\log p-\nu_{\mathrm{H}}\log K$$

where s is the saturation, p is the partial pressure of O_2, K is a constant (not the binding constant for one ligand), and ν_{H} is the *Hill coefficient*, which varies from 1, for no cooperativity, to N, for all-or-none binding of N ligands ($N=4$ in Hb). The Hill coefficient for myoglobin is 1, and for haemoglobin it is 2.8. (a) Determine the constant K for both Mb and Hb from the graph of fractional saturation (at $s=0.5$) and then calculate the fractional saturation of Mb and Hb for the following values of p/kPa: 1.0, 1.5, 2.5, 4.0, 8.0. (b) Calculate the value of s at the same p values assuming ν_{H} has the theoretical maximum value of 4.

73.12 Here we investigate the molecular basis for the observation that the hydrolysis of ATP is exergonic at pH = 7.0 and 310 K. (a) It is thought that the exergonicity of ATP hydrolysis is due in part to the fact that the standard entropies of hydrolysis of polyphosphates are positive. Why would an increase in entropy accompany the hydrolysis of a triphosphate group into a diphosphate and a phosphate group? (b) Under identical conditions, the Gibbs energies of hydrolysis of H_4ATP and $MgATP^{2-}$, a complex between the Mg^{2+} ion and ATP^{4-}, are less negative than the Gibbs energy of hydrolysis of ATP^{4-}. This observation has been used to support the hypothesis that electrostatic repulsion between adjacent phosphate groups is a factor that controls the exergonicity of ATP hydrolysis. Provide a rationale for the hypothesis and discuss how the experimental evidence supports it. Do these electrostatic effects contribute to the $\Delta_r H$ or $\Delta_r S$ terms that determine the exergonicity of the reaction? *Hint*: In the $MgATP^{2-}$complex, the Mg^{2+} ion and ATP^{4-} anion form two bonds: one that involves a negatively charged oxygen belonging to the terminal phosphate group of ATP^{4-} and another that involves a negatively charged oxygen belonging to the phosphate group adjacent to the terminal phosphate group of ATP^{4-}.

73.13 To get a sense of the effect of cellular conditions on the ability of ATP to drive biochemical processes, compare the standard Gibbs energy of hydrolysis of ATP to ADP with the reaction Gibbs energy in an environment at 37 °C in which pH = 7.0 and the ATP, ADP, and P_i^- concentrations are all $1.0\,\mu\mathrm{mol\,dm^{-3}}$.

73.14 Under biochemical standard conditions, aerobic respiration produces approximately 38 molecules of ATP per molecule of glucose that is completely oxidized. (a) What is the percentage efficiency of aerobic respiration under biochemical standard conditions? (b) The following conditions are more likely to be observed in a living cell: $p_{CO_2}=5.3\times10^{-2}$ atm, $p_{O_2}=0.132$ atm, $[\text{glucose}]=5.6\times10^{-2}\,\mathrm{mol\,dm^{-3}}$, $[\text{ATP}]=[\text{ADP}]=[P_i]=1.0\times10^{-4}\,\mathrm{mol\,dm^{-3}}$, pH = 7.4, $T=310$ K. Assuming that activities can be replaced by the numerical values of molar concentrations, calculate the efficiency of aerobic respiration under these physiological conditions. (c) A typical diesel engine operates between $T_c=873$ K and $T_h=1923$ K with an efficiency that is approximately 75 per cent of the theoretical limit of $(1-T_c/T_h)$ (see Topic 61). Compare the efficiency of a typical diesel engine with that of aerobic respiration under typical physiological conditions (see part b). Why is biological energy conversion more or less efficient than energy conversion in a diesel engine?

73.15 In anaerobic bacteria, the source of carbon may be a molecule other than glucose and the final electron acceptor is some molecule other than O_2. Could a bacterium evolve to use the ethanol/nitrate pair instead of the glucose/O_2 pair as a source of metabolic energy?

73.16‡ Nitric acid hydrates have received much attention as possible catalysts for heterogeneous reactions which bring about the Antarctic ozone hole. Worsnop, et al. investigated the thermodynamic stability of these hydrates under conditions typical of the polar winter stratosphere (D.R. Worsnop, et al. *Science* **259**, 71 (1993)). Standard reaction Gibbs energies can be computed for the following reactions at 190 K from their data:

(i) $H_2O(g)\rightarrow H_2O(s)$ $\quad\Delta_r G^\ominus=-23.6\,\mathrm{kJ\,mol^{-1}}$

(ii) $H_2O(g)+HNO_3(g)\rightarrow HNO_3{\cdot}H_2O(s)$ $\quad\Delta_r G^\ominus=-57.2\,\mathrm{kJ\,mol^{-1}}$

(iii) $2\,H_2O(g)+HNO_3(g)\rightarrow HNO_3{\cdot}2H_2O(s)$ $\quad\Delta_r G^\ominus=-85.6\,\mathrm{kJ\,mol^{-1}}$

(iv) $3\,H_2O(g)+HNO_3(g)\rightarrow HNO_3{\cdot}3H_2O(s)$ $\quad\Delta_r G^\ominus=-112.8\,\mathrm{kJ\,mol^{-1}}$

Which solid is thermodynamically most stable at 190 K if $p_{H_2O}=1.3\times10^{-7}$ and $p_{HNO_3}=4.1\times10^{-10}$? *Hint*: Try computing $\Delta_r G$ for each reaction under the prevailing conditions; if more than one solid forms spontaneously, examine $\Delta_r G$ for the conversion of one solid to another.

Topic 74 The statistical description of equilibrium

Discussion question

74.1 Use concepts of statistical thermodynamics to describe the molecular features that determine the magnitudes of equilibrium constants and their variation with temperature.

Exercises

74.1(a) Calculate the value of K for the reaction $I_2(g)\rightleftharpoons 2\,I(g)$ at 1000 K from the following data for I_2: $\tilde{\nu}=214.36\,\mathrm{cm^{-1}}$, $\tilde{B}=0.0373\,\mathrm{cm^{-1}}$, $D_e=1.5422$ eV. The ground state of the I atoms is $^2P_{3/2}$, implying fourfold degeneracy.

74.1(b) Calculate the value of K at 298 K for the gas-phase isotopic exchange reaction $2\,{}^{79}\mathrm{Br}^{81}\mathrm{Br}\rightleftharpoons{}^{79}\mathrm{Br}^{79}\mathrm{Br}+{}^{81}\mathrm{Br}^{81}\mathrm{Br}$. The Br_2 molecule has a non-degenerate ground state, with no other electronic states nearby. Base the calculation on the wavenumber of the vibration of $^{79}\mathrm{Br}^{81}\mathrm{Br}$, which is $323.33\,\mathrm{cm^{-1}}$.

Problems

74.1 Calculate and plot as a function of temperature, in the range 300 K to 1000 K, the equilibrium constant for the reaction $CD_4(g)+HCl(g) \rightleftharpoons CHD_3(g)+DCl(g)$ using the following data (numbers in parentheses are degeneracies): $\tilde{\nu}(CHD_3)/cm^{-1}=2993(1),\ 2142(1),\ 1003(3),\ 1291(2),\ 1036(2)$; $\tilde{\nu}(CD_4)/cm^{-1}=2109(1),\ 1092(2),\ 2259(3),\ 996(3)$; $\tilde{\nu}(HCl)/cm^{-1}=2991$; $\tilde{\nu}(DCl)/cm^{-1}=2145$; $\tilde{B}(HCl)/cm^{-1}=10.59$; $\tilde{B}(DCl)/cm^{-1}=5.445$; $\tilde{A}(CHD_3)/cm^{-1}=3.28$; $\tilde{B}(CHD_3)/cm^{-1}=2.63$; $\tilde{B}(CD_4)/cm^{-1}=2.63$.

74.2 The exchange of deuterium between acid and water is an important type of equilibrium, and we can examine it using spectroscopic data on the molecules. Calculate the equilibrium constant at (a) 298 K and (b) 800 K for the gas-phase exchange reaction $H_2O+DCl \rightleftharpoons HDO+HCl$ from the following data: $\tilde{\nu}(H_2O)/cm^{-1}=3656.7,\ 1594.8,\ 3755.8$; $\tilde{\nu}(HDO)/cm^{-1}=2726.7,\ 1402.2,\ 3707.5$; $\tilde{A}(H_2O)/cm^{-1}=27.88$; $\tilde{B}(H_2O)/cm^{-1}=14.51$; $\tilde{C}(H_2O)/cm^{-1}=9.29$; $\tilde{A}(HDO)/cm^{-1}=23.38$; $\tilde{B}(HDO)/cm^{-1}=9.102$; $\tilde{C}(HDO)/cm^{-1}=6.417$; $\tilde{B}(HCl)/cm^{-1}=10.59$; $\tilde{B}(DCl)/cm^{-1}=5.449$; $\tilde{\nu}(HCl)/cm^{-1}=2991$; $\tilde{\nu}(DCl)/cm^{-1}=2145$.

Topic 75 The response of equilibria to the conditions

Discussion questions

75.1 Account for Le Chatelier's principle in terms of thermodynamic quantities. Can you think of a reason why the principle might fail?

75.2 State the limits to the generality of the van 't Hoff equation, written as in eqn 75.5.

Exercises

75.1(a) Calculate the percentage change in K_x for the reaction $H_2CO(g) \rightleftharpoons CO(g)+H_2(g)$ when the total pressure is increased from 1.0 bar to 3.0 bar at constant temperature.

75.1(b) Calculate the percentage change in K_x for the reaction $CH_3OH(g)+NOCl(g) \rightleftharpoons HCl(g)+CH_3NO_2(g)$ when the total pressure is increased from 1.0 bar to 4.0 bar at constant temperature.

75.2(a) The standard reaction enthalpy of $Zn(s)+H_2O(g) \rightarrow ZnO(s)+H_2(g)$ is approximately constant at $+224\,kJ\,mol^{-1}$ from 920 K up to 1280 K. The standard reaction Gibbs energy is $+33\,kJ\,mol^{-1}$ at 1280 K. Estimate the temperature at which the equilibrium constant becomes greater than 1.

75.2(b) The standard enthalpy of a certain reaction is approximately constant at $+125\,kJ\,mol^{-1}$ from 800 K up to 1500 K. The standard reaction Gibbs energy is $+22\,kJ\,mol^{-1}$ at 1120 K. Estimate the temperature at which the equilibrium constant becomes greater than 1.

75.3(a) The equilibrium constant of the reaction $2\,C_3H_6(g) \rightleftharpoons C_2H_4(g)+C_4H_8(g)$ is found to fit the expression $\ln K=A+B/T+C/T^2$ between 300 K and 600 K, with $A=-1.04$, $B=-1088\,K$, and $C=1.51\times10^5\,K^2$. Calculate the standard reaction enthalpy and standard reaction entropy at 450 K.

75.3(b) The equilibrium constant of a reaction is found to fit the expression $\ln K=A+B/T+C/T^3$ between 400 K and 600 K with $A=-2.01$, $B=-1170\,K$, and $C=2.2\times10^7\,K^3$. Calculate the standard reaction enthalpy and standard reaction entropy at 500 K.

75.4(a) What is the standard enthalpy of a reaction for which the equilibrium constant is (a) doubled, (b) halved when the temperature is increased by 10 K at 298 K?

75.4(b) What is the standard enthalpy of a reaction for which the equilibrium constant is (a) doubled, (b) halved when the temperature is increased by 15 K at 310 K?

75.5(a) Estimate the temperature at which $CaCO_3$(calcite) decomposes.

75.5(b) Estimate the temperature at which $CuSO_4{\cdot}5H_2O$ undergoes dehydration.

75.6(a) From information in the *Resource section*, calculate the standard Gibbs energy and the equilibrium constant at (a) 298 K and (b) 400 K for the reaction $PbO(s)+CO(g) \rightleftharpoons Pb(s)+CO_2(g)$. Assume that the reaction enthalpy is independent of temperature.

75.6(b) From information in the *Resource section*, calculate the standard Gibbs energy and the equilibrium constant at (a) 25 °C and (b) 50 °C for the reaction $CH_4(g)+3\,Cl_2(g) \rightleftharpoons CHCl_3(l)+3\,HCl(g)$. Assume that the reaction enthalpy is independent of temperature.

Problems

75.1 The dissociation vapour pressure of NH_4Cl at 427 °C is 608 kPa but at 459 °C it has risen to 1115 kPa. Calculate (a) the equilibrium constant, (b) the standard reaction Gibbs energy, (c) the standard enthalpy, (d) the standard entropy of dissociation, all at 427 °C. Assume that the vapour behaves as a perfect gas and that $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ are independent of temperature in the range given.

75.2 Consider the dissociation of methane, $CH_4(g)$, into the elements $H_2(g)$ and C(s, graphite). (a) Given that $\Delta_f H^{\ominus}(CH_4, g)=-74.85\,kJ\,mol^{-1}$ and that $\Delta_f S^{\ominus}(CH_4, g)=-80.67\,J\,K^{-1}\,mol^{-1}$ at 298 K, calculate the value of the equilibrium constant at 298 K. (b) Assuming that $\Delta_f H^{\ominus}$ is independent of temperature, calculate K at 50 °C.

75.3 The equilibrium pressure of H_2 over U(s) and UH_3(s) between 450 K and 715 K fits the expression $\ln(p/Pa)=A+B/T+C\ln(T/K)$, with $A=69.32$, $B=-1.464\times10^4\,K$, and $C=-5.65$. Find an expression for the standard enthalpy of formation of UH_3(s) and from it calculate $\Delta_r C_p^{\ominus}$.

75.4 The degree of dissociation, $\alpha_e = (n_{\text{initial}} - n_{\text{equilibrium}})/n_{\text{initial}}$, of $CO_2(g)$ into $CO(g)$ and $O_2(g)$ at high temperatures was found to vary with temperature as follows:

T/K	1395	1443	1498
$\alpha_e/10^{-4}$	1.44	2.50	4.71

Assuming $\Delta_r H^\ominus$ to be constant over this temperature range, calculate $\Delta_r H^\ominus$ and, at each of the above three temperatures, K, $\Delta_r G^\ominus$, and $\Delta_r S^\ominus$. Make any justifiable approximations.

75.5 The standard reaction enthalpy for the decomposition of $CaCl_2{\cdot}NH_3(s)$ into $CaCl_2(s)$ and $NH_3(g)$ is nearly constant at $+78\,\text{kJ mol}^{-1}$ between 350 K and 470 K. The equilibrium pressure of NH_3 in the presence of $CaCl_2{\cdot}NH_3$ is 1.71 kPa at 400 K. Find an expression for the temperature dependence of $\Delta_r G^\ominus$ in the same range.

75.6 Acetic acid was evaporated in a container of volume $21.45\,\text{cm}^3$ at 437 K and at an external pressure of 200 kPa. The container was then sealed. The mass of acid present in the sealed container was 0.0519 g. The experiment was repeated with the same container but at 471 K, and it was found that 0.0380 g of acetic acid was present. Calculate the equilibrium constant for the dimerization of the acid in the vapour and the enthalpy of vaporization.

75.7 The dissociation of I_2 can be monitored by measuring the total pressure, and three sets of results are as follows:

T/K	973	1073	1173
$100p$/atm	6.244	7.500	9.181
$10^4 n_I$	2.4709	2.4555	2.4366

where n_I is the amount of I atoms per mole of I_2 molecules in the mixture, which occupied $342.68\,\text{cm}^3$. Calculate the equilibrium constants of the dissociation and the standard enthalpy of dissociation at the mean temperature.

75.8‡ Suppose that an iron catalyst at a particular manufacturing plant produces ammonia in the most cost-effective manner at 450 °C when the pressure is such that $\Delta_r G$ for the reaction $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$ is equal to $-500\,\text{J mol}^{-1}$. (a) What pressure is needed? (b) Now suppose that a new catalyst is developed that is most cost-effective at 400 °C when the pressure gives the same value of $\Delta_r G$. What pressure is needed when the new catalyst is used? What are the advantages of the new catalyst? Assume that (i) all gases are perfect gases or that (ii) all gases are van der Waals gases. Isotherms of $\Delta_r G(T,p)$ in the pressure range $100\,\text{atm} \le p \le 400\,\text{atm}$ are needed to derive the answer. (c) Do the isotherms you plotted confirm Le Chatelier's principle concerning the response of equilibrium to changes in temperature and pressure?

75.9 Find an expression for the standard reaction Gibbs energy at a temperature T' in terms of its value at another temperature T and the coefficients a, b, and c in the expression for the molar heat capacity listed in Table 56.1. Evaluate the standard Gibbs energy of formation of $H_2O(l)$ at 372 K from its value at 298 K.

75.10‡ The dimerization of ClO in the Antarctic winter stratosphere is believed to play an important part in that region's severe seasonal depletion of ozone. The following equilibrium constants are based on measurements by Cox and Hayman (R. A. Cox and G. D. Hayman, *Nature* **332**, 796 (1988)) on the reaction $2\,ClO(g) \rightarrow (ClO)_2(g)$.

T/K	233	248	258	268	273
K	4.13×10^8	5.00×10^7	1.45×10^7	5.37×10^6	3.20×10^6

T/K	280	288	295	303
K	9.62×10^5	4.28×10^5	1.67×10^5	7.02×10^4

(a) Derive the values of $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ for this reaction. (b) Compute the standard enthalpy of formation and the standard molar entropy of $(ClO)_2$ given $\Delta_f H^\ominus(ClO) = +101.8\,\text{kJ mol}^{-1}$ and $S_m^\ominus(ClO) = 226.6\,\text{J K}^{-1}\,\text{mol}^{-1}$.

Topic 76 Electrochemical cells

Discussion questions

76.1 Describe the various types of galvanic and electrolytic cells.

76.2 Explain why salt bridges are used in electrochemical cell measurements.

Exercise

76.1(a) Write the cell reaction and electrode half-reactions of each of the following cells:

(a) $Zn(s)|ZnSO_4(aq)\|AgNO_3(aq)|Ag(s)$

(b) $Cd(s)|CdCl_2(aq)\|HNO_3(aq)|H_2(g)|Pt(s)$

(c) $Pt(s)|K_3[Fe(CN)_6](aq),K_4[Fe(CN)_6](aq)\|CrCl_3(aq)|Cr(s)$

(d) $Pt(s)|Fe^{3+}(aq),Fe^{2+}(aq)\|Sn^{4+}(aq),Sn^{2+}(aq)|Pt(s)$

76.1(b) Write the cell reaction and electrode half-reactions of each of the following cells:

(a) $Pt(s)|K_3[Fe(CN)_6](aq),K_4[Fe(CN)_6](aq)\|Mn^{2+}(aq),H^+(aq)|MnO_2(s)|Pt(s)$

(b) $Cu(s)|Cu^{2+}(aq)\|Mn^{2+}(aq),H^+(aq)|MnO_2(s)|Pt(s)$

(c) $Pt(s)|Cl_2(g)|HCl(aq)\|HBr(aq)|Br_2(l)|Pt(s)$

(d) $Fe(s)|Fe^{2+}(aq)\|Mn^{2+}(aq),H^+(aq)|MnO_2(s)|Pt(s)$

Problems

76.1 A fuel cell develops an electric potential from the chemical reaction between reagents supplied from an outside source. What is the potential of a cell fuelled by (a) hydrogen and oxygen, (b) the complete oxidation of benzene at 1.0 bar and 298 K?

76.2 A fuel cell is constructed in which both electrodes make use of the oxidation of methane. The left-hand electrode makes use of the complete oxidation of methane to carbon dioxide and water; the right-hand electrode makes use of the partial oxidation of methane to carbon monoxide and water. (a) Which electrode is the cathode? (b) What is the cell potential at 25 °C when all gases are at 1 bar?

Topic 77 Standard electrode potentials

Discussion questions

77.1 Discuss how the electrochemical series can be used to determine if a redox reaction is spontaneous under standard conditions.

77.2 Describe a method for the determination of the standard potential of a redox couple.

77.3 Describe at least one non-calorimetric experimental method for determining a standard reaction enthalpy.

Exercises

77.1(a) Calculate the standard potential of the Ce^{4+}/Ce couple from the values for the Ce^{3+}/Ce and Ce^{4+}/Ce^{3+} couples.
77.1(b) Calculate the standard potential of the Au^{3+}/Au^{+} couple from the values for the Au^{3+}/Au and Au^{+}/Au couples.

77.2(a) Can mercury produce zinc metal from aqueous zinc sulfate under standard conditions?
77.2(b) Can chlorine gas oxidize water to oxygen gas under standard conditions in basic solution?

77.3(a) The potential of the cell $Ag(s)|AgI(s)|AgI(aq)|Ag(s)$ is +0.9509 V at 25 °C. Calculate (a) the solubility of AgI and (b) the equilibrium constant for the dissolution of AgI(s).
77.3(b) The potential of the cell $Bi(s)|Bi_2S_3(s)|Bi_2S_3(aq)|Bi(s)$ is −0.96 V at 25 °C. Calculate (a) the solubility of Bi_2S_3 and (b) the equilibrium constant for the dissolution of $Bi_2S_3(s)$.

77.4(a) The standard potential of the cell $Pt(s)|H_2(g)|HCl(aq)|Hg_2Cl_2(s)|Hg(l)$ was found to be +0.2699 V at 293 K and +0.2669 V at 303 K. Evaluate the standard reaction Gibbs energy, enthalpy, and entropy at 298 K of the reaction $Hg_2Cl_2(s)+H_2(g) \rightarrow 2\ Hg(l)+2\ HCl(aq)$.
77.4(b) The standard potential of the cell $Pt(s)|H_2(g)|HBr(aq)|AgBr(s)|Ag(s)$ was found to be +0.07372 V at 293 K and +0.06873 V at 303 K. Evaluate the standard reaction Gibbs energy, enthalpy, and entropy at 298 K of the reaction $AgBr(s)+\tfrac{1}{2}\ H_2(g) \rightarrow Ag(s)+HBr(aq)$.

77.5(a) Calculate the standard cell potential and the value of $\Delta_r G^{\ominus}$ at 25 °C for the reactions in the following cells:

(a) $Zn(s)|ZnSO_4(aq)||AgNO_3(aq)|Ag(s)$

(b) $Cd(s)|CdCl_2(aq)||HNO_3(aq)|H_2(g)|Pt(s)$

(c) $Pt(s)|K_3[Fe(CN)_6](aq),K_4[Fe(CN)_6](aq)||CrCl_3(aq)|Cr(s)$

(d) $Pt(s)|Fe^{3+}(aq),Fe^{2+}(aq)||Sn^{4+}(aq),Sn^{2+}(aq)|Pt(s)$

77.5(b) Calculate the standard cell potential and the value of $\Delta_r G^{\ominus}$ at 25 °C for the reactions in the following cells:

(a) $Pt(s)|K_3[Fe(CN)_6](aq),K_4[Fe(CN)_6](aq)||Mn^{2+}(aq),H^{+}(aq)|MnO_2(s)|Pt(s)$

(b) $Cu(s)|Cu^{2+}(aq)||Mn^{2+}(aq),H^{+}(aq)|MnO_2(s)|Pt(s)$

(c) $Pt(s)|Cl_2(g)|HCl(aq)||HBr(aq)|Br_2(l)|Pt(s)$

(d) $Fe(s)|Fe^{2+}(aq)||Mn^{2+}(aq),H^{+}(aq)|MnO_2(s)|Pt(s)$

77.6(a) Devise cells in which the following are the reactions and calculate the standard cell potential in each case:

(a) $Fe(s)+PbSO_4(aq) \rightarrow FeSO_4(aq)+Pb(s)$

(b) $Hg_2Cl_2(s)+H_2(g) \rightarrow 2\ HCl(aq)+2\ Hg(l)$

(c) $2\ H_2(g)+O_2(g) \rightarrow 2\ H_2O(l)$

77.6(b) Devise cells in which the following are the reactions and calculate the standard cell potential in each case:

(a) $H_2(g)+O_2(g) \rightarrow H_2O_2(aq)$

(b) $H_2(g)+I_2(g) \rightarrow 2\ HI(aq)$

(c) $2\ CuCl(aq) \rightarrow Cu(s)+CuCl_2(aq)$

77.7(a) Consider the cell $Ag|AgBr(s)|KBr(aq,\ 0.050\ mol\ kg^{-1})||Cd(NO_3)_2(aq,\ 0.010\ mol\ kg^{-1})|Cd$. (a) Write the cell reaction. (b) Write the Nernst equation for the cell. (c) Use the Debye–Hückel limiting law and the Nernst equation to estimate the cell potential at 25 °C.
77.7(b) Consider the cell $Pt|H_2(g,p^{\ominus})|HCl(aq,\ 0.010\ mol\ kg^{-1})|AgCl(s)|Ag$. (a) Write the cell reaction. (b) Write the Nernst equation for the cell. (c) Use the Debye–Hückel limiting law and the Nernst equation to estimate the cell potential at 25 °C.

77.8(a) Calculate the equilibrium constants of the following reactions at 25 °C from standard potential data:

(a) $Sn(s)+Sn^{4+}(aq) \rightleftharpoons 2\ Sn^{2+}(aq)$

(b) $Fe(s)+Hg(NO_3)_2(aq) \rightleftharpoons Hg(l)+Fe(NO_3)_2(aq)$

77.8(b) Calculate the equilibrium constants of the following reactions at 25 °C from standard potential data:

(a) $Cd(s)+CuSO_4(aq) \rightleftharpoons Cu(s)+CdSO_4(aq)$

(b) $3\ Au^{2+}(aq) \rightleftharpoons Au(s)+2\ Au^{3+}(aq)$

Problems

77.1 Given that $\Delta_r G^{\ominus}=-212.7\ kJ\ mol^{-1}$ for the reaction in the Daniell cell at 25 °C, and $b(CuSO_4)=1.0\times10^{-3}\ mol\ kg^{-1}$ and $b(ZnSO_4)=3.0\times10^{-3}\ mol\ kg^{-1}$, calculate (a) the ionic strengths of the solutions, (b) the mean ionic activity coefficients in the compartments, (c) the reaction quotient, (d) the standard cell potential, and (e) the cell potential. (Take $\gamma_+=\gamma_-=\gamma_\pm$ in the respective compartments.)

77.2 Although the hydrogen electrode may be simple conceptually, it is cumbersome to use and several substitutes have been devised. One of these alternatives is the quinhydrone electrode (quinhydrone, $Q{\cdot}QH_2$, is a complex of quinone, $C_6H_4O_2=Q$, and hydroquinone, $C_6H_4O_2H_2=QH_2$). The electrode half-reaction is $Q(aq)+2\,H^+(aq)+e^-\rightarrow QH_2(aq)$, $E^{\ominus}=+0.6994$ V. If the cell $Hg|Hg_2Cl_2(s)|HCl(aq)|Q{\cdot}QH_2|Au$ is prepared, and the measured cell potential is +0.190 V, what is the pH of the HCl solution? Assume that the Debye–Hückel limiting law is applicable.

77.3 Consider the cell, $Zn(s)|ZnCl_2(0.0050\ mol\ kg^{-1})|Hg_2Cl_2(s)|Hg(l)$, for which the cell reaction is $Hg_2Cl_2(s)+Zn(s)\rightarrow 2\,Hg(l)+2\,Cl^-(aq)+Zn^{2+}(aq)$. Given that $E^{\ominus}(Zn^{2+},Zn)=-0.7628$ V, $E^{\ominus}(Hg_2Cl_2,Hg)=+0.2676$ V, and that the cell potential is +1.2272 V, (a) write the Nernst equation for the cell. Determine (b) the standard cell potential; (c) Δ_rG, $\Delta_rG^{\ominus}$, and K for the cell reaction; (d) the mean activity and activity coefficient of $ZnCl_2$ from the measured cell potential; and (e) the mean activity coefficient of $ZnCl_2$ from the Debye–Hückel limiting law. (f) Given that $(\partial E/\partial T)_p=-4.52\times10^{-4}\ \mathrm{V\,K^{-1}}$, calculate Δ_rS and Δ_rH.

77.4 The potential of the cell $Pt(s)|H_2(g,p^{\ominus})|HCl(aq,b)|Hg_2Cl_2(s)|Hg(l)$ has been measured with high precision (G. J. Hills and D. J. G. Ives, *J. Chem. Soc.*, 311 (1951)), with the following results at 25 °C:

$b/(\mathrm{mmol\,kg^{-1}})$	1.6077	3.0769	5.0403	7.6938	10.9474
E/V	0.60080	0.56825	0.54366	0.52267	0.50532

Determine the standard potential of the cell and the mean activity coefficient of HCl at these molalities. (Make a least-squares fit of the data to the best straight line.)

77.5 Careful measurements of the potential of the cell $Pt(s)|H_2(g,p^{\ominus})|NaOH(aq,0.0100\ mol\ kg^{-1}), NaCl(aq,0.01125\ mol\ kg^{-1})|AgCl(s)|Ag(s)$ have been reported (C.P. Bezboruah, et al. *J. Chem. Soc. Faraday Trans. I* **69**, 949 (1973)). Among the data is the following information:

θ/°C	20.0	25.0	30.0
E/V	1.04774	1.04864	1.04942

Calculate pK_w at these temperatures and the standard enthalpy and entropy of the autoprotolysis of water at 25.0 °C.

77.6 Measurements of the potentials of cells of the type $Ag(s)|AgX(s)MX(b_1)|M_xHg|MX(b_2)|AgX(s)|Ag(s)$, where M_xHg denotes an amalgam and the electrolyte is an alkali metal halide dissolved in ethylene glycol, have been reported (U. Sen, *J. Chem. Soc. Faraday Trans. I* **69**, 2006 (1973)), and some values for LiCl are given below. Estimate the activity coefficient at the concentration marked * and then use this value to calculate activity coefficients from the measured cell potential at the other concentrations. Base your answer on the Davies equation (eqn 72.29, $\log\gamma_\pm=-AI^{1/2}/(1+BI^{1/2})+CI$) for the mean ionic activity, with $A=1.461$, $B=1.70$, $k=0.20$, and $I=b/b^{\ominus}$. For $b_2=0.09141\ \mathrm{mol\,kg^{-1}}$:

$b_1/(\mathrm{mol\,kg^{-1}})$	0.0555	0.09141*	0.1652	0.2171	1.040	1.350
E/V	−0.0220	0.0000	0.0263	0.0379	0.1156	0.1336

77.7 The standard potential of the AgCl/Ag,Cl⁻ couple has been measured very carefully over a range of temperature (R.G. Bates and V.E. Bowers, *J. Res. Nat. Bur. Stand.* **53**, 283 (1954)) and the results were found to fit the expression

$$\begin{aligned}E^{\ominus}/\mathrm{V}=0.23659\ -\ 4.8564\times10^{-4}(\theta/°\mathrm{C})-3.4205\times10^{-6}(\theta/°\mathrm{C})^2\\+5.869\times10^{-9}(\theta/°\mathrm{C})^3\end{aligned}$$

Calculate the standard Gibbs energy and enthalpy of formation of $Cl^-(aq)$ and its entropy at 298 K.

77.8‡ The table below summarizes the potential observed for the cell $Pd(s)|H_2(g,1\ bar)|BH(aq,b), B(aq,b)|AgCl(s)|Ag(s)$. Each measurement is made at equimolar concentrations of 2-aminopyridinium chloride (BH) and 2-aminopyridine (B). The data are for 25 °C and it is found that $E^{\ominus}=0.22251$ V. Use the data to determine pK_a for the acid at 25 °C and the mean activity coefficient ($\gamma_\pm$) of BH as a function of molality (b) and ionic strength (I). Use the Davies equation for the mean activity coefficient (see Problem 77.6) with $A=0.5091$. Draw a graph of the mean activity coefficient with $b=0.04\ \mathrm{mol\,kg^{-1}}$ and $0\le I\le0.1$.

$b/(\mathrm{mol\,kg^{-1}})$	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10
$E^{\ominus}$(25 °C)/V	0.74452	0.72853	0.71928	0.71314	0.70809	0.70380	0.70059	0.69790	0.69571	0.69338

Hint: Use mathematical software or a spreadsheet.

77.9 Show that if the ionic strength of a solution of the sparingly soluble salt MX and the freely soluble salt NX is dominated by the concentration C of the latter, and if it is valid to use the Debye–Hückel limiting law, the solubility S' in the mixed solution is given by

$$S'=\frac{K_s e^{4.606AC^{1/2}}}{C}$$

when K_s is small (in a sense to be specified).

77.10 If the mitochondrial electric potential between matrix and the intermembrane space were 70 mV, as is common for other membranes, how much ATP could be synthesized from the transport of 4 mol H⁺, assuming the pH difference remains the same?

77.11 The standard potentials of proteins are not commonly measured by the methods described in this Topic because proteins often lose their native structure and function when they react on the surfaces of electrodes. In an alternative method, the oxidized protein is allowed to react with an appropriate electron donor in solution. The standard potential of the protein is then determined from the Nernst equation, the equilibrium concentrations of all species in solution, and the known standard potential of the electron donor. We shall illustrate this method with the protein cytochrome *c*. The one-electron reaction between cytochrome *c*, cyt, and 2,6-dichloroindophenol, D, can be followed spectrophotometrically because each of the four species in solution has a distinct colour, or absorption spectrum. We write the reaction as $cyt_{ox}+D_{red}\rightleftharpoons cyt_{red}+D_{ox}$, where the subscripts 'ox' and 'red' refer to oxidized and reduced states, respectively. (a) Consider $E^{\ominus}_{cyt}$ and $E^{\ominus}_{D}$ to be the standard potentials of cytochrome *c* and D, respectively. Show that, at equilibrium ('eq'), a plot of $\ln([D_{ox}]_{eq}/[D_{red}]_{eq})$ versus $\ln([cyt_{ox}]_{eq}/[cyt_{red}]_{eq})$ is linear with slope of 1 and *y*-intercept $F(E^{\ominus}_{cyt}-E^{\ominus}_{D})/RT$, where equilibrium activities are replaced by the numerical values of equilibrium molar concentrations. (b) The following data were obtained for the reaction between oxidized cytochrome *c* and reduced D in a pH = 6.5 buffer at 298 K. The ratios $[D_{ox}]_{eq}/[D_{red}]_{eq}$ and $[cyt_{ox}]_{eq}/[cyt_{red}]_{eq}$ were adjusted by titrating a solution containing oxidized cytochrome *c* and reduced D with a solution of sodium ascorbate, which is a strong reductant. From the data and the standard potential of D of 0.237 V, determine the standard potential of cytochrome *c* at pH = 6.5 and 298 K.

$[D_{ox}]_{eq}/[D_{red}]_{eq}$	0.00279	0.00843	0.0257	0.0497	0.0748	0.238	0.534
$[cyt_{ox}]_{eq}/[cyt_{red}]_{eq}$	0.0106	0.0230	0.0894	0.197	0.335	0.809	1.39

Integrated activities

F15.1 Nitrogen dioxide, a paramagnetic compound, is in equilibrium with its dimer, dinitrogen tetroxide, a diamagnetic compound. Derive an expression in terms of the equilibrium constant, K, for the dimerization to show how the molar magnetic susceptibility varies with the pressure of the sample (Topic 39). Suggest how the susceptibility might be expected to vary as the temperature is changed at constant pressure.

F15.2 Use mathematical software, a spreadsheet, or the *Living graphs* (labelled $^{\mathrm{LG}}$) on the website of this book for the following exercises:

(a) Plot x_A and x_B against the pressure p for several values of the equilibrium constant K for a reaction of the form $\mathrm{A(g)} \rightleftharpoons 2\,\mathrm{B(g)}$.

(b) The equilibrium constant of a reaction is found to fit the expression $\ln K = a + b/(T/\mathrm{K}) + c/(T/\mathrm{K})^3$ over a range of temperatures. (a) Write expressions for $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$. (b) Plot $\ln K$ against T between 400 K and 600 K for $a = -2.0$, $b = -1.0 \times 10^3$, and $c = 2.0 \times 10^7$.

(c) Plot the variation of cell potential with the value of the reaction quotient for the cell reaction for different values of the temperature. Does the cell potential become more or less sensitive to composition as the temperature increases?

(d) For the cell described in Example 77.1, plot a family of curves of E against $b/b^{\ominus}$ for several values of the temperature T.

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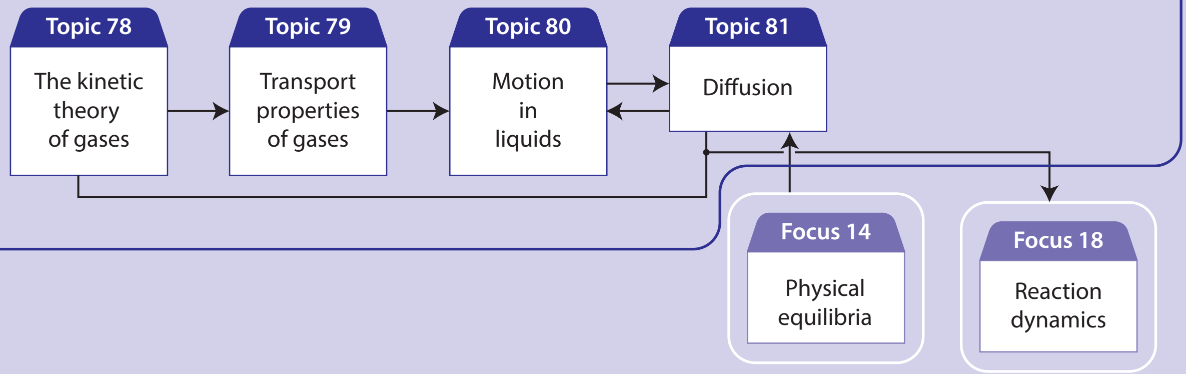
FOCUS 16 ON Molecular motion



That so many chemical reactions take place in gas and liquid phases is due in part to the mobility of molecules and ions in fluid media. To understand the rates of these reactions, which are treated as an aspect of *Reaction dynamics*, we need to know how fast molecules migrate and encounter one another.

A perfect gas is in principle very simple, and the model of a gas in which the molecules are in ceaseless chaotic motion provides a way to predict many of its properties (**Topic 78**). In fact, the kinetic theory of gases described in this Topic is a remarkable example of model-building in science, for from the flimsiest of assumptions precise predictions can be made about the pressure and the speeds of the molecules. Moreover, when molecules fly through space, they carry properties with them. By noting how far and how fast molecules move, we can build quantitative expressions for a number of these 'transport properties', including the thermal conductivity and viscosity of a perfect gas (**Topic 79**).

The motion of ions and molecules in liquids is quite different: instead of flying freely through space, a molecule or ion must migrate through a dense but mobile medium. One way to study this motion is to apply an electric field and to monitor the rate at which ions migrate under its influence (**Topic 80**). All solute particles, however, migrate by jostling their way past the surrounding solvent molecules, and their motion can be understood in terms of a 'thermodynamic force' that relies on the concept of the chemical potential introduced in *Physical equilibria*; furthermore we see that their average motion can be expressed in terms of two very powerful and general laws of diffusion (**Topic 81**). In fact, by treating the motion as a random walk, we see that there are analogies between the migration of molecules in liquids and in gases.

What is the impact of this material?

The migration of molecules and ions through matter is crucial to the occurrence of chemical reactions, but it also plays a central role in biology. In *Impact* 16.1 we examine how the transport properties of molecules are used in genomics and proteomics to establish the composition of nucleic acids and proteins. In *Impact* 16.2 we see how the experimental detection of the migration of ions across biological membranes leads to insights about the function of biological cells.

To read more about the impact of this material, scan the QR code or go to http://bcs.whfreeman.com/webpub/chemistry/qmc2e/impact/qchem_impact16.html.

TOPIC 78

The kinetic theory of gases

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➤ Why do you need to know this material?

There are 'scientific' and practical reasons for the importance of this material. The 'scientific' reason is that the discussion shows how to extract quantitative information from a qualitative model. The practical importance of the material is that it is used in the discussion of the properties of gases (Topic 36), in the discussion of catalysis (Topic 97), and in the discussion of reaction rates in gases (Topic 87).

➤ What is the key idea?

According to the kinetic model, a gas consists of molecules of negligible size in ceaseless random motion and obeying the laws of classical mechanics in their collisions.

➤ What do you need to know already?

You need to be aware of Newton's second law of motion, that the acceleration of a body is proportional to the force acting on it (*Foundations*, Topic 2).

In the **kinetic theory** of gases (which is sometimes called the *kinetic-molecular theory*, KMT) it is assumed that the only contribution to the energy of the gas is from the kinetic energies of the molecules. The kinetic model is one of the most remarkable—and arguably most beautiful—models in physical chemistry, for from a set of very slender assumptions, powerful quantitative conclusions can be reached.

78.1 The kinetic model

The kinetic model of a pure gas (of identical molecules) is based on four assumptions:

1. The gas consists of molecules of mass m in ceaseless random motion obeying the laws of classical mechanics.
2. The size of the molecules is negligible, in the sense that their diameters are much smaller than the average distance travelled between collisions.
3. Because the forces between molecules are assumed to have a short range, the molecules interact only through brief collisions.
4. The collisions are elastic.

An **elastic collision** is a collision in which the total translational kinetic energy of the molecules is conserved. The theory is applicable to a sample consisting of a large number of molecules in which it is safe to consider the average behaviour of the molecules and to ignore fluctuations from the mean.

(a) Pressure and molecular speeds

From the very economical assumptions of the kinetic model, we show in the following *Justification* that the pressure, p, and volume, V, of the gas are related by

$$pV=\tfrac{1}{3}nMv_{\text{rms}}^2$$

Perfect gas Pressure (78.1)

where $M=mN_{\text{A}}$, the molar mass of the molecules of mass m, n is the amount of molecules in the sample, and v_{rms} is the square root of the mean of the squares of the speeds, v, of the molecules:

$$v_{\text{rms}}=\langle v^2\rangle^{1/2}$$

Definition Root mean square speed (78.2)

Justification 78.1 The pressure of a gas according to the kinetic model

Consider the arrangement in Fig. 78.1. When a particle of mass m that is travelling with a component of velocity v_x parallel to the x-axis collides with the wall on the right and is reflected, its linear momentum changes from mv_x before the collision to $-mv_x$ after the collision (when it is travelling in the opposite direction). The x-component of momentum therefore changes by $2mv_x$ on each collision (the y- and z-components are unchanged). Many molecules collide with the wall in an interval Δt, and the total change of momentum is the product of the change in momentum of each molecule multiplied by the number of molecules that reach the wall during the interval.

Because a molecule with velocity component v_x can travel a distance $v_x\Delta t$ along the x-axis in an interval Δt, all the molecules within a distance $v_x\Delta t$ of the wall will strike it if they are travelling towards it (Fig. 78.2). It follows that if the wall has area A, then all the particles in a volume $A\times v_x\Delta t$ will reach the wall (if they are travelling towards it). The number density of particles is nN_{A}/V, where n is the total amount of molecules in the container of volume V and N_{A} is Avogadro's constant, so the number of molecules in the volume $Av_x\Delta t$ is $(nN_{\text{A}}/V)\times Av_x\Delta t$.

At any instant, half the particles are moving to the right and half are moving to the left. Therefore, the average number of collisions with the wall during the interval Δt is $\tfrac{1}{2}nN_A Av_x\Delta t/V$. The total momentum change in that interval is the product of this number and the change $2mv_x$:

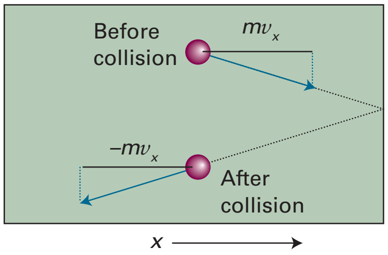


Figure 78.1 The pressure of a gas arises from the impact of its molecules on the walls. In an elastic collision of a molecule with a wall perpendicular to the x-axis, the x-component of velocity is reversed but the y- and z-components are unchanged.

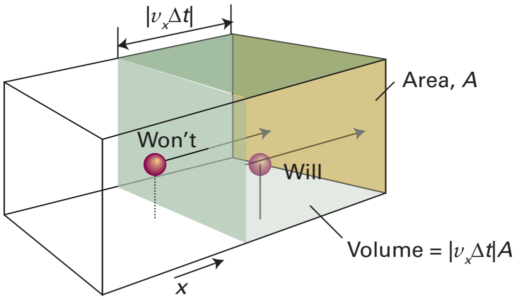


Figure 78.2 A molecule will reach the wall on the right within an interval Δt if it is within a distance $v_x\Delta t$ of the wall and travelling to the right.

$$\text{Momentum change}=\frac{nN_{\text{A}}Av_x\Delta t}{2V}\times 2mv_x$$

$$=\frac{n\overbrace{mN_{\text{A}}}^{M}Av_x^2\Delta t}{V}=\frac{nMAv_x^2\Delta t}{V}$$

Next, to find the force, we calculate the rate of change of momentum, which is this change of momentum divided by the interval Δt during which it occurs:

$$\text{Rate of change of momentum}=\frac{nMAv_x^2}{V}$$

This rate of change of momentum is equal to the force (by Newton's second law of motion). It follows that the pressure, the force divided by the area, is

$$\text{Pressure}=\frac{nMv_x^2}{V}$$

Not all the molecules travel with the same velocity, so the detected pressure, p, is the average (denoted $\langle\ldots\rangle$) of the quantity just calculated:

$$p=\frac{nM\langle v_x^2\rangle}{V}$$

This expression already resembles the perfect gas equation of state.

To write an expression for the pressure in terms of the root mean square speed, we begin by writing the speed of a single molecule, v, as $v^2=v_x^2+v_y^2+v_z^2$. Because the root mean square speed, v_{rms}, is defined as $v_{\text{rms}}=\langle v^2\rangle^{1/2}$ (as in eqn 78.2), it follows that

$$v_{\text{rms}}^2=\langle v^2\rangle=\langle v_x^2\rangle+\langle v_y^2\rangle+\langle v_z^2\rangle$$

However, because the molecules are moving randomly, all three averages are the same. It follows that $v_{\text{rms}}^2=3\langle v^2\rangle$. Equation 78.1 follows immediately by substituting $\langle v_x^2\rangle=\tfrac{1}{3}v_{\text{rms}}^2$ into $p=nM\langle v_x^2\rangle/V$.

Equation 78.1 is one of the key results of the kinetic model. We see that, if the root mean square speed of the molecules depends only on the temperature, then at constant temperature

$$pV = \text{constant}$$

which is the content of Boyle's law. Moreover, for eqn 78.1 to be the equation of state of a perfect gas, its right-hand side must be equal to nRT. It follows that the root mean square speed of the molecules in a gas at a temperature T must be

$$v_{\text{rms}} = \left(\frac{3RT}{M}\right)^{1/2} \qquad (78.3)$$

Perfect gas Root mean square speed

It is also possible to confirm that the right-hand side of eqn 78.1 is equal to nRT by appealing to the Boltzmann distribution. To do so, we proceed in two steps. First, in the following *Justification* we show that the fraction of molecules that have a speed in the range v to $v+\mathrm{d}v$ is $f(v)\mathrm{d}v$, where

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 \mathrm{e}^{-Mv^2/2RT} \qquad (78.4)$$

Perfect gas Maxwell–Boltzmann distribution

Justification 78.2 The Maxwell–Boltzmann distribution of speeds

The Boltzmann distribution implies that the fraction of molecules with velocity components v_x, v_y, and v_z is proportional to an exponential function of their kinetic energy: $f(v) = K\mathrm{e}^{-\varepsilon/kT}$, where K is a constant of proportionality. The kinetic energy is

$$\varepsilon = \tfrac{1}{2}mv_x^2 + \tfrac{1}{2}mv_y^2 + \tfrac{1}{2}mv_z^2$$

Therefore, we can use the relation $a^{x+y+z} = a^x a^y a^z$ to write

$$f(v) = K\mathrm{e}^{-(mv_x^2+mv_y^2+mv_z^2)/2kT} = K\mathrm{e}^{-mv_x^2/2kT}\mathrm{e}^{-mv_y^2/2kT}\mathrm{e}^{-mv_z^2/2kT}$$

The distribution factorizes into three terms, and we can write $f(v) = f(v_x)f(v_y)f(v_z)$ and $K = K_xK_yK_z$, with

$$f(v_x) = K_x\mathrm{e}^{-mv_x^2/2kT}$$

and likewise for the other two axes.

To determine the constant K_x, we note that a molecule must have a velocity component somewhere in the range $-\infty < v_x < \infty$, so

$$\int_{-\infty}^{\infty} f(v_x)\mathrm{d}v_x = 1$$

Substitution of the expression for $f(v_x)$ and use of Integral G.1 in the *Resource section* then gives

$$1 = K_x\int_{-\infty}^{\infty} \mathrm{e}^{-mv_x^2/2kT}\mathrm{d}v_x = K_x\left(\frac{2\pi kT}{m}\right)^{1/2}$$

Therefore, $K_x = (m/2\pi kT)^{1/2}$ and at this stage we can write

$$f(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} \mathrm{e}^{-mv_x^2/2kT}$$

The probability that a molecule has a velocity in the range v_x to $v_x+\mathrm{d}v_x$, v_y to $v_y+\mathrm{d}v_y$, v_z to $v_z+\mathrm{d}v_z$ is therefore

$$\begin{aligned} f(v_x)f(v_y)f(v_z)\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z &= \left(\frac{m}{2\pi kT}\right)^{3/2} \mathrm{e}^{-mv_x^2/2kT}\mathrm{e}^{-mv_y^2/2kT}\mathrm{e}^{-mv_z^2/2kT}\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z \\ &= \left(\frac{m}{2\pi kT}\right)^{3/2} \mathrm{e}^{-mv^2/2kT}\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z \end{aligned}$$

where $v^2 = v_x^2 + v_y^2 + v_z^2$.

To evaluate the probability that the molecules have a speed in the range v to $v+\mathrm{d}v$ regardless of direction we think of the three velocity components as defining three coordinates in 'velocity space', with the same properties as ordinary space except that the coordinates are labelled (v_x,v_y,v_z) instead of (x,y,z). Just as the volume element in ordinary space is $\mathrm{d}x\mathrm{d}y\mathrm{d}z$, so the volume element in velocity space is $\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$. The sum of all the volume elements in ordinary space that lie at a distance r from the centre is the volume of a spherical shell of radius r and thickness $\mathrm{d}r$. That volume is the product of its surface area, $4\pi r^2$, and its thickness, $\mathrm{d}r$, and is therefore $4\pi r^2\mathrm{d}r$. Similarly, the analogous volume in velocity space is the volume of a shell of radius v and thickness $\mathrm{d}v$, namely $4\pi v^2\mathrm{d}v$ (Fig. 78.3). Now, because $f(v_x)f(v_y)f(v_z)$, the term in blue in the last equation, depends only on v^2, and has the same value everywhere in a shell of radius v, the total probability of the molecules possessing a speed in the range v to $v+\mathrm{d}v$ is the product

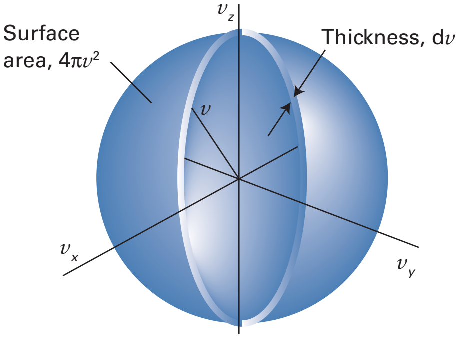


Figure 78.3 To evaluate the probability that a molecule has a speed in the range v to $v+\mathrm{d}v$, we evaluate the total probability that the molecule will have a speed that is anywhere on the surface of a sphere of radius $v = (v_x^2+v_y^2+v_z^2)^{1/2}$ by summing the probabilities that it is in a volume element $\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$ at a distance v from the origin.

of the term in blue and the volume of the shell of radius v and thickness $\mathrm{d}v$. If this probability is written $f(v)\mathrm{d}v$, it follows that

$$f(v)\mathrm{d}v = 4\pi v^2\mathrm{d}v\left(\frac{m}{2\pi kT}\right)^{3/2}\mathrm{e}^{-mv^2/2kT}$$

and $f(v)$ itself, after minor rearrangement, is

$$f(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}v^2\mathrm{e}^{-mv^2/2kT}$$

Because $m/k = M/R$, this expression is eqn 78.4.

The function $f(v)$ is called the **Maxwell–Boltzmann distribution of speeds**. Then we use this distribution to calculate the average value of v^2.

The important features of the Maxwell–Boltzmann distribution are as follows (and are shown pictorially in Fig. 78.4):

Physical interpretation

- Equation 78.4 includes a decaying exponential function (more specifically, a Gaussian function). Its presence implies that the fraction of molecules with very high speeds will be very small because e^{-x^2} becomes very small when x is large.
- The factor $M/2RT$ multiplying v^2 in the exponent is large when the molar mass, M, is large, so the exponential factor goes most rapidly towards zero when M is large. That is, heavy molecules are unlikely to be found with very high speeds.
- The opposite is true when the temperature, T, is high: then the factor $M/2RT$ in the exponent is small, so the exponential factor falls towards zero relatively slowly as v increases. In other words, a greater fraction of the molecules can be expected to have high speeds at high temperatures than at low temperatures.
- A factor v^2 (the term before the e) multiplies the exponential. This factor goes to zero as v goes to zero, so the fraction of molecules with very low speeds will also be very small whatever their mass.
- The remaining factors (the term in parentheses in eqn 78.4 and the 4π) simply ensure that, when we sum the fractions over the entire range of speeds from zero to infinity, we get 1.

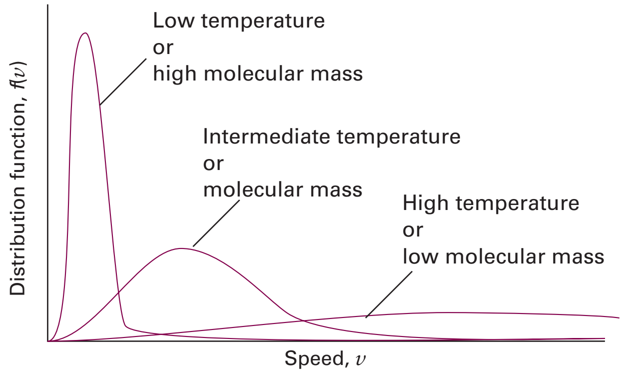


Figure 78.4 The distribution of molecular speeds with temperature and molar mass. Note that the most probable speed (corresponding to the peak of the distribution) increases with temperature and with decreasing molar mass, and simultaneously the distribution becomes broader.

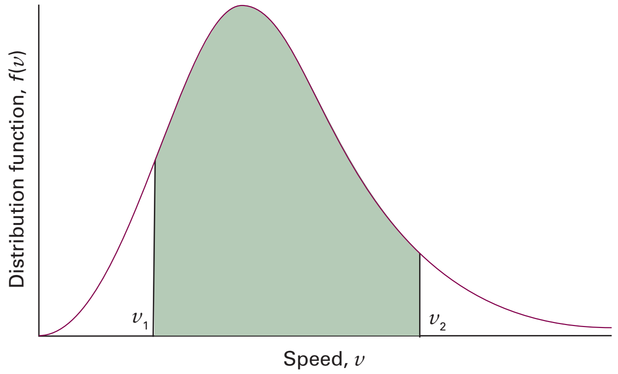


Figure 78.5 To calculate the probability that a molecule will have a speed in the range v_1 to v_2, we integrate the distribution between those two limits; the integral is equal to the area of the curve between the limits, as shown shaded here.

The Maxwell–Boltzmann distribution can be used to evaluate the fraction of molecules in the range from v_1 to v_2 by evaluating the integral

$$F(v_1,v_2) = \int_{v_1}^{v_2} f(v)\mathrm{d}v \qquad (78.5)$$

This integral is the area under the graph of f as a function of v and in general has to be evaluated numerically by using mathematical software (Fig. 78.5).

Brief illustration 78.1 The number of molecules with a range of speeds

To evaluate the number of N_2 molecules that have speeds in the range 200 to 220 m s^{-1} at 400 K we need to evaluate the integral in eqn 78.5 with $M = 28.02\ \mathrm{g\,mol^{-1}}$. First, we write

$$\frac{M}{2RT} = \frac{2.802\times10^{-2}\ \mathrm{kg\,mol^{-1}}}{2\times(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(400\ \mathrm{K})} = 4.21\ldots\times10^{-6}\ \mathrm{m^{-2}\,s^{2}}$$

and denote it a^2. Then (by using mathematical software to evaluate the integral),

$$F(200\,\mathrm{m\,s^{-1}},220\,\mathrm{m\,s^{-1}}) = 4\pi\overbrace{\left(\frac{a^2}{\pi}\right)^{3/2}}^{1.95\times10^{-8}\,\mathrm{m^{-3}\,s^3}}\overbrace{\int_{200\,\mathrm{m\,s^{-1}}}^{220\,\mathrm{m\,s^{-1}}} v^2 e^{-a^2v^2}\,\mathrm{d}v}^{7.32\times10^5\,\mathrm{m^3\,s^{-3}}}$$

$$=0.0143$$

That is, 1.43 per cent of the molecules lie in the specified range.

Self-test 78.1 Calculate the fraction of CO_2 molecules that have speeds in the range 400 to 500 m s^{-1} at 298 K.

Answer: 0.199

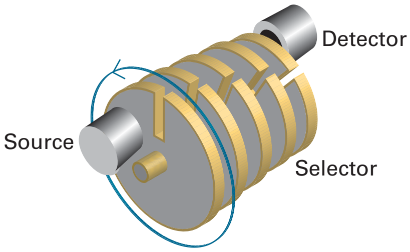


Figure 78.6 A velocity selector. The molecules are produced in the source (which may be an oven with a small hole in one wall), and travel in a beam towards the rotating discs. Only if the speed of a molecule is such as to carry it through the sequence of slits will it reach the detector. Thus, the number of slow molecules can be counted by rotating the discs slowly, and the number of fast molecules counted by rotating the discs rapidly.

The Maxwell–Boltzmann distribution has been verified experimentally. For example, molecular speeds can be measured directly with a velocity selector (Fig. 78.6). The spinning cylinder has channels that permit the passage of only those molecules moving through them at the appropriate speed, and the number of molecules can be determined by collecting them at a detector.

(b) Mean values

Once we have the Maxwell–Boltzmann distribution, we can calculate the mean value of any power of the speed by evaluating the appropriate integral (see *The chemist's toolkit* 78.1). Thus, to evaluate the average value of v^n we calculate

$$\langle v^n\rangle=\int_0^\infty v^n f(v)\mathrm{d}v \tag{78.6}$$

In particular, integration with $n=2$ results in eqn 78.3 for the mean square speed (v_{rms}^2) of the molecules at a temperature T. We can conclude that the root mean square speed of the molecules of a gas is proportional to the square root of the temperature and inversely proportional to the square root of the molar mass. That is, the higher the temperature, the higher the root mean square speed of the molecules, and, at a given temperature, heavy molecules travel more slowly than light molecules. Sound waves are pressure waves, and for them to propagate the molecules of the gas must move to form regions of high and low pressure. Therefore, we should expect the root mean square speeds of molecules to be comparable to the speed of sound in air (340 m s^{-1}). The root mean square speed of N_2 molecules, for instance, is found from eqn 78.3 to be 515 m s^{-1} at 298 K.

The chemist's toolkit 78.1 Mean values

The mean value (also called the *expectation value*) $\langle x\rangle$ of a property (such as the speed v) is calculated by first multiplying each discrete value x_i that the property can have (such as v_1, v_2, …, v_N) by the probability p_i that x_i occurs and then summing these products over all possible N values:

$$\langle x\rangle=\sum_{i=1}^{N}p_ix_i$$

When N is very large and the x_i values are so closely spaced that the property can be regarded as varying continuously (as is the case with molecular speeds), it is useful to express the probability that it can have a value between x and $x+\mathrm{d}x$ as

$$\text{Probability of finding a value between } x \text{ and } x+\mathrm{d}x = f(x)\mathrm{d}x$$

where the function $f(x)$ is the *probability density*. It follows that the probability that the property has a value between $x=a$ and $x=b$ is

$$\text{Probability of finding a value between } a \text{ and } b=\int_a^b f(x)\mathrm{d}x$$

The integral is equivalent to the area beneath the graph of the function $f(x)$ between the limits a and b. If $g(x)$ is a function of the property (for instance, a power of x, such as x^2; in the case of speeds, v^2), then its mean value in the range is

$$\langle g(x)\rangle=\int_a^b g(x)f(x)\mathrm{d}x$$

The mean value if x spans an infinite but positive range (like molecular speeds) is

$$\langle g(x)\rangle=\int_0^\infty g(x)f(x)\mathrm{d}x$$

Example 78.1 Calculating the mean speed of molecules in a gas

Calculate the mean speed, v_{mean}, of N_2 molecules in air at 25 °C.

Method The mean speed, v_{mean}, is obtained by evaluating the integral

$$v_{\text{mean}} = \int_0^\infty v f(v)\,dv$$

with $f(v)$ given in eqn 78.4. Either use mathematical software or use Integral G.4 given in the *Resource section*.

Answer The integral required is

$$\begin{aligned} v_{\text{mean}} &= 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_0^\infty v^3 e^{-mv^2/2kT}\,dv \\ &= 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\times\frac{1}{2}\left(\frac{2RT}{M}\right)^{2} = \left(\frac{8RT}{\pi M}\right)^{1/2} \end{aligned}$$

Substitution of the data then gives

$$v_{\text{mean}} = \left(\frac{8\times(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})\times(298\,\text{K})}{\pi\times(28.02\times10^{-3}\,\text{kg}\,\text{mol}^{-1})}\right)^{1/2} = 475\,\text{m}\,\text{s}^{-1}$$

We have used 1 J = 1 kg m^2 s^{-2}.

Self-test 78.2 Evaluate the root mean square speed of N_2 molecules at 25 °C by integration. Use mathematical software or Integral G.5 of the *Resource Section*.

Answer: $v_{\text{rms}} = (3RT/M)^{1/2} = 515\,\text{m}\,\text{s}^{-1}$

As shown in Example 78.1, we can use the Maxwell–Boltzmann distribution to evaluate the **mean speed**, v_{mean}, of the molecules in a gas:

$$v_{\text{mean}} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

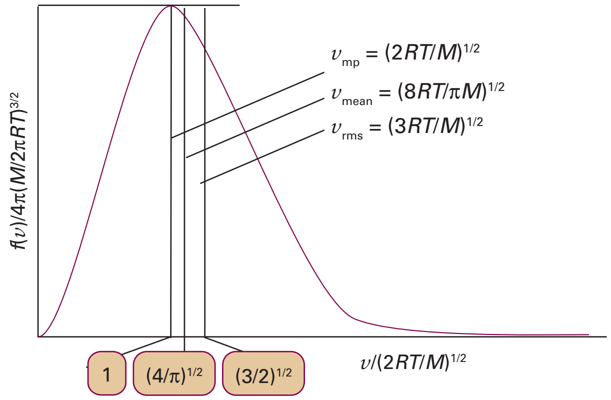
Perfect gas Mean speed (78.7)

We can identify the **most probable speed**, v_{mp}, from the location of the peak of the distribution:

$$v_{\text{mp}} = \left(\frac{2RT}{M}\right)^{1/2}$$

Perfect gas Most probable speed (78.8)

The location of the peak of the distribution is found by differentiating $f(v)$ with respect to v and looking for the value of v at which the derivative is zero (other than at $v=0$ and $v=\infty$; see Problem 78. 5). Figure 78.7 summarizes these results.



Figuer 78.7 A summary of the conclusions that can be deduced from the Maxwell–Boltzmann distribution for molecules of molar mass M at a temperature T: v_{mp} is the most probable speed, v_{mean} is the mean speed, and v_{rms} is the root mean square speed.

The mean relative speed, v_{rel}, the mean speed with which one molecule approaches another of the same kind, can also be calculated from the distribution:

$$v_{\text{rel}} = 2^{1/2} v_{\text{mean}}$$

Perfect gas, identical molecules Mean relative speed (78.9a)

This result is much harder to derive, but the diagram in Fig. 78.8 should help to show that it is plausible. For the relative mean speed of two dissimilar molecules of masses m_A and m_B,

$$v_{\text{rel}} = \left(\frac{8RT}{\pi\mu}\right)^{1/2} \qquad \mu = \frac{M_A M_B}{M_A + M_B}$$

Perfect gas Mean relative speed (78.9b)

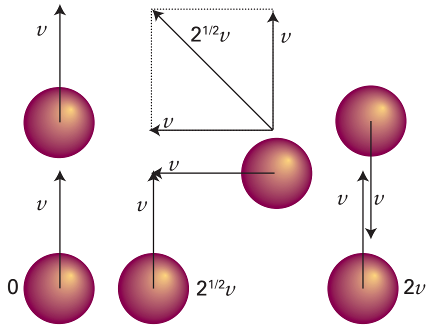


Figure 78.8 A simplified version of the argument to show that the mean relative speed of molecules in a gas is related to the mean speed. When the molecules are moving in the same direction, the relative speed is zero; it is $2v$ when the molecules are approaching each other. A typical mean direction of approach is from the side, and the speed of approach is then $2^{1/2}v$. The last direction of approach is the most characteristic, so the speed of approach can be expected to be about $2^{1/2}v$. This value is confirmed by more detailed calculation.

Equation 78.9b turns into eqn 78.9a when the molecules are identical (that is when $M_A = M_B = M$ so $\mu = M/2$).

(c) The collision frequency

Although the kinetic-molecular theory assumes that the molecules are point-like, we can count a 'hit' whenever the centres of two molecules come within a distance d of each other, where d, the **collision diameter**, is of the order of the actual diameters of the molecules (for impenetrable hard spheres d is the diameter). As we show in the following *Justification*, we can use the kinetic model to deduce that the **collision frequency**, z, the number of collisions made by one molecule divided by the time interval during which the collisions are counted, when there are N molecules in a volume V, is

$$z = \sigma v_{\text{rel}} \mathcal{N} \qquad \textit{Perfect gas} \qquad \text{Collision frequency} \qquad (78.10a)$$

with $\mathcal{N} = N/V$, the number density, and $\bar{v}_{\text{rel}}$ given by eqn 78.9. The area $\sigma = \pi d^2$ is called the **collision cross-section** of the molecules. Some typical collision cross-sections are given in Table 78.1. In terms of the pressure (as is also shown in the following *Justification*),

$$z = \frac{\sigma v_{\text{rel}} p}{kT} \qquad \textit{Perfect gas} \qquad \text{Collision frequency} \qquad (78.10b)$$

Table 78.1* Collision cross-sections

	σ/nm^2
C_6H_6	0.88
CO_2	0.52
He	0.21
N_2	0.43

* More values are given in the *Resource section*.

Justification 78.3 The collision frequency

Consider the positions of all the molecules except one to be frozen. Then note what happens as one mobile molecule travels through the gas with a mean relative speed v_{rel} for a time Δt. In doing so it sweeps out a 'collision tube' of cross-sectional area $\sigma = \pi d^2$ and length $v_{\text{rel}}\Delta t$ and therefore of volume $\sigma v_{\text{rel}}\Delta t$ (Fig. 78.9). The number of stationary molecules with centres inside the collision tube is given by the volume of the tube multiplied by the number density $\mathcal{N} = N/V$, and is $\mathcal{N}\sigma v_{\text{rel}}\Delta t$. The number of hits scored in the interval Δt is equal to this number, so the number of collisions divided by the time interval is $\mathcal{N}\sigma v_{\text{rel}}$, which is eqn 78.10a. The expression in terms of the pressure of the gas is obtained by using the perfect gas equation and $R = kN_A$ to write

$$\mathcal{N} = \frac{N}{V} = \frac{nN_A}{V} = \frac{nN_A}{nRT/p} = \frac{p}{kT}$$

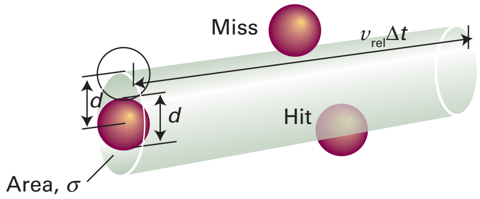


Figure 78.9 In an interval Δt, a molecule of diameter d sweeps out a tube of radius d and length $v_{\text{rel}}\Delta t$. As it does so it encounters other molecules with centres that lie within the tube, and each such encounter counts as one collision. In reality, the tube is not straight, but changes direction at each collision. Nevertheless, the volume swept out is the same, and this straightened version of the tube can be used as a basis of the calculation.

Equation 78.10a shows that, at constant volume, the collision frequency increases with increasing temperature. Equation 78.10b shows that, at constant temperature, the collision frequency is proportional to the pressure. Such a proportionality is plausible because the greater the pressure, the greater the number density of molecules in the sample, and the rate at which they encounter one another is greater even though their average speed remains the same.

Brief illustration 78.2 Molecular collisions

For an N_2 molecule in a sample at 1.00 atm (101 kPa) and 25 °C, from Example 78.1 we know that $v_{\text{mean}} = 475\ \text{m s}^{-1}$, so from eqn 78.9a, $v_{\text{rel}} = 2^{1/2} \times 475\ \text{m s}^{-1}$. Therefore, from eqn 78.10b, and taking $\sigma = 0.43\ \text{nm}^2$ (corresponding to $0.43 \times 10^{-18}\ \text{m}^2$) from Table 78.1,

$$\begin{aligned} z &= \frac{(0.43\times10^{-18}\ \text{m}^2)\times(2^{1/2}\times475\ \text{m s}^{-1})\times(1.01\times10^5\ \text{Pa})}{(1.381\times10^{-23}\ \text{J K}^{-1})\times(298\ \text{K})} \\ &= 7.1\times10^9\ \text{s}^{-1} \end{aligned}$$

so a given molecule collides about 7×10^9 times each second. We are beginning to appreciate the timescale of events in gases.

Self-test 78.3 Evaluate the collision frequency between H_2 molecules in a gas under the same conditions.

Answer: $1.7 \times 10^{10}\ \text{s}^{-1}$

(d) The mean free path

Once we have the collision frequency, we can calculate the **mean free path**, λ (lambda), the average distance a molecule travels between collisions. If a molecule collides with a frequency z, it spends a time $1/z$ in free flight between collisions, and therefore travels a distance $(1/z)v_{\text{rel}}$. It follows that the mean free path is

$$\lambda = \frac{v_{\text{rel}}}{z} \qquad \textit{Perfect gas} \quad \text{Mean free path} \tag{78.11}$$

Substitution of the expression for z in eqn 78.10b gives

$$\lambda = \frac{kT}{\sigma p} \qquad \textit{Perfect gas} \quad \text{Mean free path} \tag{78.12}$$

Doubling the pressure reduces the mean free path by half.

Brief illustration 78.3 The mean free path

In *Brief illustration* 78.2 we noted that $v_{\text{rel}} = 2^{1/2} \times 475\,\text{m}\,\text{s}^{-1}$ for N_2 molecules at 25 °C, and $z = 7.1 \times 10^9\,\text{s}^{-1}$ when the pressure is 1.00 atm. Under these circumstances, the mean free path of N_2 molecules is

$$\lambda = \frac{2^{1/2} \times 475\,\text{m}\,\text{s}^{-1}}{7.1 \times 10^9\,\text{s}^{-1}} = 9.5 \times 10^{-8}\,\text{m}$$

or 95 nm, about 10^3 molecular diameters.

Self-test 78.4 Evaluate the mean free path of benzene molecules at 25 °C in a sample where the pressure is 0.10 atm.

Answer: 460 nm

Although the temperature appears in eqn 78.12, in a sample of constant volume, the pressure is proportional to T, so T/p remains constant when the temperature is increased. Therefore, the mean free path is independent of the temperature in a sample of gas in a container of fixed volume: the distance between collisions is determined by the number of molecules present in the given volume, not by the speed at which they travel.

In summary, a typical gas (N_2 or O_2) at 1 atm and 25 °C can be thought of as a collection of molecules travelling with a mean speed of about 500 m s⁻¹. Each molecule makes a collision within about 1 ns, and between collisions it travels about 10^3 molecular diameters. The kinetic model of gases is valid and the gas behaves nearly perfectly if the diameter of the molecules is much smaller than the mean free path ($d \ll \lambda$), for then the molecules spend most of their time far from one another.

78.2 Collisions with walls and surfaces

The key result for accounting for transport in the gas phase is the rate at which molecules strike an area (which may be an imaginary area embedded in the gas, or part of a real wall). The **collision flux**, Z_W is the number of collisions with the area in a given time interval divided by the area and the duration of the interval.

(a) The collision flux

The collision frequency, the number of hits per second, is obtained by multiplication of the collision flux by the area of interest. We show in the following *Justification* that the collision flux is

$$Z_W = \frac{p}{(2\pi mkT)^{1/2}} \qquad \textit{Perfect gas} \quad \text{Collision flux} \tag{78.13}$$

Brief illustration 78.4 The collision flux

The collision flux of O_2 molecules, with $m = M/N_A$ and $M = 32.00\,\text{g}\,\text{mol}^{-1}$, at 25 °C and at 1.00 bar is

$$\begin{aligned} Z_W &= \frac{1.00 \times 10^5\ \overbrace{\text{Pa}}^{\text{kg}\,\text{m}^{-1}\,\text{s}^{-2}}}{\{2\pi \times (32.00 \times 10^{-3}\,\text{kg}\,\text{mol}^{-1}/6.022 \times 10^{23}\,\text{mol}^{-1}) \times (1.381 \times 10^{-23}\,\text{J}\,\text{K}^{-1}) \times (298\,\text{K})\}^{1/2}} \\ &= 2.70 \times 10^{27}\,\text{m}^{-2}\,\text{s}^{-1} \end{aligned}$$

This flux corresponds to $2.70 \times 10^{23}\,\text{cm}^{-2}\,\text{s}^{-1}$.

Self-test 78.5 Evaluate the collision flux of H_2 molecules under the same conditions.

Answer: $1.07 \times 10^{28}\,\text{m}^{-2}\,\text{s}^{-1}$

Justification 78.4 The collision flux

Consider a wall of area A perpendicular to the x-axis (as in Fig. 78.2). If a molecule has $v_x > 0$ (that is, it is travelling in the direction of positive x), then it will strike the wall within an interval Δt if it lies within a distance $v_x\Delta t$ of the wall. Therefore, all molecules in the volume $Av_x\Delta t$, and with positive x-component of velocities, will strike the wall in the interval Δt. The total number of collisions in this interval is therefore the volume $Av_x\Delta t$ multiplied by the number density, $\mathcal{N}$, of molecules. However, to take account of the presence of a range of velocities in the sample, we must sum the result over all the positive values of v_x weighted by the probability distribution of velocities given in *Justification* 78.2:

$$\text{Number of collisions} = \mathcal{N}A\Delta t\int_0^\infty v_x f(v_x)\mathrm{d}v_x$$

The collision flux is the number of collisions divided by A and Δt, so

$$Z_\mathrm{W} = \mathcal{N}\int_0^\infty v_x f(v_x)\mathrm{d}v_x$$

Then, using the velocity distribution $f(v_x)$ found in *Justification* 78.2 and Integral G.2 from the *Resource section*, we find

$$\int_0^\infty v_x f(v_x)\mathrm{d}v_x = \left(\frac{m}{2\pi kT}\right)^{1/2}\int_0^\infty v_x \mathrm{e}^{-mv_x^2/2kT}\mathrm{d}v_x = \left(\frac{kT}{2\pi m}\right)^{1/2}$$

Therefore,

$$Z_\mathrm{W} = \mathcal{N}\left(\frac{kT}{2\pi m}\right)^{1/2}$$

Substitution of $\mathcal{N}=p/kT$ then gives eqn 78.13.

(b) Effusion

The essential empirical observations on effusion are summarized by **Graham's law of effusion**, which states that the rate of effusion is inversely proportional to the square root of the molar mass. The basis of this result is that, as remarked above, the mean speed of molecules is inversely proportional to $M^{1/2}$, so the rate at which they strike the area of the hole is also inversely proportional to $M^{1/2}$. However, by using the expression for the rate of collisions, we can obtain a more detailed expression for the rate of effusion and hence use effusion data more effectively.

When a gas at a pressure p and temperature T is separated from a vacuum by a small hole, the rate of escape of its molecules is equal to the rate at which they strike the area of the hole, which is the product of the area and collision flux. Therefore, for a hole of area A_0

$$\text{Rate of effusion} = Z_\mathrm{W}A_0 = \frac{pA_0}{(2\pi mkT)^{1/2}} \qquad \textit{Perfect gas} \qquad \text{Effusion} \qquad (78.14)$$

Because $M=mN_\mathrm{A}$, this rate is inversely proportional to $M^{1/2}$, in accord with Graham's law.

Equation 78.14 is the basis of the **Knudsen method** for the determination of the vapour pressures of liquids and solids, particularly of substances with very low vapour pressures. In this technique, a sample of the substance is enclosed in a cavity with a small hole and its mass is monitored as a function of time. The value of the vapour pressure, p, is then obtained by applying eqn 78.14.

Example 78.2 Calculating the vapour pressure from a mass loss

Caesium (m.p. 29 °C, b.p. 686 °C) was introduced into a container and heated to 500 K. When a hole of diameter 0.50 mm was opened in the container for 100 s, a mass loss of 385 mg was measured. Calculate the vapour pressure of liquid caesium at 500 K.

Method The pressure of vapour is constant inside the container despite the effusion of atoms because the hot liquid metal replenishes the vapour. The rate of effusion is therefore constant, and given by eqn 78.14. To express the rate in terms of mass, multiply the number of atoms that escape by the mass of each atom.

Answer The mass loss Δm in an interval Δt is related to the collision flux by $\Delta m = Z_\mathrm{W}A_0 m\Delta t$, where A_0 is the area of the hole and m is the mass of one atom. It follows from eqn 78.14 that

$$\Delta m = \frac{pA_0 m\Delta t}{(2\pi mkT)^{1/2}} = \frac{pA_0 m^{1/2}\Delta t}{(2\pi kT)^{1/2}}$$

and therefore that

$$p = \left(\frac{2\pi kT}{m}\right)^{1/2}\frac{\Delta m}{A_0\Delta t} = \left(\frac{2\pi RT}{M}\right)^{1/2}\frac{\Delta m}{A_0\Delta t}$$

Substitution of the data and $M = 132.9\ \mathrm{g\,mol^{-1}}$ gives

$$\begin{aligned} p &= \left(\frac{2\pi\times(8.3145\,\mathrm{J\,K^{-1}})\times(500\,\mathrm{K})}{132.9\times10^{-3}\,\mathrm{kg\,mol^{-1}}}\right)^{1/2} \\ &\quad\times\frac{385\times10^{-6}\,\mathrm{kg}}{\pi\times(0.25\times10^{-3}\,\mathrm{m})^2\times(100\,\mathrm{s})} \\ &= 8.7\times10^3\,\overbrace{\mathrm{kg\,m^{-1}s^{-2}}}^{\mathrm{Pa}} \end{aligned}$$

or 8.7 kPa.

Self-test 78.6 How long would it take 1.0 g of Cs atoms to effuse out of the oven under the same conditions?

Answer: 260 s

Checklist of concepts

☐ **1.** In the **kinetic theory** (or *kinetic-molecular theory*, KMT) of gases it is assumed that the only contribution to the energy of the gas is from the kinetic energies of the molecules.

☐ **2.** An **elastic collision** is a collision in which the total translational kinetic energy of the molecules is conserved.

☐ **3.** The **Maxwell–Boltzmann distribution of speeds** gives the probability that a molecule will have a given speed (see below).

☐ **4.** The **root mean square speed** of the molecules of a gas is proportional to the square root of the temperature and inversely proportional to the square root of the molar mass.

☐ **5.** The **collision frequency** is the number of collisions made by one molecule divided by the time interval during which the collisions are counted.

☐ **6.** The **mean free path** is the average distance a molecule travels between collisions.

☐ **7.** The **collision flux** is the number of collisions with the area in a given time interval divided by the area and the duration of the interval.

☐ **8.** **Graham's law of effusion** states that the rate of effusion is inversely proportional to the square root of the molar mass.

☐ **9.** The **Knudsen method** is a technique for the determination of the vapour pressures of liquids and solids by monitoring mass loss by effusion.

Checklist of equations

Property	Equation	Comment	Equation number
Pressure	$pV=\frac{1}{3}nMv_{\rm rms}^2$	KMT*	78.1
Root mean square speed	$v_{\rm rms}=\langle v^2\rangle^{1/2}$	Definition	78.2
	$v_{\rm rms}=(3RT/M)^{1/2}$	KMT	78.3
Maxwell–Boltzmann distribution	$f(v)=4\pi\left(M/2\pi RT\right)^{3/2}v^2{\rm e}^{-Mv^2/2RT}$	KMT	78.4
Mean speed	$v_{\rm mean}=(8RT/\pi M)^{1/2}$	KMT	78.7
Most probable speed	$v_{\rm mp}=(2RT/M)^{1/2}$	KMT	78.8
Mean relative speed	$v_{\rm rel}=(8RT/\pi\mu)^{1/2}$	$\mu=M_AM_B/(M_A+M_B)$, KMT	78.9b
Collision frequency	$z=\sigma v_{\rm rel}\mathcal{N}$	KMT	78.10a
Mean free path	$\lambda=v_{\rm rel}/z$	KMT	78.11
Collision flux	$Z_W=p/(2\pi mkT)^{1/2}$	KMT	78.13
Rate of effusion	Rate of effusion $=Z_WA_0$	KMT; rate in terms of number, not amount	78.14

* KMT denotes a result derived on the basis of kinetic-molecular theory of gases.

TOPIC 79

Transport properties of gases

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➤ Why do you need to know this material?

The transport of properties by gas molecules plays an important role in the atmosphere. It also extends the approach of kinetic theory, showing how to extract quantitative expressions from simple models.

➤ What is the key idea?

A molecule carries properties through space for about the distance of its mean free path.

➤ What do you need to know already?

This Topic builds on and extends the kinetic theory of gases (Topic 78) and you need to be familiar with the expressions from that Topic for the mean speed of molecules and with the significance of the mean free path and its pressure dependence. It also uses the expression for the collision flux.

Transport properties are commonly expressed in terms of a number of 'phenomenological' equations, equations that are empirical summaries of experimental observations. These phenomenological equations apply to all kinds of properties and media. In the following sections, we introduce the equations for the general case and then show how to calculate the parameters that appear in them.

79.1 The phenomenological equations

By a 'phenomenological equation', a term encountered commonly in the study of fluids, we mean an equation that summarizes empirical observations on phenomena without, initially at least, being based on an understanding of the molecular processes responsible for the property.

The net rate of transport of a property is measured by its **flux**, *J*, the quantity of that property passing through a given area in a given time interval divided by the area and the duration of the interval. If matter is flowing (as in diffusion), we speak of a **matter flux** of so many molecules per square metre per second; if the property is the energy of thermal motion (as in thermal conduction), then we speak of the **energy flux** and express it in joules per square metre per second, and so on.

Experimental observations on transport properties show that the flux of a property is usually proportional to the first derivative of some other related property. For example, the flux of matter diffusing parallel to the *z*-axis of a container is found to be proportional to the first derivative of the concentration:

$$J(\text{matter}) \propto \frac{d\mathcal{N}}{dz} \tag{79.1}$$

where $\mathcal{N}$ is the number density of particles with units number per metre cubed (m^{-3}). The SI units of J are number per square metre per second ($\text{m}^{-2}\,\text{s}^{-1}$). The proportionality of the flux of matter to the concentration gradient is sometimes called **Fick's first law of diffusion**: the law implies that if the concentration varies steeply with position, then diffusion will be fast.[1]

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[1] Fick's 'second law' is treated in Topic 81.

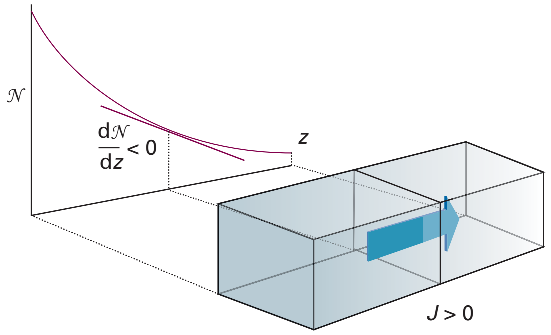

Figure 79.1 The flux of particles down a concentration gradient. Fick's first law states that the flux of matter (the number of particles passing through an imaginary window in a given time interval divided by the area of the window and the length of the interval) is proportional to the density gradient at that point.

There is no net flux if the concentration is uniform ($d\mathcal{N}/dz = 0$). Similarly, the rate of thermal conduction (the flux of the energy associated with thermal motion) is found to be proportional to the temperature gradient:

$$J(\text{energy of thermal motion}) \propto \frac{dT}{dz} \qquad (79.2)$$

The SI units of this flux are joules per square metre per second ($\mathrm{J\,m^{-2}\,s^{-1}}$).

A positive value of J signifies a flux towards positive z; a negative value of J signifies a flux towards negative z. Because matter flows down a concentration gradient, from high concentration to low concentration, J is positive if $d\mathcal{N}/dz$ is negative (Fig. 79.1). Therefore, the coefficient of proportionality in eqn 79.1 must be negative, and we write it $-D$, with D a positive constant:

$$J(\text{matter}) = -D\frac{d\mathcal{N}}{dz} \qquad \textit{Definition} \quad \text{Diffusion coefficient} \qquad (79.3)$$

The constant D is called the **diffusion coefficient**; its SI units are metre squared per second ($\mathrm{m^2\,s^{-1}}$). Energy of thermal motion ('heat') migrates down a temperature gradient, and the same reasoning leads to

$$J(\text{energy of thermal motion}) = -\kappa\frac{dT}{dz} \qquad \textit{Definition} \quad \text{Thermal conductivity} \qquad (79.4)$$

where κ (kappa) is the **coefficient of thermal conductivity**. The SI units of κ are joules per kelvin per metre per second, or watts per kelvin per metre ($\mathrm{J\,K^{-1}\,m^{-1}\,s^{-1}}$, or $\mathrm{W\,K^{-1}\,m^{-1}}$). Some experimental values are given in Table 79.1.

Table 79.1* Transport properties of gases at 1 atm

	$\kappa/(\mathrm{mW\,K^{-1}\,m^{-1}})$	$\eta/\mu\mathrm{P}^{\dagger}$	
	273 K	273 K	293 K
Ar	16.3	210	223
CO_2	14.5	136	147
He	144.2	187	196
N_2	24.0	166	176

* More values are given in the *Resource section*.

† $1\,\mu\mathrm{P} = 10^{-7}\,\mathrm{kg\,m^{-1}\,s^{-1}}$.

To see the connection between the flux of momentum and the viscosity, consider a fluid in a state of **Newtonian flow**, which can be imagined as occurring by a series of layers moving past one another (Fig. 79.2). The layer next to the wall of the vessel is stationary, and the velocity of successive layers varies linearly with distance, z, from the wall. Molecules ceaselessly move between the layers and bring with them the x-component of linear momentum they possessed in their original layer. A layer is retarded by molecules arriving from a more slowly moving layer because they have a low momentum in the x-direction. A layer is accelerated by molecules arriving from a more rapidly moving layer. We interpret the net retarding effect as the fluid's viscosity.

Because the retarding effect depends on the transfer of the x-component of linear momentum into the layer of interest, the viscosity depends on the flux of this x-component in the z-direction. The flux of the x-component of momentum is proportional to dv_x/dz because there is no net flux when all the layers move at the same velocity. We can therefore write

$$J(x\text{-component of momentum}) = -\eta\frac{dv_x}{dz} \qquad \textit{Definition} \quad \text{Viscosity} \qquad (79.5)$$

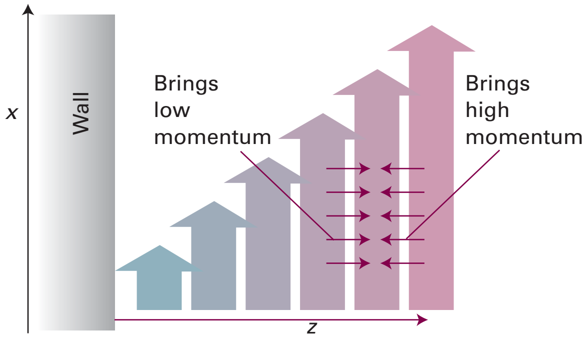

Figure 79.2 The viscosity of a fluid arises from the transport of linear momentum. In this illustration the fluid is undergoing laminar (Newtonian) flow, and particles bring their initial momentum when they enter a new layer. If they arrive with high x-component of momentum they accelerate the layer; if with low x-component of momentum they retard the layer.

The constant of proportionality, η (eta), is the **coefficient of viscosity** (or simply 'the viscosity'). Its SI units are kilogram per metre per second ($\mathrm{kg\,m^{-1}\,s^{-1}}$, which is equivalent to Pa s). Viscosities are often reported in the non-SI unit poise (P), where $1\,\mathrm{P}=10^{-1}\,\mathrm{kg\,m^{-1}\,s^{-1}}$. There is a variety of methods of determining viscosity, including monitoring the rate of flow of a fluid through a narrow tube. Some experimental values are given in Table 79.1.

Brief illustration 79.1 Energy flux

Suppose that there is a temperature difference of 10 K between two metal plates that are separated by 1.0 cm. The temperature gradient is

$$\frac{\mathrm{d}T}{\mathrm{d}z}=-\frac{10\,\mathrm{K}}{1.0\times10^{-2}\,\mathrm{m}}=-1.0\times10^{3}\,\mathrm{K\,m^{-1}}$$

Therefore, the energy flux in air (Table 79.1) is

$$J(\text{energy of thermal motion})=-(0.0241\,\mathrm{J\,K^{-1}\,m^{-1}\,s^{-1}})\times(-1.0\times10^{3}\,\mathrm{K\,m^{-1}})=+24\,\mathrm{J\,m^{-2}\,s^{-1}}$$

As a result, in 1.0 h (3600 s) the transfer of energy through an area of the opposite walls of $1.0\,\mathrm{cm}^2$ is

$$\text{Transfer}=(24\,\mathrm{J\,m^{-2}\,s^{-1}})\times(1.0\times10^{-4}\,\mathrm{m}^2)\times(3600\,\mathrm{s})=8.6\,\mathrm{J}$$

Self-test 79.1 The thermal conductivity of glass is $0.92\,\mathrm{J\,K^{-1}\,m^{-1}\,s^{-1}}$. What is the rate of energy transfer (in watts, $1\,\mathrm{W}=1\,\mathrm{J\,s^{-1}}$) through a window pane of thickness 0.50 cm and area $1.0\,\mathrm{m}^2$ when the room is at 22 °C and the exterior is at 0 °C?

Answer: 4.0 kW

79.2 The transport parameters

Here we derive expressions for the diffusion characteristics (specifically, the diffusion coefficient, the thermal conductivity, and the viscosity) of a perfect gas on the basis of the kinetic-molecular theory.

(a) The diffusion coefficient

In the following *Justification* we show that the flux of molecules through a gas is in accord with Fick's first law, and specifically that

$$J_z=-\tfrac{1}{2}v_{\text{mean}}\lambda\left(\frac{\mathrm{d}\mathcal{N}}{\mathrm{d}z}\right)_0 \qquad (79.6)$$

Justification 79.1 The diffusion coefficient

Consider the arrangement depicted in Fig. 79.3. On average, the molecules passing through the area A at $z=0$ have travelled about one mean free path λ since their last collision. Therefore, the number density where they originated is $\mathcal{N}(z)$ evaluated at $z=-\lambda$. This number density is approximately

$$\mathcal{N}(-\lambda)=\mathcal{N}(0)-\lambda\left(\frac{\mathrm{d}\mathcal{N}}{\mathrm{d}z}\right)_0$$

where we have used a Taylor expansion of the form $f(x)=f(0)+(\mathrm{d}f/\mathrm{d}x)_0x+\ldots$ truncated after the second term (see *Mathematical background* 1). Similarly, the number density at an equal distance on the other side of the area is

$$\mathcal{N}(\lambda)=\mathcal{N}(0)+\lambda\left(\frac{\mathrm{d}\mathcal{N}}{\mathrm{d}z}\right)_0$$

The average number of impacts on the imaginary window of area A_0 during an interval Δt is $Z_\mathrm{W}A_0\Delta t$, where Z_W is the collision flux (from *Justification* 78.4 and eqn 78.7 for the mean speed, $Z_\mathrm{W}=\mathcal{N}(kT/2\pi m)^{1/2}=\tfrac{1}{4}\mathcal{N}v_{\text{mean}}$). Therefore, the flux from left to right, $J(\mathrm{L}\rightarrow\mathrm{R})$, arising from the supply of molecules on the left, is

$$J(\mathrm{L}\rightarrow\mathrm{R})=\frac{\overbrace{\tfrac{1}{4}\mathcal{N}(-\lambda)v_{\text{mean}}}^{Z_\mathrm{W}}A_0\Delta t}{A_0\Delta t}=\tfrac{1}{4}\mathcal{N}(-\lambda)v_{\text{mean}}$$

There is also a flux of molecules from right to left. On average, the molecules making the journey have originated from $z=+\lambda$ where the number density is $\mathcal{N}(\lambda)$. Therefore,

$$J(\mathrm{L}\leftarrow\mathrm{R})=\tfrac{1}{4}\mathcal{N}(\lambda)v_{\text{mean}}$$

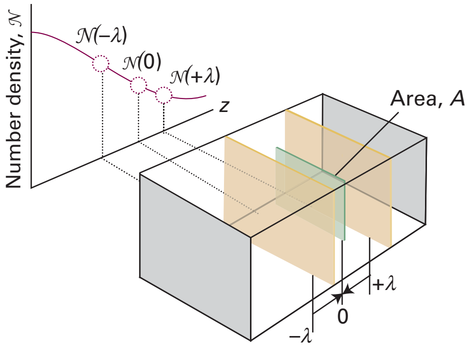

Figure 79.3 The calculation of the rate of diffusion of a gas considers the net flux of molecules through a plane of area A as a result of arrivals from on average a distance λ away in each direction, where λ is the mean free path.

The net flux from left to right is

$$\begin{aligned}J_z &= J(\mathrm{L}\rightarrow\mathrm{R}) - J(\mathrm{L}\leftarrow\mathrm{R})\\ &= \tfrac{1}{4}v_{\text{mean}}\{\mathcal{N}(-\lambda)-\mathcal{N}(\lambda)\}\\ &= \tfrac{1}{4}v_{\text{mean}}\left\{\left[\mathcal{N}(0)-\lambda\left(\frac{\mathrm{d}\mathcal{N}}{\mathrm{d}z}\right)_0\right]-\left[\mathcal{N}(0)+\lambda\left(\frac{\mathrm{d}\mathcal{N}}{\mathrm{d}z}\right)_0\right]\right\}\end{aligned}$$

That is,

$$J_z = -\tfrac{1}{2}v_{\text{mean}}\lambda\left(\frac{\mathrm{d}\mathcal{N}}{\mathrm{d}z}\right)_0$$

which is eqn 79.6.

At this stage it looks as though we can pick out a value of the diffusion coefficient by comparing eqns 79.6 and 79.3, so obtaining $D=\tfrac{1}{2}\lambda v_{\text{mean}}$. It must be remembered, however, that the calculation is quite crude, and is little more than an assessment of the order of magnitude of D. One aspect that has not been taken into account is illustrated in Fig. 79.4, which shows that although a molecule may have begun its journey very close to the window, it could have a long flight before it gets there. Because the path is long, the molecule is likely to collide before reaching the window, so it ought to be added to the graveyard of other molecules that have collided. To take this effect into account involves a lot of work, but the end result is the appearance of a factor of $\tfrac{2}{3}$ representing the lower flux. The modification results in

$$D=\tfrac{1}{3}\lambda v_{\text{mean}} \qquad \text{Diffusion coefficient} \qquad (79.7)$$

Brief illustration 79.2 The diffusion coefficient

In *Brief illustration* 78.3 of Topic 78 it is established that the mean free path of N_2 molecules in a gas at 1.0 bar is 95 nm; in Example 78.1 of the same Topic it is calculated that the mean speed of N_2 molecules at 25 °C is 475 m s⁻¹. Therefore, the diffusion coefficient for N_2 molecules under these conditions is

$$D=\tfrac{1}{3}\times(9.5\times10^{-8}\ \mathrm{m})\times475\ \mathrm{m\ s^{-1}}=1.5\times10^{-5}\ \mathrm{m^2\ s^{-1}}$$

The experimental value (for N_2 in O_2) is $2.0\times10^{-5}\ \mathrm{m^2\ s^{-1}}$.

Self-test 79.2 Evaluate D for H_2 under the same conditions.

Answer: $9.0\times10^{-5}\ \mathrm{m^2\ s^{-1}}$

There are three points to note about eqn 79.7:

- The mean free path, λ, decreases as the pressure is increased (eqn 78.12 of Topic 78, $\lambda=kT/\sigma p$), so D decreases with increasing pressure and, as a result, the gas molecules diffuse more slowly.
- The mean speed, v_{mean}, increases with the temperature (eqn 78.7 of Topic 78, $v_{\text{mean}}=(8kT/\pi m)^{1/2}$), so D also increases with temperature. As a result, molecules in a hot sample diffuse more quickly than those in a cool sample (for a given concentration gradient).
- Because the mean free path increases when the collision cross-section of the molecules decreases (eqn 78.12 of Topic 78, $\lambda=kT/\sigma p$), the diffusion coefficient is greater for small molecules than for large molecules.

Physical interpretation

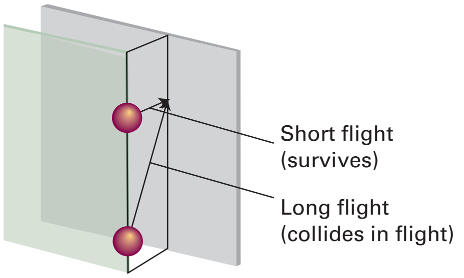

Figure 79.4 One approximation ignored in the simple treatment is that some particles might make a long flight to the plane even though they are only a short perpendicular distance away, and therefore they have a higher chance of colliding during their journey.

(b) Thermal conductivity

According to the equipartition theorem (*Foundations,* Topic 2), each molecule carries an average energy $\varepsilon=\nu kT$, where ν is a number of the order of 1. For atoms, $\nu=\tfrac{3}{2}$. When one molecule passes through the imaginary window, it transports that average energy. We suppose that the number density is uniform but that the temperature is not. Molecules arrive from the left after travelling a mean free path from their last collision in a hotter region, and therefore with a higher energy. Molecules also arrive from the right after travelling a mean free path from a cooler region. When this model is developed quantitatively, as in the following *Justification*, it turns out that the energy flux is proportional to the temperature gradient and that the thermal conductivity is

$$\kappa=\tfrac{1}{3}\nu v_{\text{mean}}\lambda\mathcal{N}k \qquad \text{Thermal conductivity} \qquad (79.8a)$$

If we identify $\mathcal{N}=nN_{\mathrm{A}}/V=[\mathrm{J}]N_{\mathrm{A}}$, where [J] is the molar concentration of the carrier particles J and N_{A} is Avogadro's constant, and identify νkN_{A} as the molar constant-volume heat capacity of a perfect gas (which follows from $C_{V,\mathrm{m}}=N_{\mathrm{A}}(\partial\varepsilon/\partial T)_V$), this expression becomes

$$\kappa=\tfrac{1}{3}v_{\text{mean}}\lambda[\mathrm{J}]C_{V,\mathrm{m}} \qquad \text{Thermal conductivity} \qquad (79.8b)$$

Yet another form is found by recognizing that $\mathcal{N}=p/kT$ and using the expression for D in eqn 79.7, for then

$$\kappa=\frac{\nu pD}{T} \qquad \text{Thermal conductivity} \qquad (79.8c)$$

Justification 79.2 Thermal conduction

The two opposing energy fluxes are

$$J(\mathrm{L}\rightarrow\mathrm{R})=\overbrace{\tfrac{1}{4}\mathcal{N}v_{\text{mean}}}^{z_\mathrm{W}}\,\varepsilon(-\lambda) \qquad J(\mathrm{L}\leftarrow\mathrm{R})=\overbrace{\tfrac{1}{4}\mathcal{N}v_{\text{mean}}}^{z_\mathrm{W}}\,\varepsilon(\lambda)$$

and the net flux is

$$\begin{aligned}J_z&=J(\mathrm{L}\rightarrow\mathrm{R})-J(\mathrm{L}\leftarrow\mathrm{R})\\&=\tfrac{1}{4}v_{\text{mean}}\mathcal{N}\{\varepsilon(-\lambda)-\varepsilon(\lambda)\}\\&=\tfrac{1}{4}v_{\text{mean}}\mathcal{N}\left\{\left[\varepsilon(0)-\lambda\left(\frac{\mathrm{d}\varepsilon}{\mathrm{d}z}\right)_0\right]-\left[\varepsilon(0)+\lambda\left(\frac{\mathrm{d}\varepsilon}{\mathrm{d}z}\right)_0\right]\right\}\end{aligned}$$

That is,

$$J_z=-\frac{1}{2}v_{\text{mean}}\lambda\mathcal{N}\left(\frac{\mathrm{d}\varepsilon}{\mathrm{d}z}\right)_0=-\frac{1}{2}\nu v_{\text{mean}}\lambda\mathcal{N}k\left(\frac{\mathrm{d}T}{\mathrm{d}z}\right)_0$$

The energy flux is proportional to the temperature gradient, as we wanted to show. As before, we multiply by $\frac{2}{3}$ to take long flight paths into account, and after comparison of this equation with eqn 79.4 arrive at eqn 79.8.

To interpret eqn 79.8, we note that:

Physical interpretation

- Because λ is inversely proportional to the pressure (eqn 78.12 of Topic 78, $\lambda=kT/\sigma p$), and hence inversely proportional to the molar concentration of the gas, and $\mathcal{N}$ is proportional to the pressure ($\mathcal{N}=p/kT$), the thermal conductivity, which is proportional to the product λp, is independent of the pressure.
- The thermal conductivity is greater for gases with a high heat capacity (eqn 79.8b) because a given temperature gradient then corresponds to a greater energy gradient.

The physical reason for the pressure independence of the thermal conductivity is that it can be expected to be large when many molecules are available to transport the energy, but the presence of so many molecules limits their mean free path and they cannot carry the energy over a great distance. These two effects balance. The thermal conductivity is indeed found experimentally to be independent of the pressure, except when the pressure is very low, when $\kappa\propto p$. At low pressures λ exceeds the dimensions of the apparatus, and the distance over which the energy is transported is determined by the size of the container and not by the other molecules present. The flux is still proportional to the number of carriers, but the length of the journey no longer depends on λ, so $\kappa\propto[\mathrm{J}]$, which implies that $\kappa\propto p$.

Brief illustration 79.3 The thermal conductivity

In *Brief illustration* 79.2 we calculated $D=1.5\times10^{-5}\,\mathrm{m^2\,s^{-1}}$ for $\mathrm{N_2}$ molecules at 25 °C. To use eqn 79.8c note that for $\mathrm{N_2}$ molecules $\nu=\frac{5}{2}$ (there are three translational modes and two rotational; whereas the rotational modes are active at room temperature, the vibrational mode is not). Therefore, at 1.0 bar,

$$\begin{aligned}\kappa&=\frac{\frac{5}{2}\times(1.0\times10^5\,\overbrace{\mathrm{Pa}}^{\mathrm{J\,m^{-3}}})\times(1.5\times10^{-5}\,\mathrm{m^2\,s^{-1}})}{298\,\mathrm{K}}\\&=1.3\times10^{-2}\,\mathrm{J\,K^{-1}\,m^{-1}\,s^{-1}}\end{aligned}$$

or $13\,\mathrm{mW\,K^{-1}\,m^{-1}}$.

Self-test 79.3 Estimate the thermal conductivity of argon gas at 25 °C and 1.0 bar.

Answer: $7.6\,\mathrm{mW\,K^{-1}\,m^{-1}}$

(c) Viscosity

Arguments very similar to those employed above, but applied to linear momentum (see the following *Justification*), show that the flux of momentum is proportional to the velocity gradient in the fluid and that the viscosity of a perfect gas is given by

$$\eta=\tfrac{1}{3}v_{\text{mean}}\lambda m\mathcal{N} \qquad \text{Viscosity} \qquad (79.9a)$$

Two alternative forms of this expression (after using $mN_\mathrm{A}=M$) are

$$\eta=MD[\mathrm{J}] \qquad \text{Viscosity} \qquad (79.9b)$$

$$\eta=\frac{pMD}{RT} \qquad \text{Viscosity} \qquad (79.9c)$$

where [J] is the molar concentration of the gas molecules and M is their molar mass.

Justification 79.3 Viscosity

Molecules travelling from the right in Fig. 79.5 (from a fast layer to a slower one) transport a momentum $mv_x(\lambda)$ to their new layer at $z=0$; those travelling from the left transport $mv_x(-\lambda)$ to it. If it is assumed that the density is uniform, the

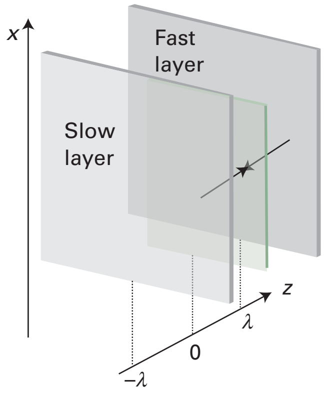

Figure 79.5 The calculation of the viscosity of a gas examines the net *x*-component of momentum brought to a plane from faster and slower layers on average a mean free path away in each direction.

collision flux is $\frac{1}{4}\mathcal{N}v_{\text{mean}}$. Those arriving from the right on average carry a momentum

$$mv_x(\lambda)=mv_x(0)+m\lambda\left(\frac{\mathrm{d}v_x}{\mathrm{d}z}\right)_0$$

Those arriving from the left bring a momentum

$$mv_x(-\lambda)=mv_x(0)-m\lambda\left(\frac{\mathrm{d}v_x}{\mathrm{d}z}\right)_0$$

The net flux of *x*-momentum in the *z*-direction is therefore

$$J_z=\tfrac{1}{4}v_{\text{mean}}\mathcal{N}\left\{\left[mv_x(0)-m\lambda\left(\frac{\mathrm{d}v_x}{\mathrm{d}z}\right)_0\right]\right.$$
$$\left.-\left[mv_x(0)+m\lambda\left(\frac{\mathrm{d}v_x}{\mathrm{d}z}\right)_0\right]\right\}=-\tfrac{1}{2}v_{\text{mean}}\lambda m\mathcal{N}\left(\frac{\mathrm{d}v_x}{\mathrm{d}z}\right)_0$$

The flux is proportional to the velocity gradient, as we wished to show. Comparison of this expression with eqn 79.5, and multiplication by $\frac{2}{3}$ in the normal way, leads to eqn 79.9.

We can interpret eqn 79.9a as follows:

Physical interpretation

- Because $\lambda \propto 1/p$ (eqn 78.12 of Topic 78, $\lambda = kT/\sigma p$)) and $[\mathrm{J}] \propto p$, it follows that $\eta \propto \lambda\mathcal{N}$ is independent of *p*. That is, the viscosity is independent of the pressure.
- Because $v_{\text{mean}} \propto T^{1/2}$ (eqn 78.7 of Topic 78, $v_{\text{mean}} = (8kT/\pi m)^{1/2}$), $\eta \propto T^{1/2}$. That is, the viscosity of a gas *increases* with temperature.

The physical reason for the pressure independence of the viscosity is the same as for the thermal conductivity: more molecules are available to transport the momentum, but they carry it less far on account of the decrease in mean free path. The increase of viscosity with temperature is explained when we remember that at high temperatures the molecules travel more quickly, so the flux of momentum is greater. By contrast, as discussed in Topic 80, the viscosity of a liquid *decreases* with increase in temperature because intermolecular interactions must be overcome.

Brief illustration 79.4 The viscosity

We have already calculated $D = 1.5\times10^{-5}\,\mathrm{m^2\,s^{-1}}$ for $\mathrm{N_2}$ at 25 °C. Because $M = 28.02\,\mathrm{g\,mol^{-1}}$, for the gas at 1.0 bar, eqn 79.9c gives

$$\eta=\frac{\left(1.0\times10^5\,\overbrace{\mathrm{Pa}}^{\mathrm{J\,m^{-3}}}\right)\times(28.02\times10^{-3}\,\mathrm{kg\,mol^{-1}})\times(1.5\times10^{-5}\,\mathrm{m^2\,s^{-1}})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})}$$
$$=1.7\times10^{-5}\,\mathrm{kg\,m^{-1}\,s^{-1}}$$

or 17 μPa s. The experimental value is 18 μPa s.

Self-test 79.4 Evaluate the viscosity of benzene vapour at 0.10 bar and 25 °C.

Answer: $1.4\times10^{-5}\,\mathrm{kg\,m^{-1}\,s^{-1}}$

Checklist of concepts

☐ 1. The **flux** of a property is the quantity of that property passing through a given area in a given time interval divided by the area and the duration of the interval.

☐ 2. **Fick's first law of diffusion** states that the flux of matter is proportional to the concentration gradient.

☐ 3. In a state of **Newtonian flow** a series of layers of the fluid are considered to move past one another.

☐ 4. The **diffusion coefficient** of a perfect gas decreases with increasing pressure and increases with temperature; it is greater for small molecules than for large molecules.

☐ 5. The **thermal conductivity** of a perfect gas is independent of the pressure and is large for gases with a high heat capacity.

☐ 6. The **viscosity** of a perfect gas is independent of the pressure and increases with temperature.

Checklist of equations

Property	Equation	Comment	Equation number
Matter flux	$J=-D\mathrm{d}\mathcal{N}/\mathrm{d}z$	Fick's first law	79.3
Energy of thermal motion flux	$J=-\kappa\mathrm{d}T/\mathrm{d}z$	'Heat flux'	79.4
x-component of momentum flux	$J=-\eta\mathrm{d}v_x/\mathrm{d}z$	Viscosity	79.5
Diffusion coefficient	$D=\frac{1}{3}\lambda v_{\text{mean}}$	KMT*	79.7
Thermal conductivity	$\kappa=\frac{1}{3}\nu v_{\text{mean}}\mathcal{N}k$	KMT	79.8a
	$\kappa=\frac{1}{3}v_{\text{mean}}\,\lambda[\mathrm{J}]C_{V,\mathrm{m}}$		79.8b
	$\kappa=\nu pD/T$		79.8c
Coefficient of viscosity	$\eta=\frac{1}{3}v_{\text{mean}}\lambda m\mathcal{N}$	KMT	79.9a
	$\eta=MD[\mathrm{J}]$		79.9b
	$\eta=pMD/RT$		79.9c

* KMT denotes that the expressions are derived on the basis of the kinetic theory of gases, a model of a perfect gas.

TOPIC 80

Motion in liquids

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➤ Why do you need to know this material?

Liquids are central to chemical reactions, and it is important to know how the mobility of their molecules and solutes in them varies with the conditions. Ionic motion is a way of exploring this motion as forces to move them can be applied electrically. From electrical measurements the properties of diffusing neutral molecules may also be inferred.

➤ What is the key idea?

Ions reach a terminal velocity when the electrical force on them is balanced by the drag due to the viscosity of the solvent, which decreases with increasing temperature.

➤ What do you need to know already?

The discussion of viscosity starts with the definition of viscosity coefficient introduced in Topic 79. One derivation uses the same argument about flux as was used in Topic 79. The final section quotes the relation between the drift speed and a generalized force acting on a solute particle, which is derived in Topic 81.

In this Topic we consider two aspects of motion in liquids. First, we deal with pure liquids, and examine how the mobilities of their molecules, as measured by their viscosity, vary with temperature. Then we consider the motion of solutes. A particularly simple and to some extent controllable type of motion through a liquid is that of an ion, and we see that the information that motion provides can be used to infer the behaviour of uncharged species too.

80.1 Pure liquids

The motion of molecules in liquids can be studied experimentally by a variety of methods. Relaxation time measurements in NMR and EPR (Topics 49 and 50) can be interpreted in terms of the mobilities of the molecules, and have been used to show that big molecules in viscous fluids typically rotate in a series of small (about 5°) steps, whereas small molecules in non-viscous fluids typically jump through about 1 radian (57°) in each step. Another important technique is **inelastic neutron scattering**, in which the energy neutrons collect or discard as they pass through a sample is interpreted in terms of the motion of its particles. The same technique is used to examine the internal dynamics of macromolecules.

More mundane than these experiments are viscosity measurements. The coefficient of viscosity, η (eta), is introduced in Topic 79 as a phenomenological coefficient, the constant of proportionality between the flux of linear momentum and the velocity gradient in a fluid:

$$J_z(x\text{-component of momentum}) = -\eta\frac{\mathrm{d}v_x}{\mathrm{d}z} \quad \text{Viscosity} \quad (80.1)$$

(This is eqn 79.5 of Topic 79.) Some values are given in Table 80.1. The SI units of viscosity are kilograms per metre per second (kg m^{-1} s^{-1}), but they may also be reported in the equivalent units of pascal seconds (Pa s). The non-SI unit poise (P) and centipoise (cP) are still widely encountered: 1 P = 10^{-1} Pa s and so 1 cP = 1 mPa s.

Table 80.1* Viscosities of liquids at 298 K

	$\eta/(10^{-3}\ \mathrm{kg\ m^{-1}\ s^{-1}})$
Benzene	0.601
Mercury	1.55
Pentane	0.224
Water†	0.891

*More values are given in the *Resource section*.
† The viscosity of water corresponds to 0.891 cP.

Unlike in a gas, for a molecule to move in a liquid it must acquire at least a minimum energy (an 'activation energy' in the language of Topic 87) to escape from its neighbours. The probability that a molecule has at least an energy E_a is proportional to $e^{-E_a/RT}$, so the mobility of the molecules in the liquid should follow this type of temperature dependence. Because the coefficient of viscosity is inversely proportional to the mobility of the particles, we should expect that

$$\eta = \eta_0 e^{E_a/RT} \quad \text{Temperature dependence of viscosity (liquid)} \quad (80.2)$$

where η_0 is a constant independent of temperature. Note the positive sign of the exponent, because the viscosity is *inversely* proportional to the mobility. This expression implies that the viscosity should decrease sharply with increasing temperature. Such a variation is found experimentally, at least over reasonably small temperature ranges (Fig. 80.1). The activation energy typical of viscosity is comparable to the mean potential energy of intermolecular interactions.

One problem with the interpretation of viscosity measurements is that the change in density of the liquid as it is heated makes a pronounced contribution to the temperature variation of the viscosity. Thus, the temperature dependence of viscosity at constant volume, when the density is constant, is much less than that at constant pressure. The intermolecular interactions between the molecules of the liquid govern the magnitude of E_a, but the problem of calculating it is immensely difficult and still largely unsolved. At low temperatures, the viscosity of water decreases as the pressure is increased. This behaviour is consistent with the need to rupture hydrogen bonds for migration to occur.

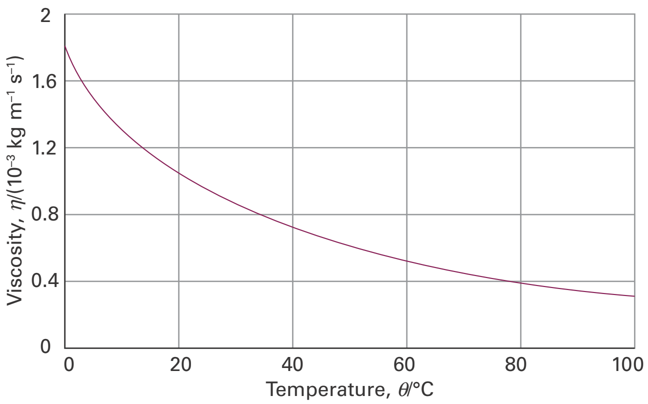

Figure 80.1 The experimental temperature dependence of the viscosity of water. As the temperature is increased, more molecules are able to escape from the potential wells provided by their neighbours, and so the liquid becomes more fluid. A plot of ln η against $1/T$ is a straight line (over a small range) with positive slope.

Brief illustration 80.1 Liquid viscosity

The viscosity of water at 25 °C and 50 °C is 0.890 mPa s and 0.547 mPa s, respectively. It follows from eqn 80.2 that the activation energy for molecular migration is the solution of

$$\frac{\eta(T_2)}{\eta(T_1)} = e^{(E_a/R)(1/T_2-1/T_1)}$$

which is

$$E_a = \frac{R\ln\{\eta(T_2)/\eta(T_1)\}}{1/T_2 - 1/T_1} = \frac{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\ln(0.547/0.890)}{1/(323\ \mathrm{K}) - 1/(298\ \mathrm{K})}$$
$$= 1.56\times10^4\ \mathrm{J\ mol^{-1}}$$

or 15.6 kJ mol^{-1}. That is comparable to the strength of a hydrogen bond (Topic 35).

Self-test 80.1 The corresponding values of the viscosity of benzene are 0.604 mPa s and 0.436 mPa s. Evaluate the activation energy for viscosity.

Answer: 10.4 kJ mol^{-1}

80.2 Electrolyte solutions

Further insight into the nature of molecular motion can be obtained by studying the net transport of charged species through solution, for ions can be dragged through the solvent by the application of a potential difference between two electrodes immersed in the sample. By studying the transport of charge through electrolyte solutions it is possible to build up a picture of the events that occur in them and, in some cases, to extrapolate the conclusions to species that have zero charge, that is, to neutral molecules.

(a) Conductivity

The fundamental measurement used to study the motion of ions is that of the electrical resistance, R, of the solution. The **conductance**, G, of a solution is the inverse of its resistance R: $G = 1/R$. As resistance is expressed in ohms, Ω, the conductance of a sample is expressed in Ω^{-1}. The reciprocal ohm used to be called the mho, but its SI designation is now the siemens, S, and $1\ \mathrm{S}=1\ \Omega^{-1}=1\ \mathrm{C\ V^{-1}\ s^{-1}}$. It is found that the conductance of a sample decreases with its length l and increases with its cross-sectional area A. We therefore write

$$G=\kappa\frac{A}{l}\qquad(80.3)$$

Definition of κ Conductance

where κ (kappa) is the electrical **conductance**. With the conductance in siemens and the dimensions in metres, it follows that the SI units of κ are siemens per metre ($\mathrm{S\ m^{-1}}$).

The conductivity of a solution depends on the number of ions present, and it is normal to introduce the **molar conductivity**, Λ_m, which is defined as

$$\Lambda_\mathrm{m}=\frac{\kappa}{c}\qquad(80.4)$$

Definition Molar conductivity

where c is the molar concentration of the added electrolyte. The SI unit of molar conductivity is siemens metre-squared per mole ($\mathrm{S\ m^2\ mol^{-1}}$), and typical values are about $10\ \mathrm{mS\ m^2\ mol^{-1}}$ (where $1\ \mathrm{mS}=10^{-3}\ \mathrm{S}$).

The values of the molar conductivity as calculated by eqn 80.4 are found to vary with the concentration. One reason for this variation is that the number of ions in the solution might not be proportional to the nominal concentration of the electrolyte. For instance, the concentration of ions in a solution of a weak electrolyte depends on the concentration of the solute in a complicated way, and doubling the concentration of the solute added does not double the number of ions. Secondly, because ions interact strongly with one another, the conductivity of a solution is not exactly proportional to the number of ions present.

In an extensive series of measurements during the nineteenth century, Friedrich Kohlrausch established what is now known as **Kohlrausch's law**, that at low concentrations the molar conductivities of strong electrolytes vary linearly with the square root of the concentration:

$$\Lambda_\mathrm{m}=\Lambda_\mathrm{m}^\circ-\mathcal{K}c^{1/2}\qquad(80.5)$$

Kohlrausch's law

The **Kohlrausch constant** $\mathcal{K}$ depends on the identity of the solute and the solvent. Kohlrausch also established that Λ_m°, the **limiting molar conductivity**, the molar conductivity in the limit of zero concentration, is the sum of contributions from its individual ions. If the limiting molar conductivity of the cations is denoted λ_+ and that of the anions λ_-, then his **law of the independent migration of ions** states that

$$\Lambda_\mathrm{m}^\circ=\nu_+\lambda_++\nu_-\lambda_-\qquad(80.6)$$

Limiting law Law of the independent migration of ions

where ν_+ and ν_- are the numbers of cations and anions per formula unit of electrolyte. For example, $\nu_+=\nu_-=1$ for HCl, NaCl, and $\mathrm{CuSO_4}$, but $\nu_+=1$, $\nu_-=2$ for $\mathrm{MgCl_2}$.

Example 80.1 Determining the limiting molar conductivity

The conductivity of KCl(aq) at 25 °C is $14.668\ \mathrm{mS\ m^{-1}}$ when $c=0.001\,00\ \mathrm{mol\ dm^{-3}}$ and $71.740\ \mathrm{mS\ m^{-1}}$ when $c=0.005\,00\ \mathrm{mol\ dm^{-3}}$. Determine the values of the limiting molar conductivity Λ_m° and the Kohlrausch constant $\mathcal{K}$.

Method Use eqn 80.4 to determine the molar conductivities at the two concentrations, then use the Kohlrausch law, eqn 80.5, in the form

$$\Lambda_\mathrm{m}(c_2)-\Lambda_\mathrm{m}(c_1)=\mathcal{K}\left(c_1^{1/2}-c_2^{1/2}\right)$$

to determine $\mathcal{K}$. Then find Λ_m° from the law in the form

$$\Lambda_\mathrm{m}^\circ=\Lambda_\mathrm{m}+\mathcal{K}c^{1/2}$$

With more data available, a better procedure is to perform a linear regression.

Answer It follows that the molar conductivity of KCl when $c=0.001\,00\ \mathrm{mol\ dm^{-3}}$ is

$$\Lambda_\mathrm{m}=\frac{14.688\,\mathrm{mS\,m^{-1}}}{0.00100\times10^3\,\mathrm{mol\,m^{-3}}}=14.688\,\mathrm{mS\,m^2\,mol^{-1}}$$

Similarly, when $c=0.005\,00\ \mathrm{mol\ dm^{-3}}$ the molar conductivity is $14.348\ \mathrm{mS\ m^2\ mol^{-1}}$. It then follows that

$$\begin{aligned}\mathcal{K}&=\frac{\Lambda_\mathrm{m}(c_2)-\Lambda_\mathrm{m}(c_1)}{c_1^{1/2}-c_2^{1/2}}=\frac{(14.348-14.688)\,\mathrm{mS\,m^2\,mol^{-1}}}{(0.00100^{1/2}-0.00500^{1/2})\ (\mathrm{mol\,dm^{-3}})^{1/2}}\\&=8.698\,\mathrm{mS\,m^2\,mol^{-1}}/(\mathrm{mol\,dm^{-3}})^{1/2}\end{aligned}$$

(It is best to keep this awkward but convenient array of units as they are rather than converting them to the equivalent $10^{-3/2}\ \mathrm{S\ m^{7/2}\ mol^{-3/2}}$.) Now we find the limiting value from the data for $c=0.001\,00\ \mathrm{mol\ dm^{-3}}$:

$$\begin{aligned}\Lambda_\mathrm{m}^\circ&=14.688\,\mathrm{mS\,m^2\,mol^{-1}}+8.698\,\frac{\mathrm{mS\ m^2\ mol^{-1}}}{(\mathrm{mol\,dm^{-3}})^{1/2}}\\&\quad\times(0.00100\,\mathrm{mol\,dm^{-3}})^{1/2}=14.963\ \mathrm{mS\ m^2\ mol^{-1}}\end{aligned}$$

Self-test 80.2 The conductivity of $\mathrm{KClO_4}$(aq) at 25 °C is $13.780\ \mathrm{mS\ m^{-1}}$ when $c=0.001\,00\ \mathrm{mol\ dm^{-3}}$ and $67.045\ \mathrm{mS\ m^{-1}}$ when $c=0.005\,00\ \mathrm{mol\ dm^{-3}}$. Determine the values of the limiting molar conductivity Λ_m° and the Kohlrausch constant $\mathcal{K}$ for this system.

Answer: $\mathcal{K}=9.491\,\mathrm{mS\,m^2\,mol^{-1}}/(\mathrm{mol\,dm^{-3}})^{1/2}$, $\Lambda_\mathrm{m}^\circ=14.08\,\mathrm{mS\,m^2\,mol^{-1}}$

Kohlrausch's law is used to provide an extrapolation procedure for determining the limiting molar conductivity of an electrolyte solution, and hence to assemble values of the limiting conductivities of individual ions. As the following section explains, those values are used to explore the mobilities of ions in solution and to construct models of their properties.

(b) The mobilities of ions

To interpret conductivity measurements we need to know why ions move at different rates, why they have different molar conductivities, and why the molar conductivities of strong electrolytes decrease with the square root of the molar concentration. The central idea in this section is that although the motion of an ion remains largely random, the presence of an electric field biases its motion, and the ion undergoes net migration through the solution.

When the potential difference between two planar electrodes a distance l apart is $\Delta\phi$, the ions in the solution between them experience a uniform electric field of magnitude (see *Foundations*, Topic 2)

$$\mathcal{E} = \frac{\Delta\phi}{l} \qquad (80.7)$$

In such a field, an ion of charge ze experiences a force of magnitude

$$\mathcal{F} = ze\mathcal{E} = \frac{ze\Delta\phi}{l} \qquad \text{Electric force} \qquad (80.8)$$

where here and throughout this section we disregard the sign of the charge number and so avoid notational complications.

A cation responds to the application of the field by accelerating towards the negative electrode and an anion responds by accelerating towards the positive electrode. However, this acceleration is short-lived. As the ion moves through the solvent it experiences a frictional retarding force, $\mathcal{F}_{\text{fric}}$, proportional to its speed. For a spherical particle of radius a travelling at a speed s, this force is given by **Stokes's law**, which was derived by considering the hydrodynamics of the passage of a sphere through a continuous fluid:

$$\mathcal{F}_{\text{fric}} = fs \quad f = 6\pi\eta a \qquad \text{Stokes's law} \qquad (80.9)$$

where η is the viscosity. In writing eqn 80.9, we have assumed that it applies on a molecular scale, and independent evidence from magnetic resonance suggests that it often gives at least the right order of magnitude.

The two forces act in opposite directions, and the ions quickly reach a terminal speed, the **drift speed**, when the accelerating force is balanced by the viscous drag. The net force is zero when $fs = ze\mathcal{E}$, or

$$s = \frac{ze\mathcal{E}}{f} \qquad \text{Drift speed} \qquad (80.10)$$

It follows that the drift speed of an ion is proportional to the strength of the applied field. We write

$$s = u\mathcal{E} \qquad \textit{Definition of } u \quad \text{Mobility} \qquad (80.11)$$

where u is called the **mobility** of the ion (Table 80.2). Comparison of the last two equations shows that

$$u = \frac{ze}{f} = \frac{ze}{6\pi\eta a} \qquad \text{Mobility} \qquad (80.12)$$

Table 80.2* Ionic mobilities in water at 298 K

	$u/(10^{-8}\ \text{m}^2\ \text{s}^{-1}\ \text{V}^{-1})$		$u/(10^{-8}\ \text{m}^2\ \text{s}^{-1}\ \text{V}^{-1})$
H^+	36.23	OH^-	20.64
Na^+	5.19	Cl^-	7.91
K^+	7.62	Br^-	8.09
Zn^{2+}	5.47	SO_4^{2-}	8.29

* More values are given in the *Resource section*.

Brief illustration 80.2 Ion mobility

For an order of magnitude estimate we can take $z = 1$ and a as the radius of an ion such as Cs^+ (which might be typical of a smaller ion plus its hydration sphere), which is 170 pm. For the viscosity, we use $\eta = 1.0$ cP (1.0 mPa s, Table 80.1). Then

$$u = \frac{1.6\times10^{-19}\ \overbrace{\text{C}}^{\text{J V}^{-1}}}{6\pi\times\left(1.0\times10^{-3}\ \underbrace{\text{Pa}}_{\text{J m}^{-3}}\ \text{s}\right)\times(170\times10^{-12}\ \text{m})} = 5.0\times10^{-8}\ \text{m}^2\ \text{V}^{-1}\ \text{s}^{-1}$$

This value means that when there is a potential difference of 1 V across a solution of length 1 cm (so $\mathcal{E} = 100\ \text{V m}^{-1}$), the drift speed is typically about 5 µm s⁻¹. That speed might seem slow, but not when expressed on a molecular scale, for it corresponds to an ion passing about 10^4 solvent molecules per second.

Self-test 80.3 The mobility of an SO_4^{2-} ion in water at 25 °C is $8.29\times10^{-8}\ \text{m}^2\ \text{V}^{-1}\ \text{s}^{-1}$. What is its effective radius? Use the viscosity given above.

Answer: 205 pm

Because the drift speed governs the rate at which charged species are transported, we might expect the conductivity to decrease with increasing solution viscosity and ion size.

Experiments confirm these predictions for bulky ions (such as R_4N^+ and RCO_2^-) but not for small ions. For example, the mobilities of the alkali metal ions in water increase from Li^+ to Cs^+ (Table 80.2) even though the ionic radii increase. The paradox is resolved when we realize that the radius a in the Stokes formula is the **hydrodynamic radius** (or 'Stokes radius') of the ion, its effective radius in the solution taking into account all the H_2O molecules it carries in its hydration shell. Small ions give rise to stronger electric fields than large ones (the electric field at the surface of a sphere of radius r is proportional to ze/r^2 and it follows that the smaller the radius, the stronger the field), so small ions are more extensively solvated than big ions. Thus, an ion of small ionic radius may have a large hydrodynamic radius because it drags many solvent molecules through the solution as it migrates. The hydrating H_2O molecules are often very labile, however, and NMR and isotope studies have shown that the exchange between the coordination sphere of the ion and the bulk solvent is very rapid for ions of low charge but may be slow for ions of high charge (Fig. 80.2).

The proton, although it is very small, has a very high mobility (Table 80.2)! Proton and ^{17}O-NMR show that the times characteristic of protons hopping from one molecule to the next are about 1.5 ps, which is comparable to the time that inelastic neutron scattering shows it takes a water molecule to reorientate through about 1 radian (1 to 2 ps). According to the **Grotthuss mechanism**, there is an effective motion of a proton that involves the rearrangement of bonds in a group of water molecules (Fig. 80.3). However, the actual mechanism is still highly contentious. The mobility of NH_4^+ in liquid ammonia is also anomalous and presumably occurs by an analogous mechanism.

(c) Mobility and conductivity

Ionic mobilities provide a link between measurable and theoretical quantities. As a first step we establish in the following *Justification* the relation between an ion's mobility and its molar conductivity:

$$\lambda = zuF \qquad \text{Ion conductivity} \qquad (80.13)$$

where F is Faraday's constant ($F = N_Ae$).

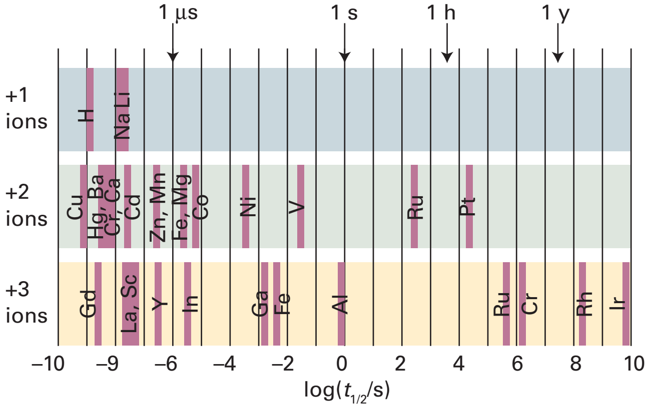

Figure 80.2 The half-lives of water molecules in the hydration spheres of ions.

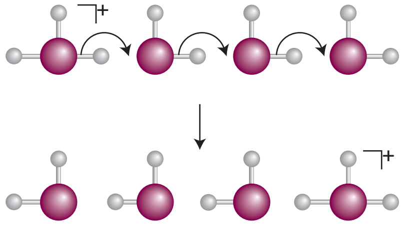

Figure 80.3 The Grotthuss mechanism of conduction by protons in water. There is a virtual transfer of a proton from one end of the chain to the other as the bonds and hydrogen bonds adjust.

Justification 80.1 The relation between ionic mobility and molar conductivity

To keep the calculation simple, we ignore signs in the following, and concentrate on the magnitudes of quantities.

Consider a solution of a fully dissociated strong electrolyte at a molar concentration c. Let each formula unit give rise to ν_+ cations of charge z_+e and ν_- anions of charge z_-e. The molar concentration of each type of ion is therefore νc (with $\nu = \nu_+$ or ν_-), and the number density of each type is νcN_A. The number of ions of one kind that pass through an imaginary window of area A during an interval Δt is equal to the number within the distance $s\Delta t$ (Fig. 80.4), and therefore to the number in the volume $s\Delta tA$. (The same sort of argument is used in Topic 79 in the discussion of the transport properties of gases.) The number of ions of that kind in this volume is equal to $s\Delta tA\nu cN_A$. The flux through the window (the number of this type of ion

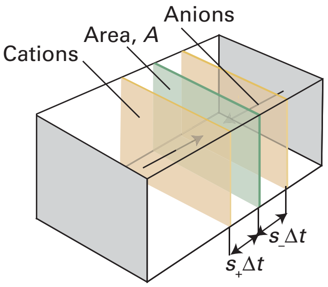

Figure 80.4 In the calculation of the current, all the cations within a distance $s_+\Delta t$ (that is, those in the volume $s_+A\Delta t$) will pass through the area A. The anions in the corresponding volume on the other side of the window will also contribute to the current similarly.

passing through the window divided by the area of the window and the duration of the interval) is therefore

$$J(\text{ions}) = \frac{s\Delta tA\nu cN_A}{\Delta tA} = s\nu cN_A$$

Each ion carries a charge ze, so the flux of charge is

$$J(\text{charge}) = zs\nu ceN_A = zs\nu cF$$

Because $s = u\mathcal{E}$, the flux is

$$J(\text{charge}) = zu\nu cF\mathcal{E}$$

The current, I, through the window due to the ions we are considering is the charge flux times the area:

$$I = JA = zu\nu cF\mathcal{E}A$$

Because the electric field is the potential gradient (eqn 80.7, $\mathcal{E} = \Delta\phi/l$), we can write

$$I = \frac{zu\nu cFA\Delta\phi}{l}$$

Current and potential difference are related by Ohm's law, $\Delta\phi = IR$, so it follows that

$$I = \frac{\Delta\phi}{R} = G\Delta\phi = \frac{\kappa A\Delta\phi}{l}$$

where we have used eqn 80.3. Comparison of the last two expressions gives $\kappa = zu\nu cF$. Division by the molar concentration of ions, νc, then results in eqn 80.13.

Equation 80.13 applies to the cations and to the anions. Therefore, for the solution itself in the limit of zero concentration (when there are no ionic interactions),

$$\Lambda_m^\circ = (z_+u_+\nu_+ + z_-u_-\nu_-)F \qquad (80.14a)$$

For a symmetrical z:z electrolyte (for example, $CuSO_4$ with $z = 2$ and $\nu_+ = \nu_- = 1$), this equation simplifies to

$$\Lambda_m^\circ = z(u_+ + u_-)F \qquad (80.14b)$$

Brief illustration 80.3 Ionic conductivity

In *Brief illustration* 80.2, we estimated the typical ionic mobility as $5.0\times10^{-8}\ \mathrm{m^2\ V^{-1}\ s^{-1}}$; so, with $z = 1$ for both the cation and anion, we can estimate that a typical limiting molar conductivity should be about

$$\begin{aligned}\lambda &= (5.0 \times 10^{-8}\ \mathrm{m^2\ V^{-1}\ s^{-1}})\times(9.648\times10^4\ \mathrm{C\,mol^{-1}})\\ &= 4.8\times10^{-3}\ \mathrm{m^2\ V^{-1}\ s^{-1}\ C\,mol^{-1}}\end{aligned}$$

But $1\ \mathrm{V^{-1}\ s^{-1}\ C} = 1\ \mathrm{S}$ (see the remark preceding eqn 80.3), so $\lambda \approx 5\ \mathrm{mS\ m^2\ mol^{-1}}$, and, from eqn 80.14b, about twice that value for Λ_m°, in accord with experiment. The experimental value for KCl, for instance, is $15\ \mathrm{mS\ m^2\ mol^{-1}}$.

Self-test 80.4 Estimate the ionic conductivity of an SO_4^{2-} ion in water at 25 °C from its mobility (Table 80.2).

Answer: $16\ \mathrm{mS\ m^2\ mol^{-1}}$

(d) The Einstein relations

An important relation between the drift speed s and a force $\mathcal{F}$ of any kind acting on a particle is derived in Topic 81:

$$s = \frac{D\mathcal{F}}{RT} \qquad \text{Drift speed} \qquad (80.15)$$

where D is the diffusion coefficient for the species and $\mathcal{F}$ is the thermodynamic force (a molar quantity). We have seen that an ion in solution has a drift speed $s = u\mathcal{E}$ in the presence of an electric field of strength $\mathcal{E}$ and experiences a thermodynamic force of magnitude $N_Aze\mathcal{E}$. Therefore, substituting these known values into eqn 80.15 and using $N_Ae = F$ gives $u\mathcal{E} = DFz\mathcal{E}/RT$ and hence, on cancelling the $\mathcal{E}$, we obtain the **Einstein relation**:

$$u = \frac{zDF}{RT} \qquad \text{Einstein relation} \qquad (80.16)$$

The Einstein relation provides a link between the molar conductivity of an electrolyte and the diffusion coefficients of its ions. First, by using eqns 80.13 and 80.16 we write

$$\lambda = zuF = \frac{z^2DF^2}{RT} \qquad (80.17)$$

for each type of ion. Then, from $\Lambda_m^\circ = \nu_+\lambda_+ + \nu_-\lambda_-$, the limiting molar conductivity is

$$\Lambda_m^\circ = \left(\nu_+z_+^2D_+ + \nu_-z_-^2D_-\right)\frac{F^2}{RT} \qquad \text{Nernst–Einstein equation} \qquad (80.18)$$

which is the **Nernst–Einstein equation**. An application of this equation is to the determination of ionic diffusion coefficients from conductivity measurements; another is to the prediction of conductivities using models of ionic diffusion.

Equations 80.12 ($u = ez/f$) and 80.16 ($u = zDF/RT$ in the form $u = zDe/kT$) relate the mobility of an ion to the frictional force and to the diffusion coefficient, respectively. We can combine the two expressions and cancel the ze and obtain the **Stokes–Einstein equation**:

$$D = \frac{kT}{f} \qquad \text{Stokes–Einstein equation} \qquad (80.19a)$$

If the frictional force is described by Stokes's law, then we also obtain a relation between the diffusion coefficient and the viscosity of the medium:

$$D=\frac{kT}{6\pi\eta a} \qquad \text{Stokes–Einstein equation} \qquad (80.19b)$$

An important feature of eqn 80.19 is that it makes no reference to the charge of the diffusing species. Therefore, the equation also applies in the limit of vanishingly small charge; that is, it also applies to neutral molecules. This feature is taken further in Topic 81 where the general features of diffusion are discussed. It must not be forgotten, however, that both equations depend on the assumption that the viscous drag is proportional to the speed.

Brief illustration 80.4 Mobility and diffusion

From Table 80.2, the mobility of SO_4^{2-} is $8.29\times10^{-8}\,\mathrm{m^2\,V^{-1}\,s^{-1}}$. It follows from eqn 80.16 in the form $D=uRT/zF$ that the diffusion coefficient for the ion in water at 25 °C is

$$D=\frac{(8.29\times10^{-8}\,\mathrm{m^2\,V^{-1}\,s^{-1}})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})}{2\times\left(9.649\times10^{4}\,\underbrace{\mathrm{C}}_{\mathrm{J\,V^{-1}}}\,\mathrm{mol^{-1}}\right)}$$
$$=1.06\times10^{-9}\,\mathrm{m^2\,s^{-1}}$$

Self-test 80.5 Repeat the calculation for the NH_4^+ ion.

Answer: $1.96\times10^{-9}\,\mathrm{m^2\,s^{-1}}$

Checklist of concepts

☐ 1. The **viscosity of a liquid** decreases with increasing temperature.

☐ 2. The **conductance** of a solution is the inverse of its resistance.

☐ 3. **Kohlrausch's law** states that at low concentrations the molar conductivities of strong electrolytes vary linearly with the square root of the concentration.

☐ 4. The **law of the independent migration of ions** states that the molar conductivity in the limit of zero concentration is the sum of contributions from its individual ions.

☐ 5. An ion reaches a **drift speed** when the acceleration due to the electrical force is balanced by the viscous drag.

☐ 6. The **hydrodynamic radius** of an ion may be greater than its geometrical radius due to solvation.

☐ 7. The high mobility of a proton in water is explained by the **Grotthuss mechanism.**

Checklist of equations

Property	Equation	Comment	Equation number
Viscosity	$\eta=\eta_0 e^{E_a/RT}$	Narrow temperature range	80.2
Conductivity	$\kappa=Gl/A$	Definition, $G=1/R$	80.3
Molar conductivity	$\Lambda_m=\kappa/c$	Definition	80.4
Kohlrausch's law	$\Lambda_m=\Lambda_m^\circ-\mathcal{K}c^{1/2}$	Empirical observation	80.5
Law of independent migration of ions	$\Lambda_m^\circ=\nu_+\lambda_++\nu_-\lambda_-$	Limiting law	80.6
Stokes's law	$\mathcal{F}_{fric}=fs, \quad f=6\pi\eta a$	Hydrodynamic radius a	80.9
Drift speed	$s=u\mathcal{E}$	Defines u	80.11
Ion mobility	$u=ze/6\pi\eta a$	Assumes Stokes's law	80.12
Conductivity and mobility	$\lambda=zuF$		80.13
Molar conductivity and mobility	$\Lambda_m^\circ=(z_+u_+\nu_++z_-u_-\nu_-)F$	Limiting law	80.14

Property	Equation	Comment	Equation number
Drift speed	$s=D\mathcal{F}/RT$		80.15
Einstein relation	$u=zDF/RT$		80.16
Nernst–Einstein relation	$\Lambda_\mathrm{m}^\circ=(\nu_+z_+^2D_++\nu_-z_-^2D_-)(F^2/RT)$		80.18
Stokes–Einstein relation	$D=kT/f$		80.19

TOPIC 81

Diffusion

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➤ Why do you need to know this material?

Diffusion is a hugely important process both in the atmosphere and in solution, and it is important to be able to predict the spread of one material through another when discussing reactions in solution and the spread of substances into the environment.

➤ What is the key idea?

Particles tend to spread and achieve a uniform distribution.

➤ What do you need to know already?

This Topic draws on arguments relating to flux that are treated in Topic 79, particularly the way to calculate the flux of particles through a window of given area. This Topic goes into more detail about the diffusion coefficient, which was introduced in Topic 79 and used in Topic 80. It uses the concept of chemical potential (Topic 69) to discuss the direction of spontaneous change. One of the mathematical manipulations draws on Stirling's approximation, which is introduced in Topic 51.

That solutes in gases, liquids, and solids have a tendency to spread can be discussed from three points of view. One viewpoint is from the Second Law of thermodynamics and the tendency for entropy to increase or, if the temperature and pressure are constant, for the Gibbs energy to decrease. When this law is applied to solutes it appears that there is a force acting to disperse the solute. That force is illusory, but it provides an interesting and useful approach to discussing diffusion. The second approach is to set up a differential equation for the change in concentration in a region by considering the flux of material through its boundaries. The resulting 'diffusion equation' can then be solved (in principle, at least) for various configurations of the system, such as the shape of a reaction vessel. The third approach is more mechanistic, and is to imagine diffusion as taking place in a series of random small steps: it enriches the thermodynamic view by providing a model of what is taking place when matter diffuses. We explore all three viewpoints in this Topic.

81.1 The thermodynamic view

In Topic 64 it is established that, at constant temperature and pressure, the maximum non-expansion work that can be done when a substance moves from a location where its Gibbs energy is G to a location where its Gibbs energy is $G+\mathrm{d}G$ is $\mathrm{d}w=\mathrm{d}G$. Since the chemical potential is the (partial) molar Gibbs energy (Topic 69), the maximum non-expansion work per mole is $\mathrm{d}w=\mathrm{d}\mu$. In a system in which the chemical potential depends on the position x,

$$\mathrm{d}w=\mathrm{d}\mu=\left(\frac{\partial\mu}{\partial x}\right)_{T,p}\mathrm{d}x$$

It is also established in *Foundations*, Topic 2 that in general work can always be expressed in terms of an opposing force (which here we write $\mathcal{F}$), and that

$$\mathrm{d}w = -\mathcal{F}\,\mathrm{d}x$$

By comparing these two expressions, we see that the slope of the chemical potential can be interpreted as an effective force per mole of molecules. We write this **thermodynamic force** as

$$\mathcal{F} = -\left(\frac{\partial \mu}{\partial x}\right)_{T,p} \qquad \text{Thermodynamic force} \qquad (81.1)$$

There is not necessarily a real force pushing the particles down the slope of the chemical potential. As we shall see, the force may represent the spontaneous tendency of the molecules to disperse as a consequence of the Second Law and the hunt for maximum entropy.

In a solution in which the activity of the solute is a, the chemical potential is $\mu = \mu^{\ominus} + RT\ln a$ (see Table 72.1 of Topic 72). If the solution is not uniform the activity depends on the position and we can write

$$\mathcal{F} = -RT\left(\frac{\partial \ln a}{\partial x}\right)_{T,p} \qquad (81.2\text{a})$$

If the solution is ideal, a may be replaced by $c/c^{\ominus}$, and then

$$\mathcal{F} = -RT\left(\frac{\partial \ln(c/c^{\ominus})}{\partial x}\right)_{T,p} = -\frac{RT}{c}\left(\frac{\partial c}{\partial x}\right)_{T,p} \qquad (81.2\text{b})$$

where we have also used the relation $\mathrm{d}\ln y/\mathrm{d}x = (1/y)(\mathrm{d}y/\mathrm{d}x)$.

Brief illustration 81.1 The thermodynamic force

Suppose a linear concentration gradient is set up across a container at 25 °C, with points separated by 1.0 cm differing in concentration by 0.10 mol dm^{-3} around a mean value of 1.0 mol dm^{-3}. According to eqn 81.2b, the solute experiences a thermodynamic force of magnitude

$$\begin{aligned}\mathcal{F} &= \frac{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})}{1.0\,\mathrm{mol\,dm^{-3}}} \times \frac{0.10\,\mathrm{mol\,dm^{-3}}}{1.0\times10^{-2}\,\mathrm{m}}\\ &= 2.5\times10^{4}\,\overbrace{\mathrm{J\,m^{-1}}}^{\mathrm{N}}\,\mathrm{mol^{-1}}\end{aligned}$$

or 25 kN mol^{-1}. Note that the thermodynamic force is a molar quantity.

Self-test 81.1 Suppose that the concentration of a solute decreases exponentially as $c(x) = c_0 \mathrm{e}^{-x/\lambda}$. Derive an expression for the thermodynamic force.

Answer: $\mathcal{F} = RT/\lambda$

In Topic 79 it is established that Fick's first law of diffusion, which we write here in the form

$$J(\text{number}) = -D\frac{\mathrm{d}\mathcal{N}}{\mathrm{d}x} \qquad \text{Fick's first law} \qquad (81.3)$$

can be deduced from the kinetic model of gases. Here we generalize that result. We show that it can be deduced more generally and that it applies to the diffusion of species in condensed phases too. To do so, we suppose that the flux of diffusing particles is motion in response to a thermodynamic force arising from a concentration gradient. The diffusing particles reach a steady 'drift speed', s, when the thermodynamic force, $\mathcal{F}$, is matched by the drag due to the viscosity of the medium. This drift speed is proportional to the thermodynamic force, and we write $s \propto \mathcal{F}$. However, the particle flux, J, is proportional to the drift speed, and the thermodynamic force is proportional to the concentration gradient, $\mathrm{d}c/\mathrm{d}x$. The chain of proportionalities ($J \propto s$, $s \propto \mathcal{F}$, and $\mathcal{F} \propto \mathrm{d}c/\mathrm{d}x$) implies that $J \propto \mathrm{d}c/\mathrm{d}x$, which is the content of Fick's law.

If we divide both sides of eqn 81.3 by Avogadro's constant, thereby converting numbers into amounts (numbers of moles), noting that $\mathcal{N}/N_\mathrm{A} = (N/V)/N_\mathrm{A} = (nN_\mathrm{A}/V)/N_\mathrm{A} = n/V = c$, the molar concentration, then Fick's law becomes

$$J(\text{amount}) = -D\frac{\mathrm{d}c}{\mathrm{d}x} \qquad (81.4)$$

In this expression, D is the diffusion coefficient and $\mathrm{d}c/\mathrm{d}x$ is the slope of the molar concentration. The flux is related to the drift speed by

$$J(\text{amount}) = sc \qquad (81.5)$$

This relation follows from the argument used in Topic 79. Thus, all particles within a distance $s\Delta t$, and therefore in a volume $s\Delta tA$, can pass through a window of area A in an interval Δt. Hence, the amount of substance that can pass through the window in that interval is $s\Delta tAc$. The particle flux is this quantity divided by the area A and the time interval Δt, and is therefore simply sc.

By combining the last two equations and using eqn 81.2

$$sc = -D\frac{\mathrm{d}c}{\mathrm{d}x} = \frac{Dc\mathcal{F}}{RT} \quad \text{or} \quad s = \frac{D\mathcal{F}}{RT} \qquad (81.6)$$

Therefore, once we know the effective force and the diffusion coefficient, D, we can calculate the drift speed of the particles (and vice versa), whatever the origin of the force. This equation is used in Topic 80 where the force is applied electrically to an ion.

Brief illustration 81.2 The thermodynamic force and the drift speed

Laser measurements showed that a molecule has a drift speed of 1.0 µm s^{-1} in water at 25 °C, with diffusion coefficient $5.0\times10^{-9}\,\mathrm{m^2\,s^{-1}}$. The corresponding thermodynamic force from eqn 81.6 in the form $\mathcal{F}=sRT/D$ is

$$\mathcal{F}=\frac{(1.0\times10^{-6}\,\mathrm{m\,s^{-1}})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})}{(5.0\times10^{-9}\,\mathrm{m^2\,s^{-1}})}$$

$$=5.0\times10^{5}\,\overbrace{\mathrm{J\,m^{-1}}}^{\mathrm{N}}\,\mathrm{mol^{-1}}$$

or about 500 kN mol^{-1}.

Self-test 81.2 What is the drift speed of a sucrose molecule in water at 25 °C if the thermodynamic force is 250 kN mol^{-1}? Use $D=5.4\times10^{-10}\,\mathrm{m^2\,s^{-1}}$.

Answer: 5.3 µm s^{-1}

81.2 The diffusion equation

We now turn to the discussion of time-dependent diffusion processes, where we are interested in the spreading of inhomogeneities with time. One example is the temperature of a metal bar that has been heated at one end: if the source of heat is removed, then the bar gradually settles down into a state of uniform temperature. When the source of heat is maintained and the bar can radiate, it settles down into a steady state of non-uniform temperature. Another example (and one more relevant to chemistry) is the concentration distribution in a solvent to which a solute is added. We shall focus on the description of the diffusion of particles, but similar arguments apply to the diffusion of physical properties, such as temperature. Our aim is to obtain an equation for the rate of change of the concentration of particles in an inhomogeneous region.

(a) Simple diffusion

The central equation of this section is the **diffusion equation**, also called 'Fick's second law of diffusion', which relates the rate of change of concentration at a point to the spatial variation of the concentration at that point:

$$\frac{\partial c}{\partial t}=D\frac{\partial^2 c}{\partial x^2} \qquad \text{Diffusion equation} \qquad (81.7)$$

We show in the following *Justification* that the diffusion equation follows from Fick's first law of diffusion.

Justification 81.1 The diffusion equation

Consider a thin slab of cross-sectional area A that extends from x to $x+\lambda$ (Fig. 81.1). Let the concentration at x be c at the time t. The rate at which the amount (in moles) of particles enter the slab is JA, so the rate of increase in molar concentration inside the slab (which has volume $A\lambda$) on account of the flux from the left is

$$\frac{\partial c}{\partial t}=\frac{JA}{A\lambda}=\frac{J}{\lambda}$$

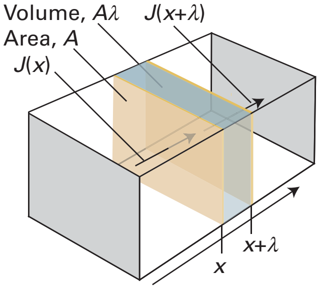

Figure 81.1 The net flux in a region is the difference between the flux entering from the region of high concentration (on the left) and the flux leaving to the region of low concentration (on the right).

There is also an outflow through the right-hand window. The flux through that window is J', and the rate of change of concentration that results is

$$\frac{\partial c}{\partial t}=-\frac{J'}{\lambda}$$

The net rate of change of concentration is therefore

$$\frac{\partial c}{\partial t}=\frac{J-J'}{\lambda}$$

Each flux is proportional to the concentration gradient at the respective window. So, by using Fick's first law, we can write

$$J-J'=-D\frac{\partial c}{\partial x}+D\frac{\partial c'}{\partial x}$$

The concentration at the right-hand window is related to that on the left by

$$c'=c+\left(\frac{\partial c}{\partial x}\right)\lambda$$

which implies that

$$J-J'=-D\frac{\partial c}{\partial x}+D\frac{\partial}{\partial x}\left\{c+\left(\frac{\partial c}{\partial x}\right)\lambda\right\}=D\lambda\frac{\partial^2 c}{\partial x^2}$$

When this relation is substituted into the expression for the rate of change of concentration in the slab, we get eqn 81.7.

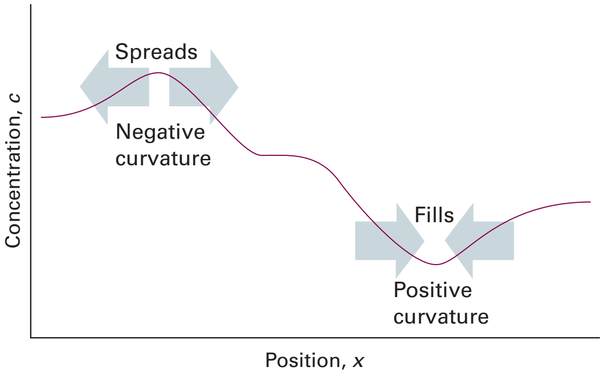

Figure 81.2 Nature abhors a wrinkle. The diffusion equation tells us that peaks in a distribution (regions of negative curvature) spread and troughs (regions of positive curvature) fill in.

The diffusion equation shows that the rate of change of concentration is proportional to the curvature (more precisely, to the second derivative) of the concentration with respect to distance. If the concentration changes sharply from point to point (if the distribution is highly wrinkled), then the concentration changes rapidly with time. Where the curvature is positive (a dip, Fig. 81.2), the change in concentration is positive; the dip tends to fill. Where the curvature is negative (a heap), the change in concentration is negative; the heap tends to spread. If the curvature is zero, then the concentration is constant in time. If the concentration decreases linearly with distance, then the concentration at any point is constant because the inflow of particles is exactly balanced by the outflow.

The diffusion equation can be regarded as a mathematical formulation of the intuitive notion that there is a natural tendency for the wrinkles in a distribution to disappear. More succinctly: Nature abhors a wrinkle.

Brief illustration 81.3 The diffusion equation

If a concentration falls linearly across a small region of space, in the sense that $c=c_0-ax$, then $\partial^2c/\partial x^2=0$ and consequently $\partial c/\partial t=0$. The concentration in the region is constant because the inward flow through one window is matched by the outward flow through the other window. If the concentration varies as $c=c_0-\frac{1}{2}ax^2$, then $\partial^2c/\partial x^2=-a$ and consequently $\partial c/\partial t=-Da$. Now the concentration decreases, because there is a greater outward flow than inward flow.

Self-test 81.3 What is the change in concentration when the concentration falls exponentially across a region? Take $c=c_0\mathrm{e}^{-x/\lambda}$.

Answer: $\partial c/\partial t=(D/\lambda^2)c$

(b) Diffusion with convection

The transport of particles arising from the motion of a streaming fluid is called **convection**. If for the moment we ignore diffusion, then the flux of particles through an area A in an interval Δt when the fluid is flowing at a velocity v can be calculated in the way we have used several times elsewhere (such as in Topic 79, by counting the particles within a distance $v\Delta t$), and is

$$J_{\text{conv}}=\frac{cAv\Delta t}{A\Delta t}=cv \qquad \text{Convective flux} \qquad (81.8)$$

This J is called the **convective flux**. The rate of change of concentration in a slab of thickness l and area A is, by the same argument as before and assuming that the velocity does not depend on the position,

$$\begin{aligned}\frac{\partial c}{\partial t}&=\frac{J_{\text{conv}}-J'_{\text{conv}}}{\lambda}=\frac{cv}{\lambda}-\left\{c+\left(\frac{\partial c}{\partial x}\right)\lambda\right\}\frac{v}{\lambda}\\&=-\left(\frac{\partial c}{\partial x}\right)v\end{aligned} \qquad \text{Convection} \qquad (81.9)$$

When both diffusion and convection occur, the total change of concentration in a region is the sum of the two effects, and the **generalized diffusion equation** is

$$\frac{\partial c}{\partial t}=D\frac{\partial^2c}{\partial x^2}-v\frac{\partial c}{\partial x} \qquad \text{Generalized diffusion equation} \qquad (81.10)$$

A further refinement, which is important in chemistry, is the possibility that the concentrations of particles may change as a result of reaction. When reactions are included in eqn 81.10 (Topic 88) we get a powerful differential equation for discussing the properties of reacting, diffusing, convecting systems and which is the basis of reactor design in chemical industry and of the utilization of resources in living cells.

Brief illustration 81.4 Convection

Here we continue the discussion of the systems treated in *Brief illustration* 81.3 and suppose that there is a convective flow v. If the concentration falls linearly across a small region of space, in the sense that $c=c_0-ax$, then $\partial c/\partial x=-a$ and the change in concentration in the region is $\partial c/\partial t=av$. There is now an increase in the region because the inward convective flow outweighs the outward flow, and there is no diffusion. If $a=0.010\,\text{mol dm}^{-3}\,\text{m}^{-1}$ and $v=+1.0\,\text{mm s}^{-1}$,

$$\begin{aligned}\frac{\partial c}{\partial t}&=(0.010\,\text{mol dm}^{-3}\,\text{m}^{-1})\times(1.0\times10^{-3}\,\text{m s}^{-1})\\&=1.0\times10^{-5}\,\text{mol dm}^{-3}\,\text{s}^{-1}\end{aligned}$$

and the concentration increases at the rate of 10 μmol dm^{-3} s^{-1}.

Self-test 81.4 What rate of flow is needed to replenish the concentration when the concentration varies exponentially as $c=c_0\mathrm{e}^{-x/\lambda}$ across the region?

Answer: $v=D/\lambda$

(c) Solutions of the diffusion equation

The diffusion equation is a second-order differential equation with respect to space and a first-order differential equation with respect to time. Therefore, we must specify two boundary conditions for the spatial dependence and a single initial condition for the time dependence (see *Mathematical background* 2).

As an illustration, consider a solvent in which the solute is initially coated on one surface of the container (for example, a layer of sugar on the bottom of a deep beaker of water). The single initial condition is that at $t=0$ all N_0 particles are concentrated on the yz-plane (of area A) at $x=0$. The two boundary conditions are derived from the requirements (1) that the concentration must everywhere be finite and (2) that the total amount (number of moles) of particles present is n_0 (with $n_0=N_0/N_A$) at all times. These requirements imply that the flux of particles is zero at the top and bottom surfaces of the system. Under these conditions it is found that

$$c(x,t)=\frac{n_0}{A(\pi Dt)^{1/2}}\mathrm{e}^{-x^2/4Dt} \qquad \text{One-dimensional diffusion} \tag{81.11}$$

as may be verified by direct substitution (Problem 81.5). Figure 81.3 shows the shape of the concentration distribution at various times, and it is clear that the concentration spreads and tends to uniformity.

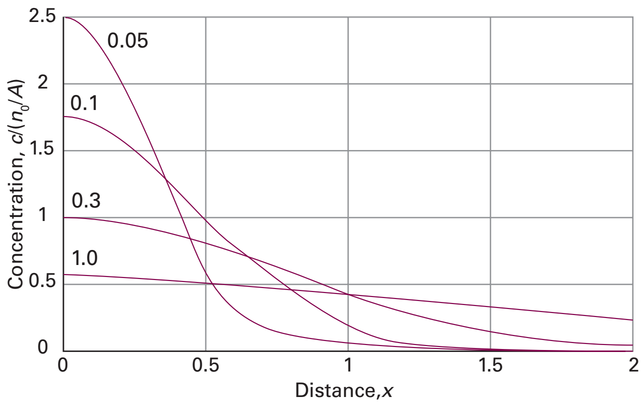

Figure 81.3 The concentration profiles above a plane from which a solute is diffusing. The curves are plots of eqn 81.11 and are labelled with different values of *Dt*. The units of *Dt* and *x* are arbitrary, but are related so that Dt/x^2 is dimensionless. For example, if *x* is in metres, *Dt* would be in metres squared; so, for $D=10^{-9}$ m^2 s^{-1}, $Dt=0.1$ m^2 corresponds to $t=10^8$ s.

Table 81.1* Diffusion coefficients at 298 K

	$D/(10^{-9}$ m^2 s$^{-1})$
H$^+$ in water	9.31
I$_2$ in hexane	4.05
Na$^+$ in water	1.33
Sucrose in water	0.522

* More values are given in the *Resource section*.

Another useful result is for a localized concentration of solute in a three-dimensional solvent (a sugar lump suspended in a large flask of water). The concentration of diffused solute is spherically symmetrical, and at a radius r is

$$c(r,t)=\frac{n_0}{8(\pi Dt)^{3/2}}\mathrm{e}^{-r^2/4Dt} \qquad \text{Three-dimensional diffusion} \tag{81.12}$$

Other chemically (and physically) interesting arrangements, such as transport of substances across biological membranes, can be treated. In many cases the solutions are more cumbersome.

The solutions of the diffusion equation are useful for experimental determinations of diffusion coefficients (Table 81.1). In the **capillary technique**, a capillary tube, open at one end and containing a solution, is immersed in a well-stirred larger quantity of solvent, and the change of concentration in the tube is monitored. The solute diffuses from the open end of the capillary at a rate that can be calculated by solving the diffusion equation with the appropriate boundary conditions, so D may be determined. In the **diaphragm technique**, the diffusion occurs through the capillary pores of a sintered glass diaphragm separating the well-stirred solution and solvent. The concentrations are monitored and then related to the solutions of the diffusion equation corresponding to this arrangement. Diffusion coefficients may also be measured by a number of techniques, including NMR spectroscopy.

The solutions of the diffusion equation can be used to predict the concentration of particles (or the value of some other physical quantity, such as the temperature in a non-uniform system) at any location. We can also use them to calculate the average displacement of the particles in a given time.

Example 81.1 Calculating the average displacement

Calculate the average displacement of particles in a time t in a one-dimensional system if they have a diffusion constant D.

Method We need to use the results of probability theory summarized in *Mathematical background* 7. In this case, we calculate the probability that a particle will be found at a certain distance from the origin, and then calculate the average by weighting each distance by that probability. You will need to use eqn 81.11 as well as Integral G.2 listed in the *Resource section*.

Answer The number of particles in a slab of thickness dx and area A at x, where the molar concentration is c, is $cAN_A\mathrm{d}x$. The probability that any of the $N_0=n_0N_A$ particles is in the slab is therefore $cAN_A\mathrm{d}x/N_0$. If the particle is in the slab, it has travelled a distance x from the origin. Therefore, the average displacement of all the particles is the sum of each x weighted by the probability of its occurrence:

$$\langle x\rangle=\int_0^\infty x\frac{c(x,t)AN_A}{\underbrace{N_0}_{n_0N_A}}\mathrm{d}x=\frac{1}{(\pi Dt)^{1/2}}\overbrace{\int_0^\infty xe^{-x^2/4Dt}\,\mathrm{d}x}^{\text{Integral G.2}}=2\left(\frac{Dt}{\pi}\right)^{1/2}$$

The average displacement varies as the square root of the lapsed time.

Self-test 81.5 Derive an expression for the root mean square distance travelled by diffusing particles in a time t in a one-dimensional system. You will need Integral G.3 listed in the *Resource section*.

Answer: $\langle x^2\rangle^{1/2}=(2Dt)^{1/2}$

As shown in Example 81.1, the average displacement of a diffusing particle in a time t in a one-dimensional system is

$$\langle x\rangle=2\left(\frac{Dt}{\pi}\right)^{1/2} \qquad \textit{One dimension} \qquad \text{Mean displacement} \qquad (81.13)$$

and the root mean square displacement in the same time is (from Self-test 81.5)

$$\langle x^2\rangle^{1/2}=(2Dt)^{1/2} \qquad \textit{One dimension} \qquad \text{Root mean square displacement} \qquad (81.14)$$

The latter is a valuable measure of the spread of particles when they can diffuse in both directions from the origin (for then $\langle x\rangle=0$ at all times). The root mean square displacement of particles with a typical diffusion coefficient ($D=5\times10^{-10}\ \mathrm{m^2\ s^{-1}}$) is illustrated in Fig. 81.4, which shows how long it takes for diffusion to increase the net distance travelled on average to about 1 cm in an unstirred solution. The graph shows that diffusion is a very slow process (which is why solutions are stirred, to encourage mixing by convection). The diffusion of pheromones in still air is also very slow, and greatly accelerated by convection.

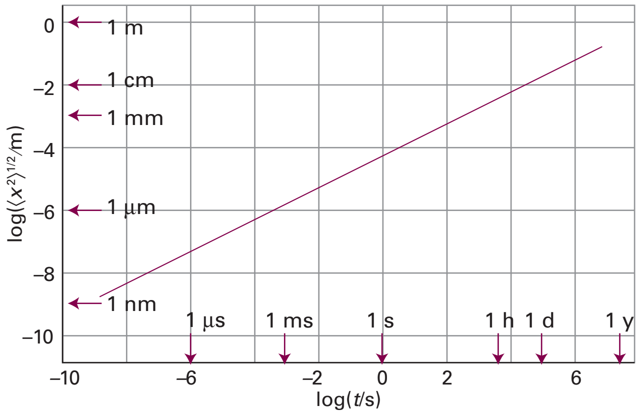

Figure 81.4 The root mean square distance covered by particles with $D=5\times10^{-10}\ \mathrm{m^2\ s^{-1}}$. Note the great slowness of diffusion.

81.3 The statistical view

An intuitive picture of diffusion is of the particles moving in a series of small steps and gradually migrating from their original positions. We explore this idea by using a model in which the particles can jump through a distance λ in a time τ. The total distance travelled by a particle in a time t is therefore $t\lambda/\tau$. However, the particle will not necessarily be found at that distance from the origin. The direction of each step may be different, and the net distance travelled must take the changing directions into account.

If we simplify the discussion by allowing the particles to travel only along a straight line (the x-axis), and for each step (to the left or the right) to be through the same distance λ, then we obtain the **one-dimensional random walk**. We show in the following *Justification* that the probability of a particle being at a distance x from the origin after a time t is

$$P(x,t)=\left(\frac{2\tau}{\pi t}\right)^{1/2}e^{-x^2\tau/2t\lambda^2} \qquad \textit{One dimension} \qquad \text{Probability} \qquad (81.15)$$

Justification 81.2 The one-dimensional random walk

Consider a one-dimensional random walk of N steps in which each step is through a distance λ to the left or right. The number of ways of performing a walk with N_R steps to the right and N_L to the left is given by the binomial coefficient (*Mathematical background* 7)

$$W=\frac{N!}{N_L!N_R!}=\frac{N!}{(N-N_R)!N_R!}$$

The total possible number of paths is 2^N as each of the N steps may be in either of two directions. The probability of the net distance walked being $n\lambda$ with $n=N_R-N_L=2N_R-N$ is therefore

$$P(n\lambda)=\frac{\text{number of paths with } N_R \text{ steps to the right}}{\text{total number of paths}}$$
$$=\frac{W}{2^N}=\frac{N!}{(N-N_R)!N_R!2^N}$$

This expression can be developed by making use of Stirling's approximation (Topic 51) in the form

$$\ln x!\approx\ln(2\pi)^{1/2}+(x+\tfrac{1}{2})\ln x-x$$

and the parameter

$$\mu=\frac{N_R}{N}-\frac{1}{2}\ll 1$$

which is small because almost exactly half the steps are to the right. The smallness of μ allows us to use the expansion

$$\ln\left(\frac{1}{2}\pm\mu\right)=-\ln 2\pm 2\mu-2\mu^2+\cdots$$

and retain terms through the order μ^2 in the overall expression for ln $P(n\lambda)$. The final result, after quite a lot of algebra (see Problem 81.10), is

$$P(n\lambda)=\frac{2^{N+1}\mathrm{e}^{-2N\mu^2}}{2^N(2\pi N)^{1/2}}=\frac{2\mathrm{e}^{-2N\mu^2}}{(2\pi N)^{1/2}}$$

At this point we recognize that

$$N\mu^2=\frac{(2N_R-N)^2}{4N}=\frac{(N_R-N_L)^2}{4N}=\frac{n^2}{4N}$$

The net distance from the origin is $x=n\lambda$ and the number of steps taken in a time t is $N=t/\tau$, so $N\mu^2=\tau x^2/4t\lambda^2$. Substitution of these quantities into the expression for P gives eqn 81.15.

The differences of detail between eqns 81.11 (for one-dimensional diffusion) and 81.15 arise from the fact that in the present calculation the particles can migrate in either direction from the origin. Moreover, they can be found only at discrete points separated by λ instead of being anywhere on a continuous line. The fact that the two expressions are so similar suggests that diffusion can indeed be interpreted as the outcome of a large number of steps in random directions.

We can now relate the coefficient D to the step length λ and the rate at which the jumps occur. Thus, by comparing the two exponents in eqn 81.11 and eqn 81.15 we can immediately write down the **Einstein–Smoluchowski equation**:

$$D=\frac{\lambda^2}{2\tau}\qquad \text{Einstein–Smoluchowski equation}\qquad (81.16)$$

Brief illustration 81.5 Random walk

Suppose an SO_4^{2-} ion jumps through its own diameter each time it makes a move in an aqueous solution. Then, because $D=1.1\times10^{-9}\ \mathrm{m^2\,s^{-1}}$ (Table 81.1) and $a=250$ pm (as deduced from mobility measurements, Topic 80), it follows from $\lambda=2a$ that

$$\tau=\frac{(2a)^2}{2D}=\frac{2a^2}{D}=\frac{2\times(250\times10^{-12}\ \mathrm{pm})^2}{1.1\times10^{-9}\ \mathrm{m^2\,s^{-1}}}=1.1\times10^{-10}\ \mathrm{s}$$

or $\tau=110$ ps. Because τ is the time for one jump, the ion makes about 1×10^{10} jumps per second.

Self-test 81.6 Suppose the activation energy for diffusion is 40 kJ mol⁻¹. What would be the jump time when the temperature was increased from 25 °C (as above) to 30 °C?

Answer: 84 ps

For a one-dimensional random walk, eqn 81.13 in combination with eqn 81.16 implies that the distance walked after $N=t/\tau$ steps of length λ is

$$\langle x\rangle=\lambda\left(\frac{2N}{\pi}\right)^{1/2}\qquad \textit{One dimension}\qquad \text{Mean distance from origin}\qquad (81.17a)$$

The corresponding expressions for the mean radius reached in a random walk in two dimensions (like a molecule migrating on a flat surface) and in three dimensions (in a solution; see Problem 81.13) are

$$\langle r\rangle=\lambda N^{1/2}\qquad \textit{Two dimensions}\qquad \text{Mean distance from origin}\qquad (81.17b)$$

$$\langle r\rangle=\lambda\left(\frac{8N}{\pi}\right)^{1/2}\qquad \textit{Three dimensions}\qquad \text{Mean distance from origin}\qquad (81.17c)$$

Note that the average distance increases as the dimensionality increases, as the particles have greater freedom to escape than in one dimension.

The Einstein–Smoluchowski equation is the central connection between the microscopic details of particle motion and the macroscopic parameters relating to diffusion (for example, the diffusion coefficient and, through the Stokes–Einstein relation, eqn 80.19b of Topic 80, $D=kT/6\pi\eta a$, the viscosity). It also brings us back full circle to the properties of the perfect gas treated in Topic 79. For if we interpret λ/τ as v_{mean}, the mean speed of the molecules, and interpret λ as a mean free path, then we can recognize in the Einstein–Smoluchowski equation essentially the same expression as we obtained from the kinetic model of gases (eqn 79.7 of Topic 79, $D=\frac{1}{3}\lambda v_{\text{mean}}$). That is, the diffusion of a perfect gas is a random walk with an average step size equal to the mean free path.

Checklist of concepts

☐ 1. The **thermodynamic force** represents the spontaneous tendency of the molecules to disperse as a consequence of the Second Law and the hunt for maximum entropy.

☐ 2. The **diffusion equation** (Fick's second law; see below) can be regarded as a mathematical formulation of the notion that there is a natural tendency for concentration to become uniform.

☐ 3. **Convection** is the transport of particles arising from the motion of a streaming fluid.

☐ 4. An intuitive picture of diffusion is of the particles moving in a series of small steps and gradually migrating from their original positions.

Checklist of equations

Property	Equation	Comment	Equation number
Thermodynamic force	$\mathcal{F}=-(\partial\mu/\partial x)_{T,p}$	Definition	81.1
Fick's first law	$J(\text{amount})=-D\mathrm{d}c/\mathrm{d}x$		81.4
Diffusive flux	$J=sc$		81.5
Drift speed	$s=D\mathcal{F}/RT$		81.6
Diffusion equation	$\partial c/\partial t=D\partial^2 c/\partial x^2$	One dimension	81.7
Convective flux	$J=cv$		81.8
Generalized diffusion equation	$\partial c/\partial t=D\partial^2 c/\partial x^2-v\partial c/\partial x$	One dimension	81.10
Mean displacement	$\langle x\rangle=2(Dt/\pi)^{1/2}$	One-dimensional diffusion	81.13
Root mean square displacement	$\langle x^2\rangle^{1/2}=(2Dt)^{1/2}$	One-dimensional diffusion	81.14
Probability of displacement	$P(x,t)=(2\tau/\pi t)^{1/2}\mathrm{e}^{-x^2\tau/2t\lambda^2}$	One-dimensional random walk	81.15
Einstein–Smoluchowski equation	$D=\lambda^2/2\tau$	One-dimensional random walk	81.16

Focus 16 on Molecular motion

Topic 78 The kinetic theory of gases

Discussion questions

78.1 Specify and analyse critically the assumptions that underlie the kinetic model of gases.

78.2 Provide molecular interpretations for the dependencies of the mean free path on the temperature, pressure, and size of gas molecules.

Exercises

78.1(a) Determine the ratios of (a) the mean speeds, (b) the mean translational kinetic energies of H_2 molecules and Hg atoms at 20 °C.
78.1(b) Determine the ratios of (a) the mean speeds, (b) the mean kinetic energies of He atoms and Hg atoms at 25 °C.

78.2(a) Calculate the root mean square speeds of H_2 and O_2 molecules at 20 °C.
78.2(b) Calculate the root mean square speeds of CO_2 molecules and He atoms at 20 °C.

78.3(a) Use the Maxwell distribution of speeds to estimate the fraction of N_2 molecules at 400 K that have speeds in the range 200 to 210 m s^{-1}.
78.3(b) Use the Maxwell distribution of speeds to estimate the fraction of CO_2 molecules at 400 K that have speeds in the range 400 to 405 m s^{-1}.

78.4(a) Calculate the most probable speed, the mean speed, and the mean relative speed of CO_2 molecules in air at 20 °C.
78.4(b) Calculate the most probable speed, the mean speed, and the mean relative speed of H_2 molecules in air at 20 °C.

78.5(a) Assume that air consists of N_2 molecules with a collision diameter of 395 pm. Calculate (a) the mean speed of the molecules, (b) the mean free path, (c) the collision frequency in air at 1.0 atm and 25 °C.
78.5(b) The best laboratory vacuum pump can generate a vacuum of about 1 nTorr. At 25 °C and assuming that air consists of N_2 molecules with a collision diameter of 395 pm, calculate (a) the mean speed of the molecules, (b) the mean free path, (c) the collision frequency in the gas.

78.6(a) At what pressure does the mean free path of argon at 20 °C become comparable to the diameter of a 100 cm^3 vessel that contains it? Take $\sigma = 0.36\,\text{nm}^2$.
78.6(b) At what pressure does the mean free path of argon at 20 °C become comparable to 10 times the diameters of the atoms themselves?

78.7(a) At an altitude of 20 km the temperature is 217 K and the pressure 0.050 atm. What is the mean free path of N_2 molecules? ($\sigma = 0.43\,\text{nm}^2$).
78.7(b) At an altitude of 15 km the temperature is 217 K and the pressure 12.1 kPa. What is the mean free path of N_2 molecules? ($\sigma = 0.43\,\text{nm}^2$).

78.8(a) How many collisions does a single Ar atom make in 1.0 s when the temperature is 25 °C and the pressure is (a) 10 atm, (b) 1.0 atm, (c) 1.0 μatm?
78.8(b) How many collisions per second does an N_2 molecule make at an altitude of 15 km? (See Exercise 78.7b for data.)

78.9(a) A solid surface with dimensions 5.0 mm × 4.0 mm is exposed to argon gas at 25 Pa and 300 K. How many collisions do the Ar atoms make with this surface in 100 s?
78.9(b) A solid surface with dimensions 2.0 cm × 10.0 cm is exposed to helium gas at 120 Pa and 1200 K. How many collisions do the He atoms make with this surface in 1.0 s?

78.10(a) If 125 cm^3 of hydrogen gas effuses through a small hole in 135 seconds, how long will it take the same volume of oxygen gas to effuse under the same temperature and pressure?
78.10(b) If 175 cm^3 of carbon dioxide effuses through a small hole in 255 seconds, how long will it take the same volume of sulfur dioxide to effuse under the same temperature and pressure?

78.11(a) An effusion cell has a circular hole of diameter 1.50 mm. If the molar mass of the solid in the cell is 300 g mol^{-1} and its vapour pressure is 0.735 Pa at 500 K, by how much will the mass of the solid decrease in a period of 1.00 h?
78.11(b) An effusion cell has a circular hole of diameter 1.00 mm. If the molar mass of the solid in the cell is 250 g mol^{-1} and its vapour pressure is 0.324 Pa at 425 K, by how much will the mass of the solid decrease in a week (use 1 week = 7 × 24 h)?

78.12(a) A manometer was connected to a bulb containing a gaseous sample under slight pressure. The gas was allowed to escape through a small pinhole, and the time for the manometer reading to drop from 74 cm to 20 cm was 152 s. When the experiment was repeated using nitrogen (for which $M = 28.02\,\text{g mol}^{-1}$) the same fall took place in 45 s. Calculate the molar mass of the sample.
78.12(b) A manometer was connected to a bulb containing nitrogen under slight pressure. The gas was allowed to escape through a small pinhole, and the time for the manometer reading to drop from 75.1 cm to 32.5 cm was 22.5 s. When the experiment was repeated using a fluorocarbon gas, the same fall took place in 135.0 s. Calculate the molar mass of the fluorocarbon.

78.13(a) A space vehicle of internal volume 3.0 m^3 is struck by a meteor and a hole of radius 0.10 mm is formed. If the oxygen pressure within the vehicle is initially 80 kPa and its temperature 298 K, how long will the pressure take to fall to 70 kPa?
78.13(b) A container of internal volume 22.0 m^3 was punctured, and a hole of radius 0.050 mm was formed. If the nitrogen pressure within the vehicle is initially 122 kPa and its temperature 293 K, how long will the pressure take to fall to 105 kPa?

Problems

78.1 The speed of molecules can also be measured with a rotating slotted-disc apparatus, which consists of five coaxial 5.0 cm diameter disks separated by 1.0 cm, the slots in their rims being displaced by 2.0° between neighbours. The relative intensities, I, of the detected beam of Kr atoms for two different temperatures and at a series of rotation rates were as follows:

ν/Hz	20	40	80	100	120
I (40 K)	0.846	0.513	0.069	0.015	0.002
I (100 K)	0.592	0.485	0.217	0.119	0.057

Find the distributions of molecular velocities, $f(v_x)$, at these temperatures, and check that they conform to the theoretical prediction for a one-dimensional system.

78.2 A Knudsen cell was used to determine the vapour pressure of germanium at 1000 °C. During an interval of 7200 s the mass loss through a hole of radius 0.50 mm amounted to 43 μg. What is the vapour pressure of germanium at 1000 °C? Assume the gas to be monatomic.

78.3 The pressure of a Knudsen cell of volume V in which a vapour is confined (with no condensed phase to replenish the vapour phase) decays exponentially with a time constant $\tau = (2\pi M/RT)^{1/2}(V/A)$ (see Problem 78.12 for the derivation of a related expression). How long would it take the pressure of barium vapour in a cell with $V = 100\,\text{cm}^3$ and $A = 0.10\,\text{mm}^2$ at 1300 °C to fall to 1/10 of its initial value?

78.4 The vapour pressure of zinc in the range 250 °C to 419 °C can be estimated from the expression $\log(p/\text{Torr}) = a - b/T$ with $a = 9.200$ and $b = 6947\,\text{K}$. Calculate and plot the beam flux (in Zn atoms per second) emerging from a hole of radius 0.20 mm as the temperature of the oven containing solid zinc is raised from 250 °C to 400 °C.

78.5 Start from the Maxwell–Boltzmann distribution and derive an expression for the most probable speed of a gas of molecules at a temperature T. Go on to demonstrate the validity of the equipartition conclusion that the average translational kinetic energy of molecules free to move in three dimensions is $\frac{3}{2}kT$.

78.6 In Topic 58 it is established that the heat capacity of a collection of molecules is proportional to the variance of their energy (the mean square deviation of the energy from its mean value). Use the Maxwell–Boltzmann distribution of speeds to calculate the translational contribution to the heat capacity of a gas by this approach.

78.7 Consider molecules that are confined to move in a plane (a two-dimensional gas). Calculate the distribution of speeds and determine the mean speed of the molecules at a temperature T.

78.8 A specially constructed velocity selector accepts a beam of molecules from an oven at a temperature T but blocks the passage of molecules with a speed greater than the mean. What is the mean speed of the emerging beam, relative to the initial value, treated as a one-dimensional problem?

78.9 What, according to the Maxwell–Boltzmann distribution, is the proportion of gas molecules having (a) more than, (b) less than the root mean square speed? (c) What are the proportions having speeds greater and smaller than the mean speed?

78.10 Calculate the fractions of molecules in a gas that have a speed in a range Δv at the speed nv_{mp} relative to those in the same range at v_{mp} itself? This calculation can be used to estimate the fraction of very energetic molecules (which is important for reactions). Evaluate the ratio for $n = 3$ and $n = 4$.

78.11 Derive an expression for $\langle v^n \rangle^{1/n}$ from the Maxwell–Boltzmann distribution of speeds. You will need Integrals G.7 and G.8 listed in the *Resource section*.

78.12 Derive an expression that shows how the pressure of a gas inside an effusion oven (a heated chamber with a small hole in one wall) varies with time if the oven is not replenished as the gas escapes. Then show that $t_{1/2}$, the time required for the pressure to decrease to half its initial value, is independent of the initial pressure. *Hint*: Begin by setting up a differential equation relating $\mathrm{d}p/\mathrm{d}t$ to $p = NkT/V$, and then integrating it.

78.13 Calculate the escape velocity (the minimum initial velocity that will take an object to infinity) from the surface of a planet of radius R. What is the value for (a) the Earth, $R = 6.37 \times 10^6$ m, $g = 9.81\,\text{m s}^{-2}$; (b) Mars, $R = 3.38 \times 10^6$ m, $m_{\text{Mars}}/m_{\text{Earth}} = 0.108$. At what temperatures do H_2, He, and O_2 molecules have mean speeds equal to their escape speeds? What proportion of the molecules have enough speed to escape when the temperature is (a) 240 K, (b) 1500 K? Calculations of this kind are very important in considering the composition of planetary atmospheres.

78.14 The kinetic model of gases is valid when the size of the particles is negligible compared with their mean free path. It may seem absurd, therefore, to expect the kinetic theory and, as a consequence, the perfect gas law, to be applicable to the dense matter of stellar interiors. In the Sun, for instance, the density is 1.50 times that of liquid water at its centre and comparable to that of water about half way to its surface. However, we have to realize that the state of matter is that of a *plasma,* in which the electrons have been stripped from the atoms of hydrogen and helium that make up the bulk of the matter of stars. As a result, the particles making up the plasma have diameters comparable to those of nuclei, or about 10 fm. Therefore, a mean free path of only 0.1 pm satisfies the criterion for the validity of the kinetic model and the perfect gas law. We can therefore use $pV = nRT$ as the equation of state for the stellar interior. (a) Calculate the pressure half way to the centre of the Sun, assuming that the interior consists of ionized hydrogen atoms, the temperature is 3.6 MK, and the mass density is $1.20\,\text{g cm}^{-3}$ (slightly higher than the density of water). (b) Combine the result from part (a) with the expression for the pressure from the kinetic model to show that the pressure of the plasma is related to its *kinetic energy density,* $\rho_k = E_k/V$, the kinetic energy of the molecules in a region divided by the volume of the region, by $p = \frac{2}{3}\rho_k$. (c) What is the kinetic energy density half way to the centre of the Sun? Compare your result with the (translational) kinetic energy density of the Earth's atmosphere on a warm day (25 °C), $1.5 \times 10^5\,\text{J m}^{-3}$ (corresponding to $0.15\,\text{J cm}^{-3}$). (d) A star eventually depletes some of the hydrogen in its core, which contracts and results in higher temperatures. The increased temperature results in an increase in the rates of nuclear reactions, some of which result in the formation of heavier nuclei, such as carbon. The outer part of the star expands and cools to produce a red giant. Assume that halfway to the centre a red giant has a temperature of 3500 K, is composed primarily of fully ionized carbon atoms and electrons, and has a mass density of $1200\,\text{kg m}^{-3}$. What is the pressure at this point? (e) If the red giant in part (d) consisted of neutral carbon atoms, what would be the pressure at the same point under the same conditions?

78.15 The principal components of the atmosphere of the Earth are diatomic molecules, which can rotate as well as translate. Given that the translational kinetic energy density of the atmosphere is $0.15\,\text{J cm}^{-3}$, what is the total kinetic energy density, including rotation?

Topic 79 Transport properties of gases

Discussion questions

79.1 Explain how Fick's first law arises from the concentration gradient of gas molecules.

79.2 Provide molecular interpretations for the dependencies of the diffusion coefficient and the viscosity on the temperature, pressure, and size of gas molecules.

79.3 What might be the effect of molecular interactions on the transport properties of a gas?

Exercises

79.1(a) Calculate the thermal conductivity of argon ($C_{V,\text{m}} = 12.5\,\text{J K}^{-1}\,\text{mol}^{-1}$, $\sigma = 0.36\,\text{nm}^2$) at 298 K.
79.1(b) Calculate the thermal conductivity of nitrogen ($C_{V,\text{m}} = 20.8\,\text{J K}^{-1}\,\text{mol}^{-1}$, $\sigma = 0.43\,\text{nm}^2$) at 298 K.

79.2(a) Calculate the diffusion constant of argon at 20 °C and (a) 1.00 Pa, (b) 100 kPa, (c) 10.0 MPa. If a pressure gradient of $1.0\,\text{bar m}^{-1}$ is established in a pipe, what is the flow of gas due to diffusion?
79.2(b) Calculate the diffusion constant of nitrogen at 20 °C and (a) 100.0 Pa, (b) 100 kPa, (c) 20.0 MPa. If a pressure gradient of $1.20\,\text{bar m}^{-1}$ is established in a pipe, what is the flow of gas due to diffusion?

79.3(a) Calculate the flux of energy arising from a temperature gradient of $10.5\,\text{K m}^{-1}$ in a sample of argon in which the mean temperature is 280 K.
79.3(b) Calculate the flux of energy arising from a temperature gradient of $8.5\,\text{K m}^{-1}$ in a sample of hydrogen in which the mean temperature is 290 K.

79.4(a) Use the experimental value of the thermal conductivity of neon (Table 79.1) to estimate the collision cross-section of Ne atoms at 273 K.
79.4(b) Use the experimental value of the thermal conductivity of nitrogen (Table 79.1) to estimate the collision cross-section of N_2 molecules at 298 K.

79.5(a) In a double-glazed window, the panes of glass are separated by 1.0 cm. What is the rate of transfer of heat by conduction from the warm room (28 °C) to the cold exterior (−15 °C) through a window of area $1.0\,\text{m}^2$? What power of heater is required to make good the loss of heat?
79.5(b) Two sheets of copper of area $2.00\,\text{m}^2$ are separated by 5.00 cm. What is the rate of transfer of heat by conduction from the warm sheet (70 °C) to the cold sheet (0 °C)? What is the rate of loss of heat?

79.6(a) Use the experimental value of the coefficient of viscosity for neon (Table 79.1) to estimate the collision cross-section of Ne atoms at 273 K.
79.6(b) Use the experimental value of the coefficient of viscosity for nitrogen (Table 79.1) to estimate the collision cross-section of the molecules at 273 K.

79.7(a) Calculate the viscosity of air at (a) 273 K, (b) 298 K, (c) 1000 K. Take $\sigma \approx 0.40\,\text{nm}^2$. (The experimental values are 173 μP at 273 K, 182 μP at 20 °C, and 394 μP at 600 °C.)
79.7(b) Calculate the viscosity of benzene vapour at (a) 273 K, (b) 298 K, (c) 1000 K. Take $\sigma \approx 0.88\,\text{nm}^2$.

Problems

79.1‡ Fenghour, et al. (*J. Phys. Chem. Ref. Data* **24**, 1649 (1995)) have compiled an extensive table of viscosity coefficients for ammonia in the liquid and vapour phases. Deduce the effective molecular diameter of NH_3 based on each of the following vapour-phase viscosity coefficients: (a) $\eta = 9.08 \times 10^{-6}\,\text{kg m}^{-1}\,\text{s}^{-1}$ at 270 K and 1.00 bar; (b) $\eta = 1.749 \times 10^{-5}\,\text{kg m}^{-1}\,\text{s}^{-1}$ at 490 K and 10.0 bar.

79.2 Calculate the ratio of the thermal conductivities of gaseous hydrogen at 300 K to gaseous hydrogen at 10 K. Be circumspect, and think about the modes of motion that are thermally active at the two temperatures.

79.3 Interstellar space is quite a different medium than the gaseous environments we commonly encounter on Earth. For instance, a typical density of the medium is about $1\,\text{atom cm}^{-3}$ and that atom is typically H; the effective temperature due to stellar background radiation is about 10 kK. Estimate the diffusion coefficient and thermal conductivity of H under these conditions. *Comment*: Energy is in fact transferred much more effectively by radiation.

Topic 80 Motion in liquids

Discussion questions

80.1 Discuss the difference between the hydrodynamic radius of an ion and its ionic radius and explain why a small ion can have a large hydrodynamic radius.

80.2 Discuss the mechanism of proton conduction in water. How could the model be tested?

80.3 Why is a proton less mobile in liquid ammonia than in water?

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‡ These problems were supplied by Charles Trapp and Carmen Giunta.

Exercises

80.1(a) The viscosity of water at 20 °C is 1.002 cP and 0.7975 cP at 30 °C. What is the energy of activation for the transport process?
80.1(b) The viscosity of mercury at 20 °C is 1.554 cP and 1.450 cP at 40 °C. What is the energy of activation for the transport process?

80.2(a) The mobility of a chloride ion in aqueous solution at 25 °C is $7.91\times10^{-8}\,\mathrm{m^2\,s^{-1}\,V^{-1}}$. Calculate the molar ionic conductivity.
80.2(b) The mobility of an acetate ion in aqueous solution at 25 °C is $4.24\times10^{-8}\,\mathrm{m^2\,s^{-1}\,V^{-1}}$. Calculate the molar ionic conductivity.

80.3(a) The mobility of a $\mathrm{Rb^+}$ ion in aqueous solution is $7.92\times10^{-8}\,\mathrm{m^2\,s^{-1}\,V^{-1}}$ at 25 °C. The potential difference between two electrodes placed in the solution is 25.0 V. If the electrodes are 7.00 mm apart, what is the drift speed of the $\mathrm{Rb^+}$ ion?
80.3(b) The mobility of a $\mathrm{Li^+}$ ion in aqueous solution is $4.01\times10^{-8}\,\mathrm{m^2\,s^{-1}\,V^{-1}}$ at 25 °C. The potential difference between two electrodes placed in the solution is 24.0 V. If the electrodes are 5.0 mm apart, what is the drift speed of the ion?

80.4(a) The limiting molar conductivities of NaI, $\mathrm{NaNO_3}$, and $\mathrm{AgNO_3}$ are $12.69\,\mathrm{mS\,m^2\,mol^{-1}}$, $12.16\,\mathrm{mS\,m^2\,mol^{-1}}$, and $13.34\,\mathrm{mS\,m^2\,mol^{-1}}$, respectively (all at 25 °C). What is the limiting molar conductivity of AgI at this temperature?
80.4(b) The limiting molar conductivities of KF, $\mathrm{KCH_3CO_2}$, and $\mathrm{Mg(CH_3CO_2)_2}$ are $12.89\,\mathrm{mS\,m^2\,mol^{-1}}$, $11.44\,\mathrm{mS\,m^2\,mol^{-1}}$, and $18.78\,\mathrm{mS\,m^2\,mol^{-1}}$, respectively (all at 25 °C). What is the limiting molar conductivity of $\mathrm{MgF_2}$ at this temperature?

80.5(a) At 25 °C the molar ionic conductivities of $\mathrm{Li^+}$, $\mathrm{Na^+}$, and $\mathrm{K^+}$ are $3.87\,\mathrm{mS\,m^2\,mol^{-1}}$, $5.01\,\mathrm{mS\,m^2\,mol^{-1}}$, and $7.35\,\mathrm{mS\,m^2\,mol^{-1}}$, respectively. What are their mobilities?
80.5(b) At 25 °C the molar ionic conductivities of $\mathrm{F^-}$, $\mathrm{Cl^-}$, and $\mathrm{Br^-}$ are $5.54\,\mathrm{mS\,m^2\,mol^{-1}}$, $7.635\,\mathrm{mS\,m^2\,mol^{-1}}$, and $7.81\,\mathrm{mS\,m^2\,mol^{-1}}$, respectively. What are their mobilities?

80.6(a) Estimate the effective radius of a sucrose molecule in water at 25 °C given that its diffusion coefficient is $5.2\times10^{-10}\,\mathrm{m^2\,s^{-1}}$ and that the viscosity of water is 1.00 cP.
80.6(b) Estimate the effective radius of a glycine molecule in water at 25 °C given that its diffusion coefficient is $1.055\times10^{-9}\,\mathrm{m^2\,s^{-1}}$ and that the viscosity of water is 1.00 cP.

Problems

80.1 The viscosity of benzene varies with temperature as shown in the following table. Use the data to infer the activation energy for viscosity (the parameter E_a in eqn 80.2).

θ/°C	10	20	30	40	50	60	70
η/cP	0.758	0.652	0.564	0.503	0.442	0.392	0.358

80.2 An empirical expression that reproduces the viscosity of water in the range 20–100 °C is

$$\log\frac{\eta}{\eta_{20}}=\frac{1.3272(20-\theta/{}^\circ\mathrm{C})-0.001053(20-\theta/{}^\circ\mathrm{C})^2}{\theta/{}^\circ\mathrm{C}+105}$$

where η_{20} is the viscosity at 20 °C. Explore (by using mathematical software) the possibility of fitting an exponential curve to this expression and hence identify an activation energy for the viscosity. This approach is taken further in Problem 80.10.

80.3 The conductivity of aqueous ammonium chloride at a series of concentrations is listed in the following table. Deduce the molar conductivity and determine the parameters that occur in Kohlrausch's law.

$c/(\mathrm{mol\,dm^{-3}})$	1.334	1.432	1.529	1.672	1.725
$\kappa/(\mathrm{mS\,cm^{-1}})$	131	139	147	156	164

80.4 Conductivities are often measured by comparing the resistance of a cell filled with the sample to its resistance when filled with some standard solution, such as aqueous potassium chloride. The conductivity of water is $76\,\mathrm{mS\,m^{-1}}$ at 25 °C and the conductivity of $0.100\,\mathrm{mol\,dm^{-3}}$ KCl(aq) is $1.1639\,\mathrm{S\,m^{-1}}$. A cell had a resistance of 33.21 Ω when filled with $0.100\,\mathrm{mol\,dm^{-3}}$ KCl(aq) and 300.0 Ω when filled with $0.100\,\mathrm{mol\,dm^{-3}}$ $\mathrm{CH_3COOH}$(aq). What is the molar conductivity of acetic acid at that concentration and temperature?

80.5 The resistances of a series of aqueous NaCl solutions, formed by successive dilution of a sample, were measured in a cell with cell constant (the constant C in the relation $\kappa = C/R$) equal to $0.2063\,\mathrm{cm^{-1}}$. The following values were found:

$c/(\mathrm{mol\,dm^{-3}})$	0.00050	0.0010	0.0050	0.010	0.020	0.050
R/Ω	3314	1669	342.1	174.1	89.08	37.14

Verify that the molar conductivity follows the Kohlrausch law and find the limiting molar conductivity. Determine the coefficient $\mathcal{K}$. Use the value of $\mathcal{K}$ (which should depend only on the nature, not the identity, of the ions) and the information that $\lambda(\mathrm{Na^+}) = 5.01\,\mathrm{mS\,m^2\,mol^{-1}}$ and $\lambda(\mathrm{I^-}) = 7.68\,\mathrm{mS\,m^2\,mol^{-1}}$ to predict (a) the molar conductivity, (b) the conductivity, (c) the resistance it would show in the cell of $0.010\,\mathrm{mol\,dm^{-3}}$ NaI(aq) at 25 °C.

80.6 What are the drift speeds of $\mathrm{Li^+}$, $\mathrm{Na^+}$, and $\mathrm{K^+}$ in water when a potential difference of 100 V is applied across a 5.00 cm conductivity cell? How long would it take an ion to move from one electrode to the other? In conductivity measurements it is normal to use alternating current: what are the displacements of the ions in (a) centimetres, (b) solvent diameters (about 300 pm) during a half-cycle of 2.0 kHz applied potential difference?

80.7‡ Bakale, et al. (*J. Phys. Chem.* **100**, 12477 (1996)) measured the mobility of singly charged $\mathrm{C_{60}^-}$ ions in a variety of nonpolar solvents. In cyclohexane at 22 °C, the mobility is $1.1\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. Estimate the effective radius of the $\mathrm{C_{60}^-}$ ion. The viscosity of the solvent is $0.93\times10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}$. Suggest a reason why there is a substantial difference between this number and the van der Waals radius of neutral $\mathrm{C_{60}}$.

80.8 Estimate the diffusion coefficients and the effective hydrodynamic radii of the alkali metal cations in water from their mobilities at 25 °C. Estimate the approximate number of water molecules that are dragged along by the cations. Ionic radii are given Table 38.2.

80.9 Nuclear magnetic resonance can be used to determine the mobility of molecules in liquids. A set of measurements on methane in carbon tetrachloride showed that its diffusion coefficient is $2.05\times10^{-9}\,\mathrm{m^2\,s^{-1}}$ at 0 °C and $2.89\times10^{-9}\,\mathrm{m^2\,s^{-1}}$ at 25 °C. Deduce what information you can about the mobility of methane in carbon tetrachloride.

80.10 In Topic 85 it is shown that a general expression for the activation energy of a chemical reaction is $E_a = RT^2(\mathrm{d}\ln k/\mathrm{d}T)$. Confirm that the same expression may be used to extract the activation energy from eqn 80.2 for the viscosity and then apply the expression to deduce the temperature dependence of the activation energy when the viscosity of water is given by the empirical expression in Problem 80.2. Plot this activation energy as a function of temperature. Suggest an explanation of the temperature dependence of E_a.

Topic 81 Diffusion

Discussion questions

81.1 Describe the origin of the thermodynamic force. To what extent can it be regarded as an actual force?

81.2 Account physically for the form of the diffusion equation.

Exercises

81.1(a) The diffusion coefficient of glucose in water at 25 °C is $6.73\times10^{-10}\,\mathrm{m^2\,s^{-1}}$. Estimate the time required for a glucose molecule to undergo a root mean square displacement of 5.0 mm.

81.1(b) The diffusion coefficient of H_2O in water at 25 °C is $2.26\times10^{-9}\,\mathrm{m^2\,s^{-1}}$. Estimate the time required for an H_2O molecule to undergo a root mean square displacement of 1.0 cm.

81.2(a) A layer of 20.0 g of sucrose is spread uniformly over a surface of area 5.0 cm² and covered in water to a depth of 20 cm. What will be the molar concentration of sucrose molecules at 10 cm above the original layer at (a) 10 s, (b) 24 h? Assume diffusion is the only transport process and take $D = 5.216\times10^{-9}\,\mathrm{m^2\,s^{-1}}$.

81.2(b) A layer of 10.0 g of iodine is spread uniformly over a surface of area 10.0 cm² and covered in hexane to a depth of 10 cm. What will be the molar concentration of sucrose molecules at 5.0 cm above the original layer at (a) 10 s, (b) 24 h? Assume diffusion is the only transport process and take $D = 4.05\times10^{-9}\,\mathrm{m^2\,s^{-1}}$.

Problems

81.1 A dilute solution of potassium permanganate in water at 25 °C was prepared. The solution was in a horizontal tube of length 10 cm, and at first there was a linear gradation of intensity of the purple solution from the left (where the concentration was $0.100\,\mathrm{mol\,dm^{-3}}$) to the right (where the concentration was $0.050\,\mathrm{mol\,dm^{-3}}$). What is the magnitude and sign of the thermodynamic force acting on the solute (a) close to the left face of the container, (b) in the middle, (c) close to the right face? Give the force per mole and force per molecule in each case.

81.2 A dilute solution of potassium permanganate in water at 25 °C was prepared. The solution was in a horizontal tube of length 10 cm, and at first there was a Gaussian distribution of concentration around the centre of the tube at $x = 0$, $c(x) = c_0\mathrm{e}^{-ax^2}$, with $c_0 = 0.100\,\mathrm{mol\,dm^{-3}}$ and $a = 0.10\,\mathrm{cm^{-2}}$. Determine the thermodynamic force acting on the solute as a function of location, x, and plot the result. Give the force per mole and force per molecule in each case. What do you expect to be the consequence of the thermodynamic force?

81.3 Instead of a Gaussian 'heap' of solute, as in Problem 81.2, suppose that there is a Gaussian dip, a distribution of the form $c(x) = c_0(1-\mathrm{e}^{-ax^2})$. Repeat the calculation in Problem 81.2 and its consequences.

81.4 A lump of sucrose of mass 10.0 g is suspended in the middle of a spherical flask of water of radius 10 cm at 25 °C. What is the concentration of sucrose at the wall of the flask after (a) 1.0 h, (b) 1.0 week? Take $D = 5.22\times10^{-10}\,\mathrm{m^2\,s^{-1}}$.

81.5 Confirm that eqn 81.11 is a solution of the diffusion equation with the correct initial value.

81.6 Confirm that

$$c(x,t) = \frac{c_0}{(4\pi Dt)^{1/2}}\,\mathrm{e}^{-(x-x_0-vt)^2/4Dt}$$

is a solution of the diffusion equation with convection (eqn 81.10) with all the solute concentrated at $x = x_0$ at $t = 0$ and plot the concentration profile at a series of times to show how the distribution spreads and its centroid drifts.

81.7 The thermodynamic force has a direction as well as a magnitude, and in a three-dimensional ideal system eqn 81.2 becomes $\mathcal{F} = -RT\nabla(\ln c)$. What is the thermodynamic force acting to bring about the diffusion summarized by eqn 81.12 (that of a solute initially suspended at the centre of a flask of solvent)? *Hint*: Use $\nabla = \boldsymbol{i}\partial/\partial x + \boldsymbol{j}\partial/\partial y + \boldsymbol{k}\partial/\partial z$.

81.8 The diffusion equation is valid when many elementary steps are taken in the time interval of interest, but the random walk calculation lets us discuss distributions for short times as well as for long. Use eqn 81.15 to calculate the probability of being six paces from the origin (that is, at $x = 6\lambda$) after (a) four, (b) six, (c) twelve steps.

81.9 Use mathematical software to calculate P in a one-dimensional random walk, and evaluate the probability of being at $x = n\lambda$ for $n = 6, 10, 14, \ldots, 60$. Compare the numerical value with the analytical value in the limit of a large number of steps. At what value of n is the discrepancy no more than 0.1 per cent?

81.10 Supply the intermediate mathematical steps in *Justification* 81.2.

81.11 The diffusion coefficient of a particular kind of t-RNA molecule is $D = 1.0\times10^{-11}\,\mathrm{m^2\,s^{-1}}$ in the medium of a cell interior. How long does it take molecules produced in the cell nucleus to reach the walls of the cell at a distance 1.0 μm, corresponding to the radius of the cell?

81.12‡ In this problem, we examine a model for the transport of oxygen from air in the lungs to blood. First, show that, for the initial and boundary conditions $c(x,t) = c(x,0) = c_\mathrm{o}$ $(0 < x < \infty)$ and $c(0,t) = c_\mathrm{s}$ $(0 \le t \le \infty)$, where c_o and c_s are constants, the concentration, $c(x,t)$, of a species is given by

$$c(x,t) = c_\mathrm{o} + (c_\mathrm{s} - c_\mathrm{o})\{1 - \mathrm{erf}(\xi)\} \qquad \xi(x,t) = \frac{x}{(4Dt)^{1/2}}$$

where $\mathrm{erf}(\xi)$ is the error function (see Integral G.6 in the *Resource section*) and the concentration $c(x,t)$ evolves by diffusion from the yz-plane of constant concentration, such as might occur if a condensed phase is absorbing a species from a gas phase. Now draw graphs of concentration profiles at several different times of your choice for the diffusion of oxygen into water at 298 K (when $D = 2.10\times10^{-9}\,\mathrm{m^2\,s^{-1}}$) on a spatial scale comparable to passage of oxygen from lungs through alveoli into the blood. Use $c_\mathrm{o} = 0$ and set c_s equal to the solubility of oxygen in water. *Hint*: Use mathematical software.

81.13 Derive eqn 81.17c for the mean radius reached in a random walk in three dimensions. Use eqn 81.12 and an argument similar to that presented in Example 81.1.

Integrated activities

F16.1 In a series of observations on the displacement of rubber latex spheres of radius 0.212 μm, the mean square displacements after selected time intervals were on average as follows:

t/s	30	60	90	120
$10^{12}\langle x^2\rangle/\text{m}^2$	88.2	113.5	128	144

These results were originally used to find the value of Avogadro's constant, but there are now better ways of determining N_A, so the data can be used to find another quantity. Find the effective viscosity of water at the temperature of this experiment (25 °C).

F16.2 Use mathematical software, a spreadsheet, or the *Living graphs* (labelled $^{\text{LG}}$) on the website of this book to carry out the following exercises:

(a) $^{\text{LG}}$ Refer to Fig. 78.4. Plot different distributions by keeping the molar mass constant at 100 g mol^{-1} and varying the temperature of the sample between 200 K and 2000 K.
(b) Evaluate numerically the fraction of molecules with speeds in the range 100 m s^{-1} to 200 m s^{-1} at 300 K and 1000 K. Based on your observations, provide a molecular interpretation of temperature.
(c) Generate a family of curves similar to that shown in Fig. 81.3 but by using eqn 81.12, which describes diffusion in three dimensions.

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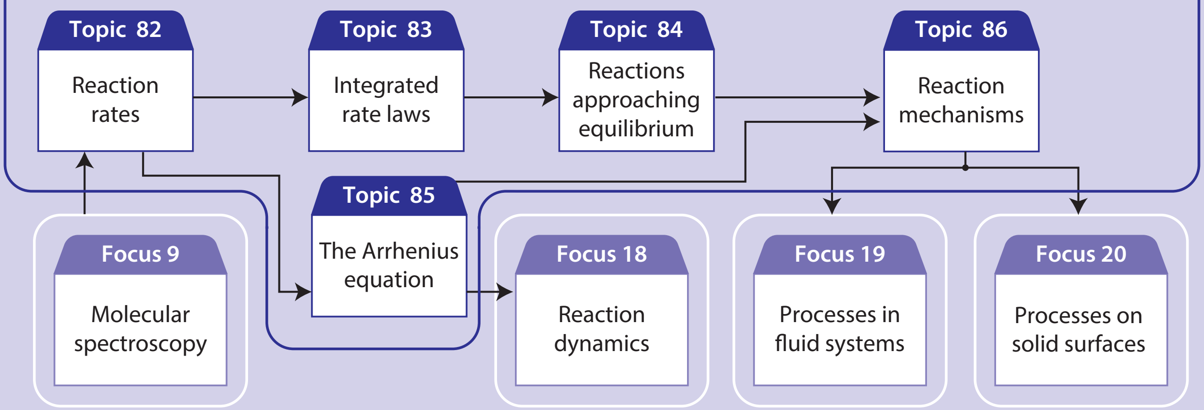
FOCUS 17 ON Chemical kinetics



'Chemical kinetics' is the study of reaction rates. The rate of a chemical reaction might depend on variables under our control, such as the pressure, the temperature, and the presence of a catalyst, and we may be able to optimize the rate by the appropriate choice of conditions. Here we begin to see how such manipulations are possible, preparing us for the study of more complicated or more specialized cases.

Topic 82 discusses the definition of reaction rate and outlines the techniques for its measurement with tools from *Molecular spectroscopy*. The results of such measurements show that reaction rates depend on the concentration of reactants (and products) and 'rate constants' that are characteristic of the reaction. This dependence can be expressed in terms of differential equations known as 'rate laws'.

'Integrated rate laws' are the solutions of the rate laws and give concentrations as a function of time (**Topic 83**). We explore simple yet very useful integrated rate laws that appear throughout this group of Topics. An important case is the inclusion of both the forward and reverse reactions, giving rise to expressions that describe the approach to equilibrium, when the forward and reverse rates are equal (**Topic 84**). A result of this analysis is a useful relation between the equilibrium constant of the overall process and the rate constants of the forward and reverse reactions in the proposed mechanism.

The rate constants of most reactions increase with increasing temperature. We see that the 'Arrhenius equation' captures this empirically determined temperature dependence by using only two parameters (**Topic 85**). This equation is developed theoretically in our discussion of *Reaction dynamics*.

The study of reaction rates also leads to an understanding of the 'mechanisms' of reactions, their analysis into a sequence of 'elementary steps' (**Topic 86**). Here we see how to construct rate laws from a proposed mechanism. The elementary steps themselves have simple rate laws which can be combined by invoking the concept of the 'rate-determining step' of a reaction or either making the 'steady-state approximation' or assuming the existence of a 'pre-equilibrium'. The stage is now set for detailed study of *Processes in fluid systems* and *Processes on solid surfaces*.

What is the impact of this material?

Synthetic polymers, such as nylon and polystyrene, are manufactured by stringing together and in some cases cross-linking smaller units known as 'monomers'. In *Impact* 17.1 we explore the formation of polymers and show how the kinetics of their formation affects their properties and through those properties their technological applications.

To read more about the impact of this material, scan the QR code or go to http://bcs.whfreeman.com/webpub/chemistry/qmc2e/impact/qchem_impact17.html.

TOPIC 82

Reaction rates

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➤ **Why do you need to know this material?**

Studies of the rates of disappearance of reactants and appearance of products allow us to predict how quickly a reaction mixture approaches equilibrium. Furthermore, studies of reaction rates lead to detailed descriptions of the molecular events that transform reactants into products.

➤ **What is the key idea?**

Reaction rates can be expressed mathematically in terms of the concentrations of reactants and, in some cases, products.

➤ **What do you need to know already?**

To understand the experimental techniques used to study the progress of chemical reactions, you should review the basic concepts of spectroscopy (Topic 40).

This Topic introduces the principles of **chemical kinetics**, the study of reaction rates, by showing how the rates of reactions may be measured and interpreted. The results of such measurements show that reaction rates depend on the concentration of reactants (and products) in characteristic ways that can be expressed in terms of differential equations known as rate laws.

82.1 Monitoring the progress of a reaction

The first steps in the kinetic analysis of reactions are to establish the stoichiometry of the reaction and identify any side reactions. The basic data of chemical kinetics are then the concentrations of the reactants and products at different times after a reaction has been initiated.

(a) General considerations

The rates of most chemical reactions are sensitive to the temperature, so in conventional experiments the temperature of the reaction mixture must be held constant throughout the course of the reaction. This requirement puts severe demands on the design of an experiment. Gas-phase reactions, for instance, are often carried out in a vessel held in contact with a substantial block of metal. Liquid-phase reactions, including flow reactions, must be carried out in an efficient thermostat. Special efforts have to be made to study reactions at low temperatures, as in the study of the kinds of reactions that take place in interstellar clouds. Thus, supersonic expansion of the reaction gas can be used to attain temperatures as low as 10 K. For work in the liquid phase and the solid phase, very low temperatures are often reached by flowing cold liquid or cold gas around the reaction vessel. Alternatively, the entire reaction vessel is immersed in a thermally insulated container filled with a cryogenic liquid, such as liquid helium (for work at around 4 K) or liquid nitrogen (for work at around 77 K). Non-isothermal conditions are sometimes employed. For instance, the shelf-life of an expensive pharmaceutical may be explored by slowly raising the temperature of a single sample.

Spectroscopy is widely applicable to the study of reaction kinetics, and is especially useful when one substance in the reaction mixture has a strong characteristic absorption in a conveniently accessible region of the electromagnetic spectrum. For example, the progress of the reaction $H_2(g)+Br_2(g)\rightarrow 2\,HBr(g)$ can be followed by measuring the absorption of visible light by bromine. A reaction that changes the number or type of ions present in a solution may be followed by monitoring the electrical conductivity of the solution. The replacement of neutral molecules by ionic products can result in dramatic changes in the conductivity, as in the reaction $(CH_3)_3CCl(aq)+H_2O(l)\rightarrow(CH_3)_3COH(aq)+H^+(aq)+Cl^-(aq)$. If hydrogen ions are produced or consumed, the reaction may be followed by monitoring the pH of the solution.

Other methods of determining composition include emission spectroscopy (Topic 46), mass spectrometry, gas chromatography, nuclear magnetic resonance (Topics 47–49), and electron paramagnetic resonance (for reactions involving radicals or paramagnetic d-metal ions; see Topic 50).

A reaction in which at least one component is a gas might result in an overall change in pressure in a system of constant volume, so its progress may be followed by recording the variation of pressure with time.

Example 82.1 Monitoring the variation in pressure

Predict how the total pressure varies during the gas-phase decomposition $2\,N_2O_5(g)\rightarrow 4\,NO_2(g)+O_2(g)$ in a constant-volume container.

Method The total pressure (at constant volume and temperature and assuming perfect gas behaviour) is proportional to the number of gas-phase molecules. Therefore, because each mole of N_2O_5 gives rise to $\frac{5}{2}$ mol of gas molecules, we can expect the pressure to rise to $\frac{5}{2}$ times its initial value. To confirm this conclusion, express the progress of the reaction in terms of the fraction, α, of N_2O_5 molecules that have reacted.

Answer Let the initial pressure be p_0 and the initial amount of N_2O_5 molecules present be n. When a fraction α of the N_2O_5 molecules has decomposed, the amounts of the components in the reaction mixture are:

	N_2O_5	NO_2	O_2	Total
Amount:	$n(1-\alpha)$	$2\alpha n$	$\frac{1}{2}\alpha n$	$n\left(1+\frac{3}{2}\alpha\right)$

When $\alpha=0$ the pressure is p_0, so at any stage the total pressure is

$$p=\left(1+\frac{3}{2}\alpha\right)p_0$$

When the reaction is complete, the pressure will have risen to $\frac{5}{2}$ times its initial value.

Self-test 82.1 Repeat the calculation in Example 82.1 for $2\,NOBr(g)\rightarrow 2\,NO(g)+Br_2(g)$.

Answer: $p=\left(1+\frac{1}{2}\alpha\right)p_0$

(b) Special techniques

The method used to monitor concentrations depends on the species involved and the rapidity with which their concentrations change. Many reactions reach equilibrium over periods of minutes or hours, and several techniques may then be used to follow the changing concentrations. In a **real-time analysis** the composition of the system is analysed while the reaction is in progress. Either a small sample is withdrawn or the bulk solution is monitored. In the **flow method** the reactants are mixed as they flow together in a chamber (Fig. 82.1). The reaction continues as the thoroughly mixed solutions flow through the outlet tube, and observation of the composition at different positions along the tube is equivalent to the observation of the reaction mixture at different times after mixing. The disadvantage of conventional flow techniques is that a large volume of reactant solution is necessary. This makes the study of fast reactions particularly difficult because to spread the reaction over a length of tube the flow must be rapid. This disadvantage is avoided by the **stopped-flow technique**, in which the reagents are mixed very quickly in a small chamber fitted with a syringe instead of an outlet tube (Fig. 82.2). The flow ceases when the plunger of the syringe reaches a stop, and the reaction continues in the mixed solutions. Observations, commonly using spectroscopic techniques such as ultraviolet–visible absorption and fluorescence emission (all introduced in Topics 40, 45, and 46), are made on the sample as a function of time. The technique allows for the study of reactions that occur on the millisecond to second timescale. The suitability of the stopped-flow

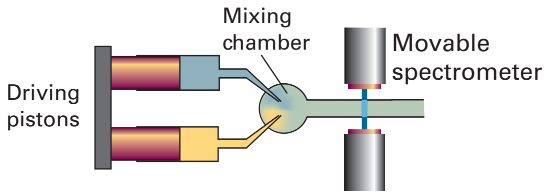

Figure 82.1 The arrangement used in the flow technique for studying reaction rates. The reactants are injected into the mixing chamber at a steady rate. The location of the spectrometer corresponds to different times after initiation.

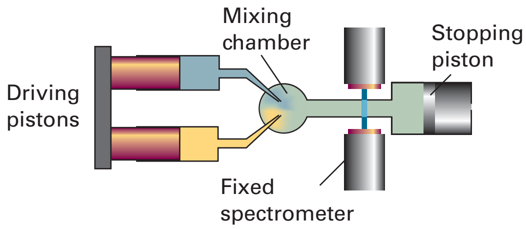

Figure 82.2 In the stopped-flow technique the reagents are driven quickly into the mixing chamber by the driving pistons and then the time dependence of the concentrations is monitored.

method to the study of small samples means that it is appropriate for many biochemical reactions, and it has been widely used to study the kinetics of protein folding and enzyme action.

Very fast reactions can be studied by **flash photolysis**, in which the sample is exposed to a brief flash of light that initiates the reaction and then the contents of the reaction chamber are monitored. The apparatus used for flash photolysis studies is based on the experimental design for time-resolved spectroscopy, in which reactions occurring on a picosecond or femtosecond timescale may be monitored by using electronic absorption or emission, infrared absorption, or Raman scattering (Topic 40).

In contrast to real-time analysis, **quenching methods** are based on stopping, or quenching, the reaction after it has been allowed to proceed for a certain time. In this way the composition is analysed at leisure and reaction intermediates may be trapped. These methods are suitable only for reactions that are slow enough for there to be little reaction during the time it takes to quench the mixture. In the **chemical quench flow method**, the reactants are mixed in much the same way as in the flow method but the reaction is quenched by another reagent, such as a solution of acid or base, after the mixture has travelled along a fixed length of the outlet tube. Different reaction times can be selected by varying the flow rate along the outlet tube. An advantage of the chemical quench flow method over the stopped-flow method is that spectroscopic fingerprints are not needed in order to measure the concentration of reactants and products. Once the reaction has been quenched, the solution may be examined by 'slow' techniques, such as gel electrophoresis, mass spectrometry, and chromatography. In the **freeze–quench method**, the reaction is quenched by cooling the mixture within milliseconds, with the concentrations of reactants, intermediates, and products measured spectroscopically.

82.2 The rates of reactions

Reaction rates depend on the composition and the temperature of the reaction mixture. The next few sections look at these observations in more detail.

(a) The definition of rate

Consider a reaction of the form $A+2\,B\rightarrow 3\,C+D$, in which at some instant the molar concentration of a participant J is [J] and the volume of the system is constant. The instantaneous **rate of consumption** of one of the reactants at a given time is $-d[R]/dt$, where R is A or B. This rate is a positive quantity (Fig. 82.3). The **rate of formation** of one of the products (C or D, which we denote P) is $d[P]/dt$ (note the difference in sign). This rate is also positive.

It follows from the stoichiometry of the reaction $A+2\,B\rightarrow 3\,C+D$ that

$$\frac{d[D]}{dt}=\frac{1}{3}\frac{d[C]}{dt}=-\frac{d[A]}{dt}=-\frac{1}{2}\frac{d[B]}{dt}$$

so there are several rates connected with the reaction. The undesirability of having different rates to describe the same reaction is avoided by using the extent of reaction, ξ (xi, the quantity introduced in Topic 73),

$$\xi=\frac{n_J-n_{J,0}}{\nu_J} \qquad \textit{Definition} \quad \text{Extent of reaction} \qquad (82.1)$$

where ν_J is the stoichiometric number of species J (Topic73), and defining the unique **rate of reaction**, v, as the rate of change of the extent of reaction:

$$v=\frac{1}{V}\frac{d\xi}{dt} \qquad \textit{Definition} \quad \text{Rate of reaction} \qquad (82.2)$$

where V is the volume of the system. It follows that

$$v=\frac{1}{\nu_J}\times\frac{1}{V}\frac{dn_J}{dt} \qquad (82.3a)$$

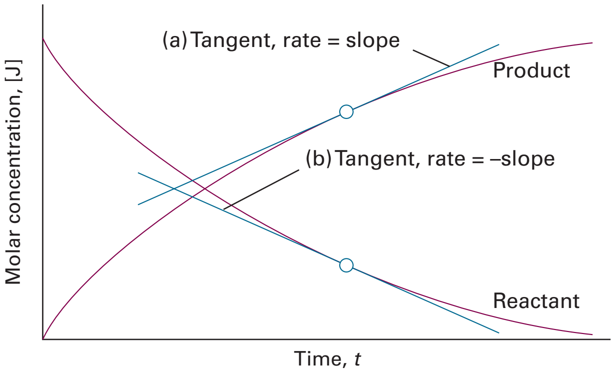

Figure 82.3 The definition of (instantaneous) rate as the slope of the tangent drawn to the curve showing the variation of concentration of (a) products, (b) reactants with time. For negative slopes, the sign is changed when reporting the rate, so all reaction rates are positive.

(Remember that ν_J is negative for reactants and positive for products.) For a homogeneous reaction in a constant-volume system the volume V can be taken inside the differential and we use $[J]=n_J/V$ to write

$$v=\frac{1}{\nu_J}\frac{d[J]}{dt} \tag{82.3b}$$

For a heterogeneous reaction, we use the (constant) surface area, A, occupied by the species in place of V and use $\sigma_J=n_J/A$ to write

$$v=\frac{1}{\nu_J}\frac{d\sigma_J}{dt} \tag{82.3c}$$

In each case there is now a single rate for the entire reaction (for the chemical equation as written). With molar concentrations in moles per cubic decimetre and time in seconds, reaction rates of homogeneous reactions are reported in moles per cubic decimetre per second (mol dm^{-3} s^{-1}) or related units. For gas-phase reactions, such as those taking place in the atmosphere, concentrations are often expressed in molecules per cubic centimetre (molecules cm^{-3}) and rates in molecules per cubic centimetre per second (molecules cm^{-3} s^{-1}). For heterogeneous reactions, rates are expressed in moles per square metre per second (mol m^{-2} s^{-1}) or related units.

Brief illustration 82.1 Reaction rates from balanced chemical equations

If the rate of formation of NO in the reaction $2\,\mathrm{NOBr(g)}\rightarrow 2\,\mathrm{NO(g)}+\mathrm{Br_2(g)}$ is reported as 0.16 mmol dm^{-3} s^{-1}, we use $\nu_{NO}=+2$ to report that $v=0.080$ mmol dm^{-3} s^{-1}. Because $\nu_{NOBr}=-2$ it follows that $d[NOBr]/dt=-0.16$ mmol dm^{-3} s^{-1}. The rate of consumption of NOBr is therefore 0.16 mmol dm^{-3} s^{-1}, or 9.6×10^{16} molecules cm^{-3} s^{-1}.

Self-test 82.2 The rate of change of molar concentration of CH_3 radicals in the reaction $2\,\mathrm{CH_3(g)}\rightarrow \mathrm{CH_3CH_3(g)}$ was reported as $d[CH_3]/dt=-1.2$ mol dm^{-3} s^{-1} under particular conditions. What is (a) the rate of reaction and (b) the rate of formation of CH_3CH_3?

Answer: (a) 0.60 mol dm^{-3} s^{-1}, (b) 0.60 mol dm^{-3} s^{-1}

(b) Rate laws and rate constants

The rate of reaction is often found to be proportional to the concentrations of the reactants raised to a power. For example, the rate of a reaction may be proportional to the molar concentrations of two reactants A and B, so we write

$$v=k_r[A][B] \tag{82.4}$$

with each concentration raised to the first power. The coefficient k_r is called the **rate constant** for the reaction. The rate constant is independent of the concentrations but depends on the temperature. An experimentally determined equation of this kind is called the **rate law** of the reaction. More formally, a rate law is an equation that expresses the rate of reaction as a function of the concentrations of all the species present in the overall chemical equation for the reaction at some time:

$$v=f([A],[B],\ldots) \tag{82.5a}$$

General form Rate law in terms of concentrations

For homogeneous gas-phase reactions, it is often more convenient to express the rate law in terms of partial pressures, which are related to molar concentrations by $p_J=RT[J]$. In this case, we write

$$v=f(p_A,p_B,\ldots) \tag{82.5b}$$

General form Rate law in terms of partial pressures

The rate law of a reaction is determined experimentally, and cannot in general be inferred from the chemical equation for the reaction. The reaction of hydrogen and bromine, for example, has a very simple stoichiometry, $\mathrm{H_2(g)}+\mathrm{Br_2(g)}\rightarrow 2\,\mathrm{HBr(g)}$, but its rate law is complicated:

$$v=\frac{k_a[H_2][Br_2]^{3/2}}{[Br_2]+k_b[HBr]} \tag{82.6}$$

In certain cases the rate law does reflect the stoichiometry of the reaction, but that is either a coincidence or reflects a feature of the underlying reaction mechanism (see Topic 86).

> *A note on good (or, at least, our) practice* We denote a general rate constant k_r to distinguish it from the Boltzmann constant k. In some texts k is used for the former and k_B for the latter. When expressing the rate constants in a more complicated rate law, such as that in eqn 82.6, we use k_a, k_b, and so on.

The units of k_r are always such as to convert the product of concentrations into a rate expressed as a change in concentration divided by time. For example, if the rate law is the one shown in eqn 82.4, with concentrations expressed in mol dm^{-3}, then the units of k_r will be dm^3 mol^{-1} s^{-1} because

$$\mathrm{dm^3\,mol^{-1}\,s^{-1}\times mol\,dm^{-3}\times mol\,dm^{-3}=mol\,dm^{-3}\,s^{-1}}$$

In gas-phase studies, including studies of the processes taking place in the atmosphere, concentrations are commonly expressed in molecules cm^{-3}, so the rate constant for the reaction above would be expressed in cm^3 molecule^{-1} s^{-1}. We can use the approach just developed to determine the units of the rate constant from rate laws of any form. For example, the rate constant for a reaction with rate law of the form $k_r[A]$ is commonly expressed in s^{-1}.

Brief illustration 82.2 Rate constants with different units

The rate constant for the reaction $O(g) + O_3(g) \rightarrow 2\ O_2(g)$ is 8.0×10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K. To express this rate constant in dm^3 mol^{-1} s^{-1}, we make use of the two relations 1 cm = 10^{-1} dm and 1 molecule = (1 mol)/(6.022×10^{23}). It follows that

$$\begin{aligned}k_r &= 8.0\times10^{-15}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}\\ &= 8.0\times10^{-15}(10^{-1}\,\text{dm})^3\left(\frac{1\,\text{mol}}{6.022\times10^{23}}\right)^{-1}\text{s}^{-1}\\ &= 8.0\times10^{-15}\times10^{-3}\times6.022\times10^{23}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}\\ &= 4.8\times10^{6}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}\end{aligned}$$

Self-test 82.3 A reaction has a rate law of the form $k_r[A]^2[B]$. What are the units of the rate constant if the reaction rate is measured in mol dm^{-3} s^{-1}?

Answer: dm^6 mol^{-2} s^{-1}

A practical application of a rate law is that once we know the law and the value of the rate constant, we can predict the rate of reaction from the composition of the mixture. As we shall see later, by knowing the rate law, we can go on to predict the composition of the reaction mixture at a later stage of the reaction. Moreover, a rate law is a guide to the mechanism of the reaction (Topic 86), for any proposed mechanism must be consistent with the observed rate law.

(c) Reaction order

Many reactions are found to have rate laws of the form

$$v = k_r[A]^a[B]^b\cdots \tag{82.7}$$

The power to which the concentration of a species (a product or a reactant) is raised in a rate law of this kind is the **order** of the reaction with respect to that species. A reaction with the rate law in eqn 82.4 is first-order in A and first-order in B. The **overall order** of a reaction with a rate law like that in eqn 82.7 is the sum of the individual orders, $a+b+\cdots$. The rate law in eqn 82.4 is therefore second-order overall.

A reaction need not have an integral order, and many gas-phase reactions do not. For example, a reaction having the rate law

$$v = k_r[A]^{1/2}[B] \tag{82.8}$$

is half-order in A, first-order in B, and three-halves-order overall. If a reaction rate is independent of the concentration of one of the reactants, then we say that it is **zeroth-order** in that reactant (because $[J]^0=1$, independent of the value of [J], just as $x^0=1$).

Brief illustration 82.3 Rate laws

The reduction of nitrogen dioxide by carbon monoxide

$$NO_2(g)+CO(g)\rightarrow NO(g)+CO_2(g)$$

has the rate law $v=k_r[NO_2]^2$, which is second-order in NO_2 and, because no other species occurs in the rate law, second-order overall. The rate of this reaction is independent of the concentration of CO provided that some CO is present, so it is zeroth-order in CO. The experimentally determined rate law for the gas-phase reaction $H_2(g)+Br_2(g)\rightarrow 2\ HBr(g)$ is given by eqn 82.6. Although the reaction is first-order in H_2, it has an indefinite order with respect to both Br_2 and HBr and an indefinite order overall.

Self-test 82.4 Repeat this analysis for a typical rate law for the action of an enzyme E on a substrate S (see Topic 92 for the derivation of this rate law): $v=k_r[E][S]/([S]+K_M)$, where K_M is a constant.

Answer: First-order in E; no specific order with respect to S

An example of a zeroth-order reaction is the catalytic decomposition of phosphine (PH_3) on hot tungsten at high pressures, with the rate law

$$v = k_r \tag{82.9}$$

The PH_3 decomposes at a constant rate until it has almost entirely disappeared. Zeroth-order reactions typically occur when there is a bottleneck of some kind in the mechanism, as in heterogeneous reactions when the surface is saturated and the subsequent reaction slow, and in a number of enzyme reactions when there is a large excess of substrate relative to the enzyme.

As we saw in *Brief illustration* 82.3, when a rate law is not of the form in eqn 82.7, the reaction does not have an overall order and may not even have definite orders with respect to each participant.

These remarks point to three important problems:

- To identify the rate law and obtain the rate constant from the experimental data. We concentrate on this aspect in this Topic.
- To construct reaction mechanisms that are consistent with the rate law. We introduce the techniques for doing so in Topic 86.
- To account for the values of the rate constants and explain their temperature dependence. This dependence is treated in Topic 85.

(d) The determination of the rate law

The determination of a rate law is simplified by the **isolation method** in which the concentrations of all the reactants except one are in large excess. If B is in large excess in a reaction between A and B, for example, then to a good approximation its concentration is constant throughout the reaction. Although the true rate law might be $v=k_r[A][B]$, we can approximate [B] by $[B]_0$, its initial value, and write

$$v=k_r'[A] \qquad k_r'=k_r[B]_0 \tag{82.10}$$

which has the form of a first-order rate law. Because the true rate law has been forced into first-order form by assuming that the concentration of B is constant, eqn 82.10 is called a **pseudo-first-order rate law**. The dependence of the rate on the concentration of each of the reactants may be found by isolating them in turn (by having all the other substances present in large excess), and so constructing a picture of the overall rate law.

In the **method of initial rates**, which is often used in conjunction with the isolation method, the rate is measured at the beginning of the reaction for several different initial concentrations of reactants. We shall suppose that the rate law for a reaction with A isolated is $v=k_r'[A]^a$; then its initial rate, v_0, is given by the initial values of the concentration of A, and we write $v_0=k_r'[A]_0^a$. Taking logarithms gives

$$\log v_0=\log k_r'+a\log[A]_0 \tag{82.11}$$

For a series of initial concentrations, a plot of the logarithms of the initial rates against the logarithms of the initial concentrations of A should be a straight line with slope *a*.

Example 82.2 Using the method of initial rates

The recombination of iodine atoms in the gas phase in the presence of argon was investigated and the order of the reaction was determined by the method of initial rates. The initial rates of reaction of $2\,I(g)+Ar(g)\rightarrow I_2(g)+Ar(g)$ were as follows:

$[I]_0/(10^{-5}$ mol dm$^{-3})$	1.0	2.0	4.0	6.0
$v_0/($mol dm^{-3} s$^{-1})$	(a) 8.70×10^{-4}	3.48×10^{-3}	1.39×10^{-2}	3.13×10^{-2}
	(b) 4.35×10^{-3}	1.74×10^{-2}	6.96×10^{-2}	1.57×10^{-1}
	(c) 8.69×10^{-3}	3.47×10^{-2}	1.38×10^{-1}	3.13×10^{-1}

The Ar concentrations are (a) 1.0 mmol dm^{-3}, (b) 5.0 mmol dm^{-3}, and (c) 10.0 mmol dm^{-3}. Determine the orders of reaction with respect to the I and Ar atom concentrations, and the rate constant.

Method Plot the logarithm of the initial rate, $\log v_0$, against $\log [I]_0$ for a given concentration of Ar, and, separately, against $\log [Ar]_0$ for a given concentration of I. The slopes of the two lines are the orders of reaction with respect to I and Ar, respectively. The intercepts with the vertical axis give $\log k_r$.

Answer The plots are shown in Fig. 82.4. The slopes are 2 and 1, respectively, so the (initial) rate law is $v_0=k_r[I]_0^2[Ar]_0$. This rate law signifies that the reaction is second-order in [I], first-order in [Ar], and third-order overall. The intercept corresponds to $k_r=9\times10^9$ mol^{-2} dm^6 s^{-1}.

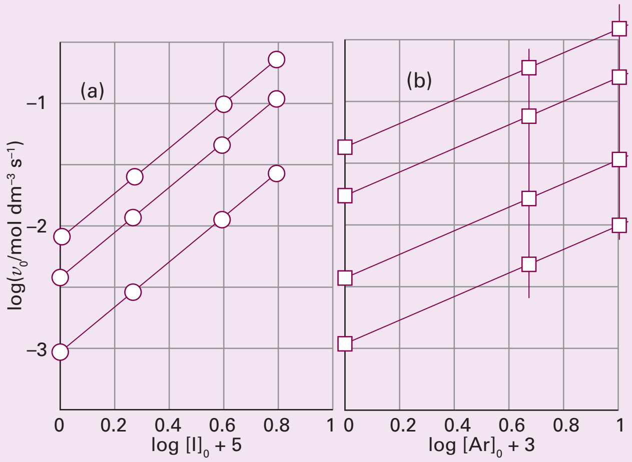

Figure 82.4 The plot of $\log v_0$ against (a) $\log [I]_0$ for a given $[Ar]_0$, and (b) $\log [Ar]_0$ for a given $[I]_0$.

A note on good practice The units of k_r come automatically from the calculation, and are always such as to convert the product of concentrations to a rate in concentration/time (for example, mol dm^{-3} s^{-1}).

Self-test 82.5 The initial rate of a reaction depended on concentration of a substance J as follows:

$[J]_0/($mmol dm$^{-3})$	5.0	8.2	17	30
$v_0/(10^{-7}$ mol dm^{-3} s$^{-1})$	3.6	9.6	41	130

Determine the order of the reaction with respect to J and calculate the rate constant.

Answer: 2, 1.4×10^{-2} dm^3 mol^{-1} s^{-1}

The method of initial rates might not reveal the full rate law, for once the products have been generated they might participate in the reaction and affect its rate. For example, products participate in the synthesis of HBr, because eqn 82.6 shows that the full rate law depends on the concentration of HBr. To avoid this difficulty, the rate law should be fitted to the data throughout the reaction. The fitting may be done, in simple cases at least, by using a proposed rate law to predict the concentration of any component at any time, and comparing it with the data. A rate law should also be tested by observing whether the addition of products or, for gas-phase reactions, a change in the surface-to-volume ratio in the reaction chamber affects the rate.

Checklist of concepts

☐ 1. The rates of chemical reactions are measured by using techniques that monitor the concentrations of species present in the reaction mixture. Examples include **real-time** and **quenching** procedures, **flow** and **stopped-flow** techniques, and **flash photolysis**.

2. The **instantaneous rate** of a reaction is the slope of the tangent to the graph of concentration against time (expressed as a positive quantity).
3. A **rate law** is an expression for the reaction rate in terms of the concentrations of the species that occur in the overall chemical reaction.

Checklist of equations

Property	Equation	Comment	Equation number
Extent of reaction	$\xi=(n_J-n_{J,0})/\nu_J$	Definition	82.1
Rate of a reaction	$v=(1/V)(\mathrm{d}\xi/\mathrm{d}t)$	Definition	82.2
Rate law (in some cases)	$v=k_r[A]^a[B]^b\cdots$	$a, b, \ldots$: orders; $a+b+\ldots$: overall order	82.7
Method of initial rates	$\log v_0=\log k_r'+a\log [A]_0$		82.11

TOPIC 83

Integrated rate laws

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➤ Why do you need to know this material?

A complete analysis of the time course of depletion of reactants and appearance of products is a required step in the formulation and verification of the mechanism of a reaction. The practical application of the material is that it enables you to predict the composition of a reaction system at any stage.

➤ What is the key idea?

A comparison between experimental data and the integrated form of the rate law leads to the verification of a proposed rate law and the determination of the order and rate constant of a reaction.

➤ What do you need to know already?

You need to be familiar with the concepts of rate law, reaction order, and rate constant (Topic 82). The manipulation of simple rate laws requires only elementary techniques of integration (see the *Resource section* for standard integrals).

Because rate laws (Topic 82) are differential equations, we must integrate them if we want to find the concentrations as a function of time. Even the most complex rate laws may be integrated numerically. However, in a number of simple cases analytical solutions, known as **integrated rate laws**, are easily obtained, and prove to be very useful. We examine a few of these simple cases here.

83.1 First-order reactions

As shown in the following *Justification*, the integrated form of the first-order rate law

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}=-k_\mathrm{r}[\mathrm{A}] \tag{83.1a}$$

is

$$\ln\frac{[\mathrm{A}]}{[\mathrm{A}]_0}=-k_\mathrm{r}t \qquad [\mathrm{A}]=[\mathrm{A}]_0\mathrm{e}^{-k_\mathrm{r}t} \tag{83.1b}$$

Integrated first-order rate law

where $[\mathrm{A}]_0$ is the initial concentration of A (at $t=0$).

Justification 83.1 First-order integrated rate law

First, we rearrange eqn 83.1a into

$$\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]}=-k_\mathrm{r}\mathrm{d}t$$

This expression can be integrated directly because k_r is a constant independent of t. Initially (at $t=0$) the concentration of A is $[\mathrm{A}]_0$, and at a later time t it is [A], so we make these values the limits of the integrals and write

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]}\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]}=-k_\mathrm{r}\int_0^t \mathrm{d}t$$

Because the integral of $1/x$ is $\ln x+$constant (Integral A.2 in the *Resource section*), eqn 83.1b is obtained immediately.

Equation 83.1b shows that if $\ln([\mathrm{A}]/[\mathrm{A}]_0)$ is plotted against t, then a first-order reaction will give a straight line of slope $-k_\mathrm{r}$. Some rate constants determined in this way are given in Table 83.1. The second expression in eqn 83.1b shows that in a first-order reaction the reactant concentration decreases exponentially with time with a rate determined by k_r (Fig. 83.1).

A useful indication of the rate of a first-order chemical reaction is the **half-life**, $t_{1/2}$, of a substance, the time taken for the concentration of a reactant to fall to half its initial value. This quantity is readily obtained from the integrated rate law. Thus, the time for [A] to decrease from $[\mathrm{A}]_0$ to $\frac{1}{2}[\mathrm{A}]_0$ in a first-order reaction is given by eqn 83.1b as

$$k_\mathrm{r}t_{1/2}=-\ln\frac{\frac{1}{2}[\mathrm{A}]_0}{[\mathrm{A}]_0}=-\ln\tfrac{1}{2}=\ln 2$$

Hence

$$t_{1/2}=\frac{\ln 2}{k_\mathrm{r}}$$

First-order reaction Half-life (83.2)

(Note that ln 2=0.693.) The main point to note about this result is that, for a first-order reaction, the half-life of a reactant is independent of its initial concentration. Therefore, if the concentration of A at some *arbitrary* stage of the reaction is [A], then it will have fallen to $\frac{1}{2}$[A] after a further interval of $(\ln 2)/k_\mathrm{r}$. Some half-lives are given in Table 83.1.

Table 83.1* Kinetic data for first-order reactions

Reaction	Phase	θ/°C	$k_\mathrm{r}/\mathrm{s}^{-1}$	$t_{1/2}$
$2\,\mathrm{N_2O_5}\rightarrow 4\,\mathrm{NO_2}+\mathrm{O_2}$	g	25	3.38×10^{-5}	5.70 h
	$\mathrm{Br_2(l)}$	25	4.27×10^{-5}	4.51 h
$\mathrm{C_2H_6}\rightarrow 2\,\mathrm{CH_3}$	g	700	5.36×10^{-4}	21.6 min

* More values are given in the *Resource section*.

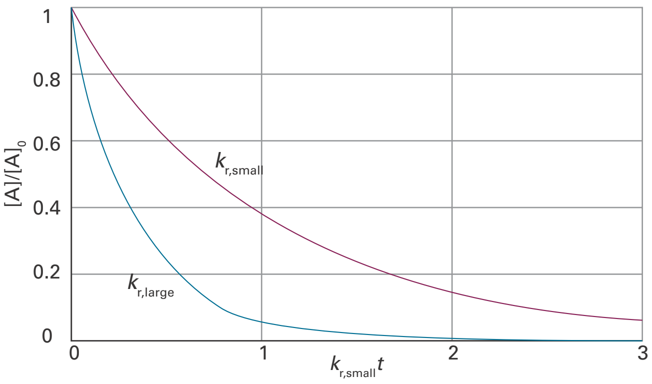

Figure 83.1 The exponential decay of the reactant in a first-order reaction. The larger the rate constant, the more rapid the decay: here $k_\mathrm{r,large}=3k_\mathrm{r,small}$.

Another indication of the rate of a first-order reaction is the **time constant**, τ (tau), the time required for the concentration of a reactant to fall to 1/e of its initial value. From eqn 83.1b it follows that

$$k_\mathrm{r}\tau=-\ln\frac{\frac{1}{\mathrm{e}}[\mathrm{A}]_0}{[\mathrm{A}]_0}=-\ln\tfrac{1}{\mathrm{e}}=1$$

That is, the time constant of a first-order reaction is the reciprocal of the rate constant:

$$\tau=\frac{1}{k_\mathrm{r}}$$

First-order reaction Time constant (83.3)

Example 83.1 Analysing a first-order reaction

The variation in the partial pressure of azomethane with time was followed at 600 K, with the results given below. Confirm that the decomposition

$$\mathrm{CH_3N_2CH_3(g)\rightarrow CH_3CH_3(g)+N_2(g)}$$

is first-order in azomethane, and find the rate constant, half-life, and time constant at 600 K.

t/s	0	1000	2000	3000	4000
p/Pa	10.9	7.63	5.32	3.71	2.59

Method As indicated in the text, to confirm that a reaction is first-order, plot $\ln([\mathrm{A}]/[\mathrm{A}]_0)$ against time and expect a straight line. Because the partial pressure of a gas is proportional to its concentration, an equivalent procedure is to plot $\ln(p/p_0)$ against t. If a straight line is obtained, its slope can be identified with $-k_\mathrm{r}$. The half-life and time constant are then calculated from k_r by using eqns 83.2 and 83.3, respectively.

Answer We draw up the following table:

t/s	0	1000	2000	3000	4000
$\ln(p/p_0)$	0	−0.357	−0.717	−1.078	−1.437

Figure 83.2 shows the plot of $\ln(p/p_0)$ against t. The plot is straight, confirming a first-order reaction, and its slope is -3.6×10^{-4}. Therefore, $k_\mathrm{r}=3.6\times10^{-4}\,\mathrm{s}^{-1}$.

A note on good practice Because the horizontal and vertical axes of graphs are labelled with pure numbers, the slope of a graph is always dimensionless. For a graph of the form $y=b+mx$ we can write $y=b+(m\text{ units})(x/\text{units})$, where 'units' are the units of x, and identify the (dimensionless) slope with 'm units'. Then m=slope/units. In the present case, because the graph shown here is a plot of $\ln(p/p_0)$ against t/s (with 'units'=s) and k_r is the negative value of the slope of $\ln(p/p_0)$ against t itself, k_r=−slope/s.

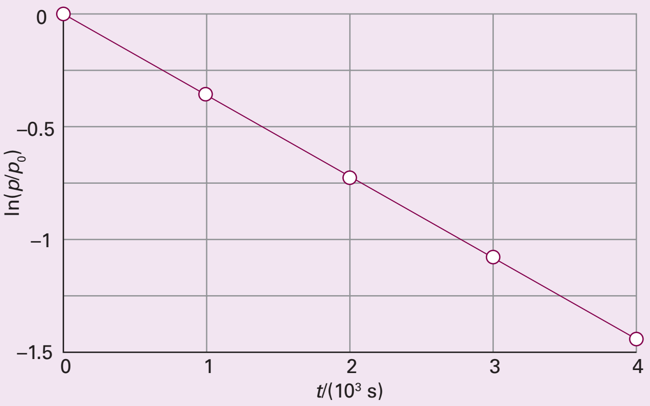

Figure 83.2 The determination of the rate constant of a first-order reaction: a straight line is obtained when ln [A]/[A]$_0$ (or, as here, ln p/p_0) is plotted against t; the slope gives k_r.

It follows from eqns 83.2 and 83.3 that the half-life and time constant are, respectively,

$$t_{1/2}=\frac{\ln 2}{3.6\times10^{4}\,\mathrm{s^{-1}}}=1.9\times10^{-5}\,\mathrm{s}\qquad \tau=\frac{1}{3.6\times10^{4}\,\mathrm{s^{-1}}}=2.8\times10^{-5}\,\mathrm{s}$$

Self-test 83.1 In a particular experiment, it was found that the concentration of N_2O_5 in liquid bromine varied with time as follows:

t/s	0	200	400	600	1000
$[N_2O_5]/(\mathrm{mol\,dm^{-3}})$	0.110	0.073	0.048	0.032	0.014

Confirm that the reaction is first-order in N_2O_5 and determine the rate constant.

Answer: $k_r=2.1\times10^{-3}\,\mathrm{s^{-1}}$

83.2 Second-order reactions

We show in the following *Justification* that the integrated form of the second-order rate law

$$\frac{d[A]}{dt}=-k_r[A]^2 \tag{83.4a}$$

is either of the following two forms:

$$\frac{1}{[A]}-\frac{1}{[A]_0}=k_r t \qquad \textit{Second-order reaction} \qquad \text{Integrated rate law} \tag{83.4b}$$

$$[A]=\frac{[A]_0}{1+k_r t[A]_0} \qquad \textit{Second-order reaction} \qquad \text{Alternative form of the integrated rate law} \tag{83.4c}$$

where $[A]_0$ is the initial concentration of A (at $t=0$).

Justification 83.2 Second-order integrated rate law

To integrate eqn 83.4a we rearrange it into

$$\frac{d[A]}{[A]^2}=-k_r dt$$

The concentration is $[A]_0$ at $t=0$ and [A] at a general time t later. Therefore,

$$-\int_{[A]_0}^{[A]}\frac{d[A]}{[A]^2}=k_r\int_0^t dt$$

Because the integral of $1/x^2$ is $-1/x+$constant (Integral A.1 in the *Resource section*), we obtain eqn 83.4b by substitution of the limits

$$\frac{1}{[A]}+\text{constant}\Bigg|_{[A]_0}^{[A]}=\frac{1}{[A]}-\frac{1}{[A]_0}=k_r t$$

We can then rearrange this expression into eqn 83.4c.

Equation 83.4b shows that to test for a second-order reaction we should plot 1/[A] against t and expect a straight line. The slope of the graph is k_r. Some rate constants determined in this way are given in Table 83.2. The rearranged form, eqn 83.4c, lets us predict the concentration of A at any time after the start of the reaction. It shows that the concentration of A approaches zero more slowly than in a first-order reaction with the same initial rate (Fig. 83.3).

It follows from eqn 83.4b by substituting $t=t_{1/2}$ and $[A]=\frac{1}{2}[A]_0$ that the half-life of a species A that is consumed in a second-order reaction is

$$t_{1/2}=\frac{1}{k_r[A]_0} \qquad \textit{Second-order reaction} \qquad \text{Half-life} \tag{83.5}$$

Therefore, unlike a first-order reaction, the half-life of a substance in a second-order reaction varies with the initial concentration. A practical consequence of this dependence is that species that decay by second-order reactions (which includes some environmentally harmful substances) may persist in low concentrations for long periods because their half-lives are long

Table 83.2* Kinetic data for second-order reactions

Reaction	Phase	θ/°C	$k_r/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})$
$2\,NOBr \rightarrow 2\,NO + Br_2$	g	10	0.80
$2\,I \rightarrow I_2$	g	23	7×10^{9}
$CH_3Cl + CH_3O^-$	$CH_3OH(l)$	20	2.29×10^{-6}

* More values are given in the *Resource section*.

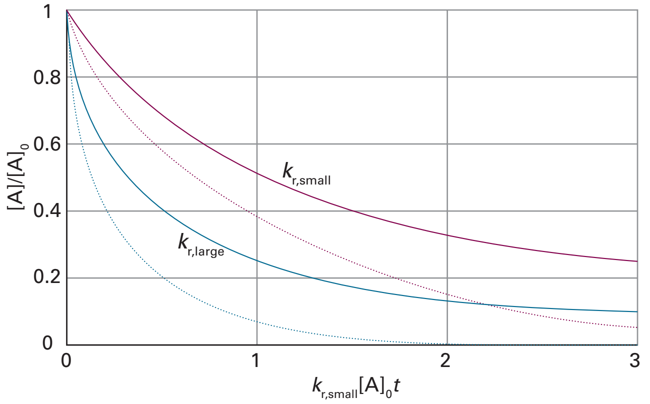

Figure 83.3 The variation with time of the concentration of a reactant in a second-order reaction. The dotted lines are the corresponding decays in a first-order reaction with the same initial rate. For this illustration, $k_{r,large}=3k_{r,small}$.

when their concentrations are low. In general, for an *n*th-order reaction (with *n* neither 0 nor 1) of the form A → products, the half-life is related to the rate constant and the initial concentration of A by (see Problem 83.16)

$$t_{1/2}=\frac{2^{n-1}-1}{(n-1)k_r[A]_0^{n-1}} \qquad \textit{nth-order reaction} \quad \text{Half-life} \qquad (83.6)$$

Another type of second-order reaction is one that is first-order in each of two reactants A and B:

$$\frac{d[A]}{dt}=-k_r[A][B] \qquad (83.7)$$

This rate law cannot be integrated until we know how the concentration of B is related to that of A. For example, if the reaction is $A+B\rightarrow P$, where P denotes products, and the initial concentrations are $[A]_0$ and $[B]_0$, then it is shown in the following *Justification* that at a time *t* after the start of the reaction, the concentrations satisfy the relation

$$\ln\frac{[B]/[B]_0}{[A]/[A]_0}=([B]_0-[A]_0)k_rt \qquad \textit{Second-order reaction of the type } A+B\rightarrow P \quad \text{Integrated rate law} \qquad (83.8)$$

Therefore, a plot of the expression on the left against *t* should be a straight line from which k_r can be obtained. As shown in the following *Brief illustration*, the rate constant may be estimated quickly by using data from only two measurements.

Brief illustration 83.1 Second-order reactions

Consider a second-order reaction of the type $A+B\rightarrow P$ carried out in solution. Initially, the concentrations of reactants were $[A]_0=0.075\ \text{mol dm}^{-3}$ and $[B]_0=0.050\ \text{mol dm}^{-3}$. After 1.0 h the concentration of B fell to $[B]=0.020\ \text{mol dm}^{-3}$. Because $\Delta[B]=\Delta[A]$, it follows that during this time interval

$$\Delta[B] = (0.020-0.050)\ \text{mol dm}^{-3}=-0.030\ \text{mol dm}^{-3}$$
$$\Delta[A] = -0.030\ \text{mol dm}^{-3}$$

Therefore, the concentrations of A and B after 1.0 h are

$$[A] = \Delta[A] + [A]_0 = (-0.030 + 0.075)\ \text{mol dm}^{-3}$$
$$= 0.045\ \text{mol dm}^{-3}$$
$$[B] = 0.020\ \text{mol dm}^{-3}$$

It follows from rearrangement of eqn 83.8 that

$$k_r(3600\,\text{s})=\frac{1}{(0.050-0.075)\,\text{mol dm}^{-3}}\ln\frac{0.020/0.050}{0.045/0.075}$$

where we have used 1 hr = 3600 s. Solving this expression for the rate constant gives

$$k_r = 4.5\times10^{-3}\,\text{dm}^3\,\text{mol}^{-1}\text{s}^{-1}$$

Self-test 83.2 Calculate the half-life of the reactants for the reaction above.

Answer: $t_{1/2}(A)=5.1\times10^3\,\text{s}$, $t_{1/2}(B)=2.1\times10^3\,\text{s}$

Justification 83.3 Overall second-order rate law

It follows from the reaction stoichiometry that when the concentration of A has fallen to $[A]_0-x$, the concentration of B will have fallen to $[B]_0-x$ (because each A that disappears entails the disappearance of one B). It follows that

$$\frac{d[A]}{dt}=-k_r([A]_0-x)([B]_0-x)$$

Because $[A]=[A]_0-x$, it follows that $d[A]/dt=-dx/dt$ and the rate law may be written as

$$\frac{dx}{dt}=k_r([A]_0-x)([B]_0-x)$$

The initial condition is that $x=0$ when $t=0$, so the integration required is

$$\int_0^x\frac{dx}{([A]_0-x)([B]_0-x)}=k_r\int_0^t dt$$

The integral on the right is simply k_rt. The integral on the left is evaluated by using the method of partial fractions (see *The chemist's toolkit* 83.1):

$$\int_0^x\frac{dx}{([A]_0-x)([B]_0-x)}=\frac{1}{[B]_0-[A]_0}\left\{\ln\frac{[A]_0}{[A]_0-x}-\ln\frac{[B]_0}{[B]_0-x}\right\}$$

The two logarithms can be combined as follows:

$$\begin{aligned}\ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]_0-x}-\ln\frac{[\mathrm{B}]_0}{[\mathrm{B}]_0-x}&=\ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]}-\ln\frac{[\mathrm{B}]_0}{[\mathrm{B}]}\\&=\ln\frac{1}{[\mathrm{A}]/[\mathrm{A}]_0}-\ln\frac{1}{[\mathrm{B}]/[\mathrm{B}]_0}\\&=\ln\frac{[\mathrm{B}]/[\mathrm{B}]_0}{[\mathrm{A}]/[\mathrm{A}]_0}\end{aligned}$$

where we have used $[\mathrm{A}]=[\mathrm{A}]_0-x$ and $[\mathrm{B}]=[\mathrm{B}]_0-x$. Combining all the results so far gives eqn 83.8. Similar calculations may be carried out to find the integrated rate laws for other orders, and some are listed in Table 83.3.

The chemist's toolkit 83.1 Integration by the method of partial fractions

To solve an integral of the form

$$I=\int\frac{1}{(a-x)(b-x)}\mathrm{d}x$$

where a and b are constants, we use the method of partial fractions, in which a fraction that is the product of terms (as in the denominator of this integrand) is written as a sum of fractions. To implement this procedure we write the integrand as

$$\frac{1}{(a-x)(b-x)}=\frac{1}{b-a}\left(\frac{1}{a-x}-\frac{1}{b-x}\right)$$

Then we integrate each term on the right. It follows that

$$\begin{aligned}I&=\frac{1}{b-a}\left(\int\frac{\mathrm{d}x}{a-x}-\int\frac{\mathrm{d}x}{b-x}\right)\\&\overset{\text{Integral A.2}}{=}\frac{1}{b-a}\left(\ln\frac{1}{a-x}-\ln\frac{1}{b-x}\right)+\text{constant}\end{aligned}$$

Table 83.3 Integrated rate laws

Order	Reaction	Rate law*	$t_{1/2}$
0	$\mathrm{A}\rightarrow\mathrm{P}$	$v=k_\mathrm{r}$ $k_\mathrm{r}t=x$ for $0\leq x\leq[\mathrm{A}]_0$	$[\mathrm{A}]_0/2k_\mathrm{r}$
1	$\mathrm{A}\rightarrow\mathrm{P}$	$v=k_\mathrm{r}[\mathrm{A}]$ $k_\mathrm{r}t=\ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]_0-x}$	$(\ln 2)/k_\mathrm{r}$
2	$\mathrm{A}\rightarrow\mathrm{P}$	$v=k_\mathrm{r}[\mathrm{A}]^2$ $k_\mathrm{r}t=\frac{x}{[\mathrm{A}]_0([\mathrm{A}]_0-x)}$	$1/k_\mathrm{r}[\mathrm{A}]_0$
	$\mathrm{A}+\mathrm{B}\rightarrow\mathrm{P}$	$v=k_\mathrm{r}[\mathrm{A}][\mathrm{B}]$ $k_\mathrm{r}t=\frac{1}{[\mathrm{B}]_0-[\mathrm{A}]_0}\ln\frac{[\mathrm{A}]_0([\mathrm{B}]_0-x)}{([\mathrm{A}]_0-x)[\mathrm{B}]_0}$	
	$\mathrm{A}+2\,\mathrm{B}\rightarrow\mathrm{P}$	$v=k_\mathrm{r}[\mathrm{A}][\mathrm{B}]$ $k_\mathrm{r}t=\frac{1}{[\mathrm{B}]_0-2[\mathrm{A}]_0}\ln\frac{[\mathrm{A}]_0([\mathrm{B}]_0-2x)}{([\mathrm{A}]_0-x)[\mathrm{B}]_0}$	
	$\mathrm{A}\rightarrow\mathrm{P}$ with autocatalysis	$v=k_\mathrm{r}[\mathrm{A}][\mathrm{P}]$ $k_\mathrm{r}t=\frac{1}{[\mathrm{A}]_0+[\mathrm{P}]_0}\ln\frac{[\mathrm{A}]_0([\mathrm{P}]_0+x)}{([\mathrm{A}]_0-x)[\mathrm{P}]_0}$	
3	$\mathrm{A}+2\,\mathrm{B}\rightarrow\mathrm{P}$	$v=k_\mathrm{r}[\mathrm{A}][\mathrm{B}]^2$ $k_\mathrm{r}t=\frac{2x}{(2[\mathrm{A}]_0-[\mathrm{B}]_0)([\mathrm{B}]_0-2x)[\mathrm{B}]_0}+\frac{1}{(2[\mathrm{A}]_0-[\mathrm{B}]_0)^2}\ln\frac{[\mathrm{A}]_0([\mathrm{B}]_0-2x)}{([\mathrm{A}]_0-x)[\mathrm{B}]_0}$	

Order	Reaction	Rate law*	$t_{1/2}$
$n \geq 2$	$A \rightarrow P$	$v = k_r[A]^n$ $k_r t = \frac{1}{n-1}\left\{\frac{1}{([A]_0 - x)^{n-1}} - \frac{1}{[A]_0{}^{n-1}}\right\}$	$\frac{2^{n-1}-1}{(n-1)k_r[A]_0{}^{n-1}}$

* $x = [P]$ and $v = dx/dt$

Checklist of concepts

☐ 1. An **integrated rate law** is an expression for the concentration of a reactant or product as a function of time (Table 83.3).

☐ 2. Analysis of experimental data using integrated rate laws allows for the prediction of the composition of a reaction system at any stage.

Checklist of equations

Property	Equation	Comment	Equation number
Integrated rate law	$\ln([A]/[A]_0) = -k_r t$ or $[A] = [A]_0 e^{-k_r t}$	First-order, $A \rightarrow P$	83.1
Half-life	$t_{1/2} = (\ln 2)/k_r$	First-order, $A \rightarrow P$	83.2
Time constant	$\tau = 1/k_r$	First-order	83.3
Integrated rate law	$1/[A] - 1/[A]_0 = k_r t$, or $[A] = [A]_0/(1 + k_r t[A]_0)$	Second-order, $A \rightarrow P$	83.4
Half-life	$t_{1/2} = 1/k_r[A]_0$	Second-order, $A \rightarrow P$	83.5
Half-life	$t_{1/2} = (2^{n-1} - 1)/(n-1)k_r[A]_0^{n-1}$	nth-order	83.6
Integrated rate law	$\ln\{([B]/[B]_0)/([A]/[A]_0)\} = ([B]_0 - [A]_0)k_r t$	Second-order $A + B \rightarrow P$	83.8

TOPIC 84

Reactions approaching equilibrium

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➤ Why do you need to know this material?

All reactions approach equilibrium, so it is important to be able to describe the changing composition as they approach this composition.

➤ What is the key idea?

Both forward and reverse reactions must be incorporated into a reaction scheme to account for the approach to equilibrium, and the analysis of the mechanism shows that there is a relation between the corresponding rate constants and the equilibrium constant.

➤ What do you need to know already?

You need to be familiar with the concepts of rate law, reaction order, and rate constant (Topic 82), integrated rate laws (Topic 83), and equilibrium constants (Topic 73). As in Topic 83, the manipulation of simple rate laws requires only elementary techniques of integration.

In practice, most kinetic studies are made on reactions that are far from equilibrium, and the reverse reactions are unimportant. For this reason, none of the laws considered so far describes the overall rate when the reaction is close to equilibrium. At that stage the products may be so abundant that the reverse reaction must be taken into account.

84.1 First-order reactions close to equilibrium

We can explore the variation of the composition with time close to chemical equilibrium by considering the reaction in which A forms B and both forward and reverse reactions are first-order (as in some isomerizations). The scheme we consider is

$$\begin{aligned} &\mathrm{A}\rightarrow\mathrm{B} \qquad v=k_\mathrm{r}[\mathrm{A}] \\ &\mathrm{B}\rightarrow\mathrm{A} \qquad v=k_\mathrm{r}'[\mathrm{B}] \end{aligned} \tag{84.1}$$

The concentration of A is reduced by the forward reaction (at a rate $k_\mathrm{r}[\mathrm{A}]$) but it is increased by the reverse reaction (at a rate $k_\mathrm{r}'[\mathrm{B}]$). The net rate of change is therefore

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}=-k_\mathrm{r}[\mathrm{A}]+k_\mathrm{r}'[\mathrm{B}] \tag{84.2}$$

If the initial concentration of A is $[\mathrm{A}]_0$, and no B is present initially, then at all times $[\mathrm{A}]+[\mathrm{B}]=[\mathrm{A}]_0$. Therefore,

$$\begin{aligned} \frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}&=-k_\mathrm{r}[\mathrm{A}]+k_\mathrm{r}'\{[\mathrm{A}]_0-[\mathrm{A}]\} \\ &=-(k_\mathrm{r}+k_\mathrm{r}')[\mathrm{A}]+k_\mathrm{r}'[\mathrm{A}]_0 \end{aligned} \tag{84.3}$$

The solution of this first-order differential equation (as may be checked by differentiation, Problem 84.1) is

$$[\mathrm{A}]=\frac{k_\mathrm{r}'+k_\mathrm{r}\mathrm{e}^{-(k_\mathrm{r}+k_\mathrm{r}')t}}{k_\mathrm{r}+k_\mathrm{r}'}[\mathrm{A}]_0 \tag{84.4}$$

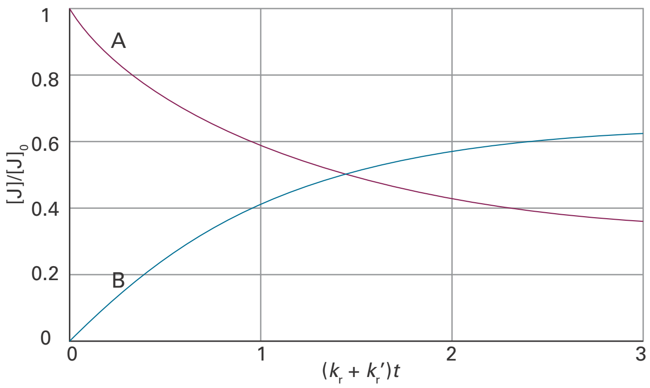

Figure 84.1 The approach of concentrations to their equilibrium values as predicted by eqn 84.4 for a reaction $\mathrm{A} \rightleftarrows \mathrm{B}$ that is first-order in each direction, and for which $k_r = 2k_r'$.

Figure 84.1 shows the time dependence predicted by this equation, with $[\mathrm{B}] = [\mathrm{A}]_0 - [\mathrm{A}]$.

As $t \rightarrow \infty$, the concentrations reach their equilibrium values, which are given by eqn 84.4 as

$$[\mathrm{A}]_{\mathrm{eq}} = \frac{k_r'[\mathrm{A}]_0}{k_r + k_r'} \qquad [\mathrm{B}]_{\mathrm{eq}} = [\mathrm{A}]_0 - [\mathrm{A}]_{\mathrm{eq}} = \frac{k_r[\mathrm{A}]_0}{k_r + k_r'} \tag{84.5}$$

It follows that the equilibrium constant of the reaction is

$$K = \frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{k_r}{k_r'} \tag{84.6}$$

(As explained in Topic 72, we are justified in replacing activities with the numerical values of molar concentrations if the latter are low.) Exactly the same conclusion can be reached—more simply, in fact—by noting that, at equilibrium, the forward and reverse rates must be the same, so

$$k_r[\mathrm{A}]_{\mathrm{eq}} = k_r'[\mathrm{B}]_{\mathrm{eq}} \tag{84.7}$$

This relation rearranges into eqn 84.6. The theoretical importance of eqn 84.6 is that it relates a thermodynamic quantity, the equilibrium constant, to quantities relating to rates. Its practical importance is that if one of the rate constants can be measured, then the other may be obtained if the equilibrium constant is known.

Equation 84.6 is valid even if the forward and reverse reactions have different orders, but in that case we need to be careful with units. For instance, if the reaction $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C}$ is second-order forward and first-order in reverse, then the condition for equilibrium is $k_r[\mathrm{A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}} = k_r'[\mathrm{C}]_{\mathrm{eq}}$ and the dimensionless equilibrium constant in full dress is

$$K = \frac{[\mathrm{C}]_{\mathrm{eq}}/c^{\ominus}}{([\mathrm{A}]_{\mathrm{eq}}/c^{\ominus})([\mathrm{B}]_{\mathrm{eq}}/c^{\ominus})} = \left(\frac{[\mathrm{C}]}{[\mathrm{A}][\mathrm{B}]}\right)_{\mathrm{eq}} c^{\ominus} = \frac{k_r}{k_r'} \times c^{\ominus}$$

The presence of $c^{\ominus} = 1\,\mathrm{mol\,dm^{-3}}$ in the last term ensures that the ratio of second-order to first-order rate constants, with their different units, is turned into a dimensionless quantity.

Brief illustration 84.1 The equilibrium constant from rate constants

The rates of the forward and reverse reactions for a dimerization reaction were found to be $8.0 \times 10^8\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ (second-order) and $2.0 \times 10^6\,\mathrm{s^{-1}}$ (first-order). The equilibrium constant for the dimerization is therefore

$$K = \frac{8.0 \times 10^8\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}}{2.0 \times 10^6\,\mathrm{s^{-1}}} \times 1\,\mathrm{mol\,dm^{-3}} = 4.0 \times 10^2$$

Self-test 84.1 The equilibrium constant for the attachment of a drug molecule to a protein was measured as 2.0×10^2. In a separate experiment, the rate constant for the second-order attachment was found to be $1.5 \times 10^8\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. What is the rate constant for the loss of the drug molecule from the protein?

Answer: $7.5 \times 10^5\,\mathrm{s^{-1}}$

For a more general reaction, the overall equilibrium constant can be expressed in terms of the rate constants for all the intermediate stages of the reaction mechanism (see Problem 84.4):

$$K = \frac{k_a}{k_a'} \times \frac{k_b}{k_b'} \times \cdots \tag{84.8}$$

The equilibrium constant in terms of the rate constants

where the *k*s are the rate constants for the individual steps and the *k*′s are those for the corresponding reverse steps.

84.2 Relaxation methods

The term **relaxation** denotes the return of a system to equilibrium. It is used in chemical kinetics to indicate that an externally applied influence has shifted the equilibrium position of a reaction, normally suddenly, and that the reaction is adjusting to the equilibrium composition characteristic of the new conditions (Fig. 84.2). We shall consider the response of reaction rates to a **temperature jump**, a sudden change in temperature. We know from Topic 75 that the equilibrium composition of a reaction depends on the temperature (provided $\Delta_r H^{\ominus}$ is nonzero), so a shift in temperature acts as a perturbation on the system. One way of achieving a temperature jump is to discharge a capacitor through a sample made conducting by the addition of ions, but laser or microwave discharges can also be used. Temperature jumps of between 5 and 10 K can be achieved in about 1 μs with electrical discharges. The high-energy output of pulsed lasers (Topic 46) is sufficient to generate temperature

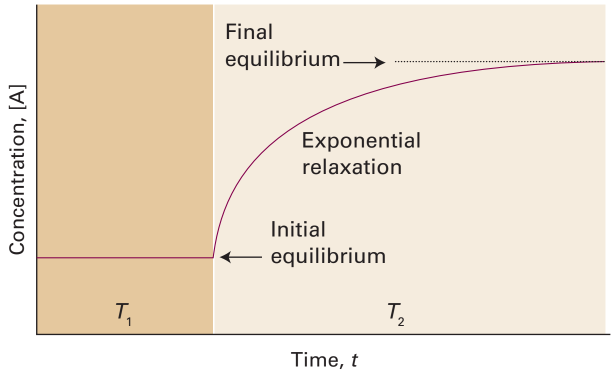

Figure 84.2 The relaxation to the new equilibrium composition when a reaction initially at equilibrium at a temperature T_1 is subjected to a sudden change of temperature, which takes it to T_2.

jumps of between 10 and 30 K within nanoseconds in aqueous samples. Some equilibria are also sensitive to pressure, and **pressure-jump techniques** may then also be used.

When a sudden temperature increase is applied to a simple $A \rightleftharpoons B$ equilibrium that is first-order in each direction, we show in the following *Justification* that the composition relaxes exponentially to the new equilibrium composition:

$$x = x_0 e^{-t/\tau} \qquad \tau = \frac{1}{k_r + k_r'} \qquad \textit{First-order reaction} \qquad \text{Relaxation after a temperature jump} \qquad (84.9)$$

where x_0 is the departure from equilibrium immediately after the temperature jump, x is the departure from equilibrium at the new temperature after a time t, and k_r and k_r' are the forward and reverse rate constants, respectively, at the new temperature.

Justification 84.1 Relaxation to equilibrium

When the temperature of a system at equilibrium is increased suddenly, the rate constants change from their earlier values to the new values k_r and k_r' characteristic of that temperature, but the concentrations of A and B remain for an instant at their old equilibrium values. As the system is no longer at equilibrium, it readjusts to the new equilibrium concentrations, which are now given by

$$k_r[A]_{eq} = k_r'[B]_{eq}$$

and it does so at a rate that depends on the new rate constants. We write the deviation of [A] from its new equilibrium value as x, so $[A] = [A]_{eq} + x$ and $[B] = [B]_{eq} - x$. The concentration of A then changes as follows:

$$\begin{aligned}\frac{d[A]}{dt} &= -k_r[A] + k_r'[B] \\ &= -k_r([A]_{eq} + x) + k_r'([B]_{eq} - x) \\ &= -(k_r + k_r')x\end{aligned}$$

because the two terms involving the equilibrium concentrations cancel. Because $d[A]/dt = dx/dt$, this equation is a first-order differential equation with a solution that resembles eqn 83.1b and is given in eqn 84.9.

Equation 84.9 shows that the concentrations of A and B relax into the new equilibrium at a rate determined by the sum of the two new rate constants. Because the equilibrium constant under the new conditions is $K \approx k_r/k_r'$, its value may be combined with the relaxation time measurement to find the individual k_r and k_r'.

Example 84.1 Analysing a temperature-jump experiment

The equilibrium constant for the autoprotolysis of water, $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$, is $K_w = a(H^+)a(OH^-) = 1.008 \times 10^{-14}$ at 298 K, where we have used the exact expression in terms of activities. After a temperature jump, the reaction returns to equilibrium with a relaxation time of 37 μs at 298 K and pH ≈ 7. Given that the forward reaction is first-order and the reverse is second-order overall, calculate the rate constants for the forward and reverse reactions.

Method We need to derive an expression for the relaxation time, τ (the time constant for return to equilibrium), in terms of k_r (forward, first-order reaction) and k_r' (reverse, second-order reaction). We can proceed as above, but it will be necessary to make the assumption that the deviation from equilibrium (x) is so small that terms in x^2 can be neglected. Relate k_r and k_r' through the equilibrium constant, but be careful with units because K_w is dimensionless.

Answer The forward rate at the final temperature is $k_r[H_2O]$ and the reverse rate is $k_r'[H^+][OH^-]$. The net rate of deprotonation of H_2O is

$$\frac{d[H_2O]}{dt} = -k_r[H_2O] + k_r'[H^+][OH^-]$$

We write $[H_2O] = [H_2O]_{eq} + x$, $[H^+] = [H^+]_{eq} - x$, and $[OH^-] = [OH^-]_{eq} - x$, and obtain

$$\begin{aligned}\frac{dx}{dt} &= -\{k_r + k_r'([H^+]_{eq} + [OH^-]_{eq})\}x - k_r[H_2O]_{eq} \\ &\quad + k_r'[H^+]_{eq}[OH^-]_{eq} + k_r'x^2 \\ &\approx -\{k_r + k_r'([H^+]_{eq} + [OH^-]_{eq})\}x\end{aligned}$$

where we have neglected the term in x^2 because it is so small and have used the equilibrium condition $k_r[H_2O]_{eq} = k_r'[H^+]_{eq}[OH^-]_{eq}$ to eliminate the terms that are independent of x. It follows that

$$\frac{1}{\tau}=k_r+k_r'([H^+]_{eq}+[OH^-]_{eq})$$

At this point we note that

$$\begin{aligned}K_w&=a(H^+)a(OH^-)\approx([H^+]_{eq}/c^{\ominus})([OH^-]_{eq}/c^{\ominus})\\&=[H^+]_{eq}[OH^-]_{eq}/c^{\ominus 2}\end{aligned}$$

with $c^{\ominus}=1$ mol dm^{-3}. For this electrically neutral system, $[H^+]=[OH^-]$, so the concentration of each type of ion is $K_w^{1/2}c^{\ominus}$, and hence

$$\frac{1}{\tau}=k_r+k_r'\left(K_w^{1/2}c^{\ominus}+K_w^{1/2}c^{\ominus}\right)=k_r'\left\{\frac{k_r}{k_r'}+2K_w^{1/2}c^{\ominus}\right\}$$

At this point we note that

$$\frac{k_r}{k_r'}=\frac{[H^+]_{eq}[OH^-]_{eq}}{[H_2O]_{eq}}=\frac{K_w c^{\ominus 2}}{[H_2O]_{eq}}$$

The molar concentration of pure water is 55.6 mol dm^{-3}, so $[H_2O]_{eq}/c^{\ominus}=55.6$. If we write $K=K_w/55.6=1.81\times10^{-16}$, we obtain

$$\frac{1}{\tau}=k_r'\left(K+2K_w^{1/2}\right)c^{\ominus}$$

Hence,

$$\begin{aligned}k_r'&=\frac{1}{\tau\left(K+2K_w^{1/2}\right)c^{\ominus}}\\&=\frac{1}{(3.7\times10^{-5}\,\mathrm{s})\times(2.0\times10^{-7})\times(1\,\mathrm{mol\,dm^{-3}})}\\&=1.4\times10^{11}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}\end{aligned}$$

It follows that

$$k_r=k_r'Kc^{\ominus}=2.4\times10^{-5}\,\mathrm{s^{-1}}$$

The reaction is faster in ice, where $k_r'=8.6\times10^{12}$ dm^3 mol^{-1} s^{-1}.

A note on good practice Notice how we keep track of units through the use of $c^{\ominus}$: K and K_w are dimensionless; k_r' is expressed in dm^3 mol^{-1} s^{-1} and k_r is expressed in s^{-1}.

Self-test 84.2 Derive an expression for the relaxation time of a concentration when the reaction $A+B \rightleftharpoons C+D$ is second-order in both directions.

Answer: $1/\tau=k_r([A]+[B])_{eq}+k_r'([C]+[D])_{eq}$

Checklist of concepts

☐ **1.** There is a relation between the equilibrium constant, a thermodynamic quantity, and the rate constants of the forward and reverse reactions (see table below).

☐ **2.** In **relaxation methods** of kinetic analysis, the equilibrium position of a reaction is first shifted suddenly and then allowed to readjust to the equilibrium composition characteristic of the new conditions.

Checklist of equations

Property	Equation	Comment	Equation number
Equilibrium constant in terms of rate constants	$K=k_a/k_a'\times k_b/k_b'\times\cdots$	Include $c^{\ominus}$ as appropriate	84.8
Relaxation of an equilibrium $A\rightleftharpoons B$ after a temperature jump	$x=x_0e^{-t/\tau}$ $\tau=1/(k_r+k_r')$	First-order in each direction	84.9

TOPIC 85

The Arrhenius equation

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➤ Why do you need to know this material?

The rates of reactions depend on the temperature. Exploration of this dependence leads to the formulation of theories that can help you understand why a collection of reactants under specific conditions leads to certain products, but not others.

➤ What is the key idea?

Analysis of the temperature dependence of the rate constant provides insight into the energy requirements for reactions.

➤ What do you need to know already?

You need to know that the rate law of a chemical reaction is expressed in terms of a rate constant (Topic 82).

In this Topic we interpret the common experimental observation that chemical reactions usually go faster as the temperature is increased. We also begin to see how exploration of the temperature dependence of reaction rates can reveal some details of the energy requirements for molecular encounters that lead to the formation of products from reactants.

85.1 The temperature dependence of reaction rates

The rates of most reactions increase with temperature. More specifically, it is found experimentally for many reactions that a plot of ln k_r against $1/T$ gives a straight line with a negative slope, indicating that an increase in ln k_r (and therefore an increase in k_r) results from a decrease in $1/T$ (that is, an increase in T). This behaviour is normally expressed mathematically by introducing two parameters, one representing the intercept and the other the slope of the straight line, and writing the **Arrhenius equation**

$$\ln k_r = \ln A - \frac{E_a}{RT} \qquad \text{Arrhenius equation} \qquad (85.1)$$

The parameter A, which corresponds to the intercept of the line at $1/T=0$ (at infinite temperature, Fig. 85.1), is called the **pre-exponential factor** or the 'frequency factor'. The parameter E_a, which is obtained from the slope of the line ($-E_a/R$), is called

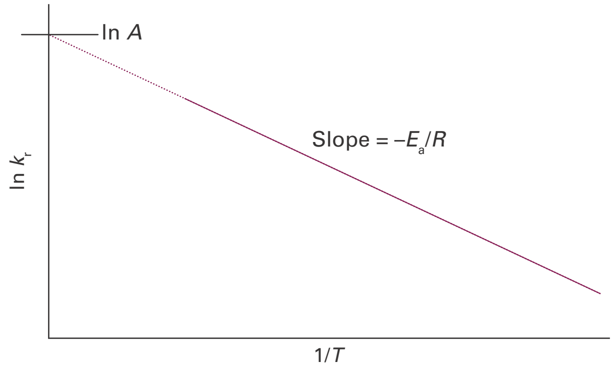

Figure 85.1 A plot of ln k_r against $1/T$ is a straight line when the reaction follows the behaviour described by the Arrhenius equation (eqn 85.1). The slope gives $-E_a/R$ and the intercept at $1/T=0$ gives ln A.

Table 85.1* Arrhenius parameters

(1) First-order reactions	$A/\mathrm{s^{-1}}$	$E_a/(\mathrm{kJ\,mol^{-1}})$
$CH_3NC \rightarrow CH_3CN$	3.98×10^{13}	160
$2\,N_2O_5 \rightarrow 4\,NO_2 + O_2$	4.94×10^{13}	103.4
(2) Second-order reactions	$A/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})$	$E_a/(\mathrm{kJ\,mol^{-1}})$
$OH + H_2 \rightarrow H_2O + H$	8.0×10^{10}	42
$NaC_2H_5O + CH_3I$ in ethanol	2.42×10^{11}	81.6

* More values are given in the *Resource section*.

the **activation energy**. Collectively the two quantities are called the **Arrhenius parameters** (Table 85.1). The activation energy is almost always a positive quantity, but under certain circumstances it can be negative (Topic 86).

Example 85.1 Determining the Arrhenius parameters

The rate of the second-order decomposition of acetaldehyde (ethanal, CH_3CHO) was measured over the temperature range 700–1000 K, and the rate constants are reported below. Find E_a and A.

T/K	700	730	760	790	810	840	910	1000
$k_r/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})$	0.011	0.035	0.105	0.343	0.789	2.17	20.0	145

Method According to eqn 85.1, the data can be analysed by plotting $\ln(k_r/\mathrm{dm^3\,mol^{-1}\,s^{-1}})$ against $1/(T/\mathrm{K})$, or more conveniently $(10^3\,\mathrm{K})/T$, and getting a straight line. Obtain the activation energy from the dimensionless slope by writing $-E_a/R = \text{slope}/\text{units}$, where in this case 'units' $=1/(10^3\,\mathrm{K})$, so $E_a = -\text{slope}\times R\times10^3\,\mathrm{K}$. The intercept at $1/T=0$ is $\ln(A/\mathrm{dm^3\,mol^{-1}\,s^{-1}})$. Use a least-squares procedure to determine the plot parameters.

Answer We draw up the following table:

$(10^3\,\mathrm{K})/T$	1.43	1.37	1.32	1.27	1.23	1.19	1.10	1.00
$\ln(k_r/\mathrm{dm^3\,mol^{-1}\,s^{-1}})$	−4.51	−3.35	−2.25	−1.07	−0.24	0.77	3.00	4.98

Now plot $\ln k_r$ against $1/T$ (Fig. 85.2). The least-squares fit results in a line with slope −22.7 and intercept 27.7. Therefore,

$$\begin{aligned} E_a &= 22.7\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(10^3\,\mathrm{K}) = 189\,\mathrm{kJ\,mol^{-1}} \\ A &= e^{27.7}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}} = 1.1\times10^{12}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}} \end{aligned}$$

Note that A has the same units as k_r.

Self-test 85.1 Determine A and E_a from the following data:

T/K	300	350	400	450	500
$k_r/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})$	7.9×10^6	3.0×10^7	7.9×10^7	1.7×10^8	3.2×10^8

Answer: $8\times10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, $23\,\mathrm{kJ\,mol^{-1}}$

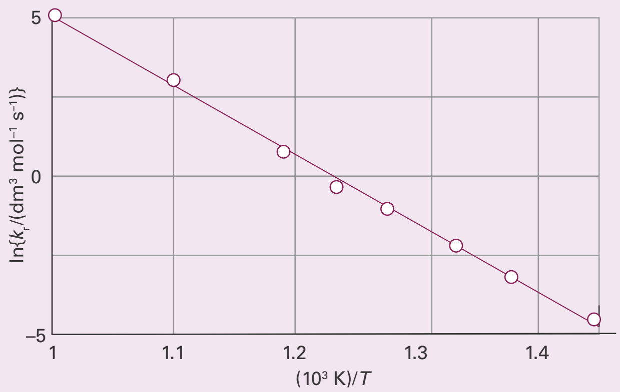

Figure 85.2 The Arrhenius plot using the data in Example 85.1.

Once the activation energy of a reaction is known, it is a simple matter to predict the value of a rate constant $k_{r,2}$ at a temperature T_2 from its value $k_{r,1}$ at another temperature T_1. To do so, we write

$$\ln k_{r,2} = \ln A - \frac{E_a}{RT_2}$$

and then subtract eqn 85.1 (with T identified as T_1 and k_r as $k_{r,1}$), so obtaining

$$\ln k_{r,2} - \ln k_{r,1} = -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

We can rearrange this expression to

$$\ln\frac{k_{r,2}}{k_{r,1}} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (85.2)$$

Temperature dependence of the rate constant

Brief illustration 85.1 The Arrhenius equation

For a reaction with an activation energy of 50 kJ mol⁻¹, an increase in the temperature from 25 °C to 37 °C (body temperature) corresponds to

$$\begin{aligned} \ln\frac{k_{r,2}}{k_{r,1}} &= \frac{50\times10^3\,\mathrm{J\,mol^{-1}}}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\left(\frac{1}{298\,\mathrm{K}} - \frac{1}{310\,\mathrm{K}}\right) \\ &= \frac{50\times10^3}{8.3145}\left(\frac{1}{298} - \frac{1}{310}\right) = 0.781\ldots \end{aligned}$$

By taking natural antilogarithms (that is, by forming e^x), $k_{r,2} = 2.18k_{r,1}$. This result corresponds to slightly more than a doubling of the rate constant as the temperature is increased from 298 K to 310 K.

Self-test 85.2 The activation energy of one of the reactions in a biochemical process is 87 kJ mol^{-1}. What is the change in rate constant when the temperature falls from 37 °C to 15 °C?

Answer: $k_r(15\,°C) = 0.076k_r(37\,°C)$

The fact that E_a is given by the slope of the plot of $\ln k_r$ against $1/T$ means that the stronger the temperature dependence of the rate constant (that is, the steeper the slope), the higher the activation energy. *A high activation energy signifies that the rate constant depends strongly on temperature.* If a reaction has zero activation energy, its rate is independent of temperature. In some cases the activation energy is negative, which indicates that the rate decreases as the temperature is raised.

The temperature dependence of some reactions is non-Arrhenius, in the sense that a straight line is not obtained when $\ln k_r$ is plotted against $1/T$. However, it is still possible to define an activation energy at any temperature as

$$E_a = RT^2\left(\frac{d\ln k_r}{dT}\right) \qquad \textit{Definition} \quad \text{Activation energy} \qquad (85.3)$$

This definition reduces to the earlier one (as the slope of a straight line) for a temperature-independent activation energy (see Problem 85.1). However, the definition in eqn 85.3 is more general than that in eqn 85.1, because it allows E_a to be obtained from the slope (at the temperature of interest) of a plot of $\ln k_r$ against $1/T$ even if the Arrhenius plot is not a straight line. Non-Arrhenius behaviour is sometimes a sign that quantum mechanical tunnelling (Topic 10) is playing a significant role in the reaction. In biological reactions it might signal that an enzyme has undergone a structural change and has become less efficient.

85.2 The interpretation of the Arrhenius parameters

For the present Topic we shall regard the Arrhenius parameters as purely empirical quantities that enable us to summarize the variation of rate constants with temperature. However, it is useful to have an interpretation in mind.

(a) A first look at the energy requirements of reactions

To interpret E_a we consider how the molecular potential energy changes in the course of a chemical reaction that begins with a collision between molecules of A and molecules of B (Fig. 85.3). In the gas phase, that is an actual collision; in solution, it is best regarded as a close encounter, possibly with excess energy, and might involve the solvent too. As the reaction event proceeds, A and B come into contact, distort, and begin to exchange or discard atoms. The **reaction coordinate** is the collection of motions, such as changes in interatomic distances and bond angles, that are directly involved in the formation of products from reactants. (The reaction coordinate is essentially a geometrical concept and quite distinct from the extent of reaction.) The potential energy rises to a maximum and the cluster of atoms that corresponds to the region close to the maximum is called the **activated complex**.

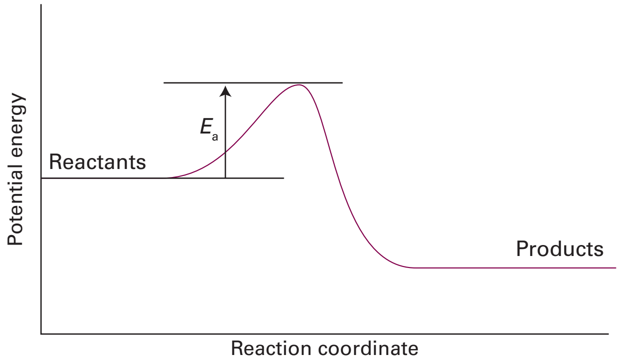

Figure 85.3 A potential energy profile for an exothermic reaction. The height of the barrier between the reactants and products is the activation energy of the reaction.

After the maximum, the potential energy falls as the atoms rearrange in the cluster, and reaches a value characteristic of the products. The climax of the reaction is at the peak of the potential energy, which corresponds to the activation energy E_a. Here two reactant molecules have come to such a degree of closeness and distortion that a small further distortion will send them in the direction of products. This crucial configuration is called the **transition state** of the reaction. Although some molecules entering the transition state might revert to reactants, if they pass through this configuration then it is inevitable that products will emerge from the encounter. (The terms 'activated complex' and 'transition state' are often used as synonyms; however, we shall preserve a distinction.)

We conclude from the preceding discussion that *the activation energy is the minimum energy reactants must have in order to form products.* For example, in a reaction mixture there are numerous molecular encounters each second, but only very few are sufficiently energetic to lead to reaction. The fraction of close encounters between reactants with energy in excess of E_a is given by the Boltzmann distribution (*Foundations*, Topic 2, and Topic 51) as $e^{-E_a/RT}$. This interpretation is confirmed by comparing this expression with the Arrhenius equation written in the form

$$k_r = Ae^{-E_a/RT} \qquad \textit{Alternative form} \quad \text{Arrhenius equation} \qquad (85.4)$$

which is obtained by taking antilogarithms of both sides of eqn 85.1. We show in the following *Justification* that the exponential factor in eqn 85.4 can be interpreted as the fraction of encounters that have enough energy to lead to reaction. This point is explored further for gas-phase reactions in Topic 87 and for reactions in solution in Topic 88.

Justification 85.1 Interpreting the activation energy

Suppose the energy levels available to the system form a uniform array of separation ε (Fig. 85.4). The Boltzmann distribution is

$$\frac{N_i}{N}=\frac{e^{-i\varepsilon\beta}}{q}=(1-e^{-\varepsilon\beta})e^{-i\varepsilon\beta}$$

where $\beta=1/kT$ and we have used the result in eqn 51.2b for the partition function q. The total number of molecules in states with energy of at least $\varepsilon_{\min}=i_{\min}\varepsilon$ is

$$\sum_{i=i_{\min}}^{\infty}N_i=\sum_{i=0}^{\infty}N_i-\sum_{i=0}^{i_{\min}-1}N_i=N-\frac{N}{q}\sum_{i=0}^{i_{\min}-1}e^{-i\varepsilon\beta}$$

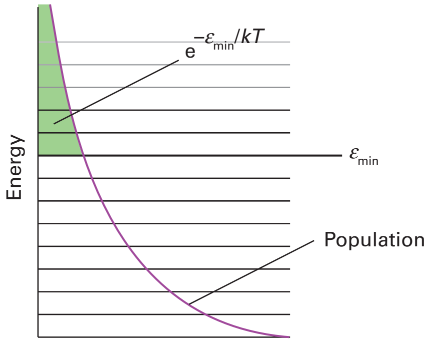

Figure 85.4 Equally spaced energy levels of an idealized system. As shown in *Justification* 85.1, the fraction of molecules with energy of at least $\varepsilon_{\min}$ is $e^{-\varepsilon_{\min}/kT}$.

The sum of the finite geometrical series is

$$\sum_{i=0}^{i_{\min}-1}e^{-i\varepsilon\beta}=\frac{1-e^{-i_{\min}\varepsilon\beta}}{1-e^{-\varepsilon\beta}}=q(1-e^{-i_{\min}\varepsilon\beta})$$

Therefore, the fraction of molecules in states with energy of at least $\varepsilon_{\min}=i_{\min}\varepsilon$ is

$$\frac{1}{N}\sum_{i=i_{\min}}^{\infty}N_i=1-(1-e^{-i_{\min}\varepsilon\beta})=e^{-i_{\min}\varepsilon\beta}$$
$$=e^{-\varepsilon_{\min}/kT}$$

Brief illustration 85.2 The fraction of reactive collisions

If we rewrite the equation for the fraction of molecules in states with energy of at least $\varepsilon_{\min}$ ($\frac{1}{N}\sum_{i=i_{\min}}^{\infty}N_i=e^{-\varepsilon_{\min}/kT}$, as in *Justification* 85.1) by

- multiplying $\varepsilon_{\min}$ and k by N_A, Avogadro's constant, and
- identifying $N_A\varepsilon_{\min}$ with E_a,

then the fraction f of molecular collisions that occur with a kinetic energy E_a becomes $f=e^{-E_a/RT}$. With $E_a=50\,\text{kJ mol}^{-1}=5.0\times10^4\,\text{J mol}^{-1}$ and $T=298\,\text{K}$, we calculate

$$f=e^{-(5.0\times10^4\,\text{J mol}^{-1})/(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}\times298\,\text{K})}=1.7\times10^{-99}$$

Self-test 85.3 At what temperature would $f=0.10$ if $E_a=50\,\text{kJ mol}^{-1}$?

Answer: 2612 K

The pre-exponential factor is a measure of the rate at which collisions occur irrespective of their energy. Hence, the product of A and the exponential factor, $e^{-E_a/RT}$, gives the rate of *successful* collisions. We develop these remarks in Topics 87 and 88 and see that they have their analogues for reactions that take place in liquids.

(b) The effect of a catalyst on the activation energy

The Arrhenius equation tells us that the rate constant of a reaction can be increased by increasing the temperature or by decreasing the energy of activation. Changing the temperature of a reaction mixture is an easy strategy. Reducing the energy of activation requires more effort, but is possible if a reaction takes place in the presence of a suitable **catalyst**, a substance that accelerates a reaction but undergoes no net chemical change. The catalyst lowers the activation energy of the reaction by providing an alternative path that avoids the slow, rate-determining step of the uncatalysed reaction (Fig 85.5). Catalysis is discussed further in Topics 92 and 97.

Brief illustration 85.3 The effect of a catalyst on the rate constant

Enzymes are biological catalysts. For example, the enzyme catalase reduces the activation energy for the decomposition of hydrogen peroxide from $76\,\text{kJ mol}^{-1}$ to $8\,\text{kJ mol}^{-1}$. From eqn

85.4 and assuming that the exponential factor is the same in both cases, it follows that the ratio of rate constants is

$$\frac{k_{\mathrm{r,\ catalysed}}}{k_{\mathrm{r,\ uncatalysed}}}=\frac{A\mathrm{e}^{-E_{\mathrm{a,catalysed}}/RT}}{A\mathrm{e}^{-E_{\mathrm{a,\ uncatalysed}}/RT}}=\mathrm{e}^{-(E_{\mathrm{a,\ catalysed}}-E_{\mathrm{a,\ uncatalysed}})/RT}$$

$$=\mathrm{e}^{(68\times10^{33}\,\mathrm{J\,mol^{-1}})/(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})}=8.3\times10^{11}$$

Self-test 85.4 Consider the decomposition of hydrogen peroxide, which can be catalysed in solution by iodide ion. By how much is the activation energy of the reaction reduced if the rate constant of reaction increases by a factor of 2000 at 298 K upon addition of the catalyst?

Answer: 25 per cent

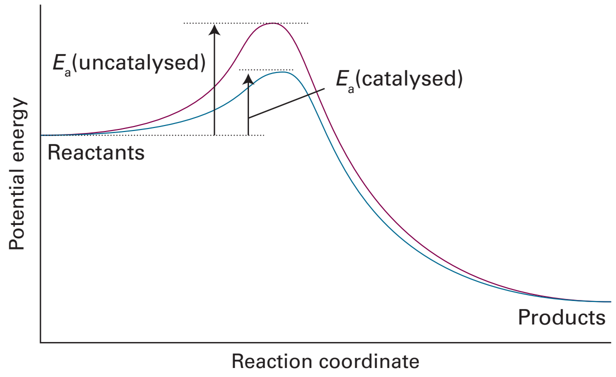

Figure 85.5 A catalyst provides a different path with a lower activation energy. The result is an increase in the rate of formation of products.

Checklist of concepts

☐ 1. The **activation energy**, the parameter E_a in the **Arrhenius equation**, is the minimum energy of close molecular encounters able to result in reaction.

☐ 2. The larger the activation energy, the more sensitive the rate constant is to the temperature.

☐ 3. The **pre-exponential factor** is a measure of the rate at which encounters occur irrespective of their energy.

☐ 4. A **catalyst** lowers the activation energy of a reaction.

Checklist of equations

Property	Equation	Comment	Equation number
Arrhenius equation	$\ln k_r = \ln A - E_a/RT$	Empirical observation	85.1
Activation energy	$E_a = RT^2(\mathrm{d}\ln k_r/\mathrm{d}T)$	Definition	85.3
Arrhenius equation	$k_r = A\mathrm{e}^{-E_a/RT}$	Alternative form	85.4

TOPIC 86

Reaction mechanisms

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➤ Why do you need to know this material?

The mechanism of a reaction not only explains why specific products are formed but also allows for careful consideration of how the yield of desired products can be optimized. It also gives insight into the atomic processes going on when reactions take place.

➤ What is the key idea?

Most chemical reactions occur as a sequence of simpler steps, with corresponding rate laws that can be combined together by applying one or more approximations.

➤ What do you need to know already?

You need to be familiar with the concept of rate laws (Topic 82) and how to integrate them (Topics 83 and 84). You also need to be familiar with the Arrhenius equation (Topic 85). Only standard techniques of calculus are necessary to make progress with mathematical analysis of rate laws.

The **mechanism** of a reaction is its analysis into a sequence of elementary steps. Here we see how simple elementary steps with simple rate laws can be combined by invoking one or more approximations.

86.1 Elementary reactions

Most reactions occur in a sequence of steps called **elementary reactions**, each of which involves only a small number of molecules or ions. A typical elementary reaction is

$$\mathrm{H} + \mathrm{Br}_2 \rightarrow \mathrm{HBr} + \mathrm{Br}$$

Note that the phase of the species is not specified in the chemical equation for an elementary reaction, and the equation represents the specific process occurring to individual molecules. This equation, for instance, signifies that an H atom attacks a Br_2 molecule to produce an HBr molecule and a Br atom. The **molecularity** of an elementary reaction is the number of molecules coming together to react in an elementary reaction. In a **unimolecular reaction**, a single molecule shakes itself apart or its atoms into a new arrangement, as in the isomerization of cyclopropane to propene. In a **bimolecular reaction** (as in the above elementary reaction), a pair of molecules collide and exchange energy, atoms, or groups of atoms, or undergo some other kind of change. It is most important to distinguish molecularity from order:

- *reaction order* is an empirical quantity, and obtained from the experimental rate law;
- *molecularity* refers to an elementary reaction proposed as an individual step in a mechanism.

The rate law of a unimolecular elementary reaction is first-order in the reactant:

$$A \rightarrow P \qquad \frac{d[A]}{dt} = -k_r[A] \tag{86.1}$$

Unimolecular elementary reaction

where P denotes products (several different species may be formed). A unimolecular reaction is first-order because the number of A molecules that decay in a short interval is proportional to the number available to decay. For instance, ten times as many decay in the same interval when there are initially 1000 A molecules as when there are only 100 present. Therefore, the rate of decomposition of A is proportional to its molar concentration at any moment during the reaction.

An elementary bimolecular reaction has a second-order rate law:

$$A + B \rightarrow P \qquad \frac{d[A]}{dt} = -k_r[A][B] \tag{86.2}$$

Bimolecular elementary reaction

A bimolecular reaction is second-order because its rate is proportional to the rate at which the reactant species meet, which in turn is proportional to their concentrations. Therefore, if we have evidence that a reaction is a single-step, bimolecular process, we can write down the rate law (and then go on to test it).

Brief illustration 86.1 The rate laws of elementary steps

Bimolecular elementary reactions are believed to account for many homogeneous reactions, such as the dimerization of alkenes and dienes and reactions such as

$$CH_3I(alc) + CH_3CH_2O^-(alc) \rightarrow CH_3OCH_2CH_3(alc) + I^-(alc)$$

(where 'alc' signifies alcohol solution). There is evidence that the mechanism of this reaction is a single elementary step:

$$CH_3I + CH_3CH_2O^- \rightarrow CH_3OCH_2CH_3 + I^-$$

This bimolecular mechanism is consistent with the observed rate law

$$v = k_r[CH_3I][CH_3CH_2O^-]$$

Self-test 86.1 The following are elementary processes: (a) the dimerization of NO(g) to form $N_2O_2(g)$, and (b) the decomposition of the $N_2O_2(g)$ dimer into NO(g) molecules. Write the rate laws for these processes.

Answer: (a) bimolecular process: $k_r[NO]^2$, (b) unimolecular process: $k_r[N_2O_2]$

We see in the following sections how to combine a series of simple steps into an overall mechanism and how to arrive at the corresponding overall rate law. For the present we emphasize that, *if the reaction is an elementary bimolecular process, then it has second-order kinetics, but if the kinetics is second-order, then the reaction might occur through the formation of a complex mechanism*. The postulated mechanism can be explored only by detailed detective work on the system, and by investigating whether side products or intermediates appear during the course of the reaction. Detailed analysis of this kind was one of the ways, for example, in which the reaction $H_2(g) + I_2(g) \rightarrow 2\,HI(g)$ was shown to proceed by a complex mechanism. For many years the reaction had been accepted on good, but insufficiently meticulous, evidence as a fine example of a simple bimolecular reaction, $H_2 + I_2 \rightarrow HI + HI$, in which atoms exchanged partners during a collision.

86.2 Consecutive elementary reactions

Some reactions proceed through the formation of an intermediate (I), as in the consecutive unimolecular reactions

$$A \xrightarrow{k_a} I \xrightarrow{k_b} P$$

Note that the intermediate occurs in the reaction steps but does not appear in the overall reaction, which in this case is A → P. An example of this type of mechanism is the decay of a radioactive family, such as

$$^{239}U \xrightarrow{23.5\,\text{min}} {}^{239}Np \xrightarrow{2.35\,\text{days}} {}^{239}Pu$$

(The times are half-lives.) The characteristics of this type of reaction are discovered by setting up the rate laws for the net rate of change of the concentration of each substance.

The rate of unimolecular decomposition of A is

$$\frac{d[A]}{dt} = -k_a[A] \tag{86.3a}$$

and A is not replenished. The intermediate I is formed from A (at a rate $k_a[\mathrm{A}]$) but decays to P (at a rate $k_b[\mathrm{I}]$). The net rate of formation of I is therefore

$$\frac{\mathrm{d[I]}}{\mathrm{d}t}=k_a[\mathrm{A}]-k_b[\mathrm{I}] \qquad (86.3b)$$

The product P is formed by the unimolecular decay of I:

$$\frac{\mathrm{d[P]}}{\mathrm{d}t}=k_b[\mathrm{I}] \qquad (86.3c)$$

We suppose that initially only A is present, and that its concentration is $[\mathrm{A}]_0$.

The first of the rate laws, eqn 86.3a, is an ordinary first-order decay, so we can write

$$[\mathrm{A}]=[\mathrm{A}]_0\,\mathrm{e}^{-k_a t} \qquad (86.4a)$$

When this equation is substituted into eqn 86.3b, we obtain after rearrangement

$$\frac{\mathrm{d[I]}}{\mathrm{d}t}+k_b[\mathrm{I}]=k_a[\mathrm{A}]_0\,\mathrm{e}^{-k_a t}$$

This differential equation has a standard form (see *Mathematical background* 2) and, after setting $[\mathrm{I}]_0=0$, the solution is

$$[\mathrm{I}]=\frac{k_a}{k_b-k_a}\left(\mathrm{e}^{-k_a t}-\mathrm{e}^{-k_b t}\right)[\mathrm{A}]_0 \qquad (86.4b)$$

At all times $[\mathrm{A}]+[\mathrm{I}]+[\mathrm{P}]=[\mathrm{A}]_0$, so it follows that

$$[\mathrm{P}]=\left\{1+\frac{k_a\mathrm{e}^{-k_b t}-k_b\mathrm{e}^{-k_a t}}{k_b-k_a}\right\}[\mathrm{A}]_0 \qquad (86.4c)$$

The concentration of the intermediate I rises to a maximum and then falls to zero (Fig. 86.1). The concentration of the product P rises from zero towards $[\mathrm{A}]_0$.

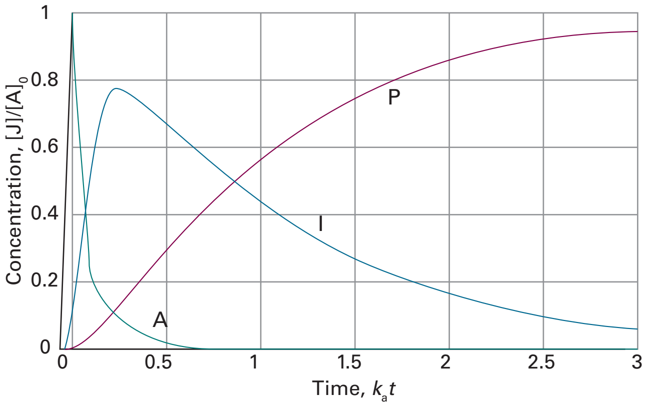

Figure 86.1 The concentrations of A, I, and P in the consecutive reaction scheme A → I → P. The curves are plots of eqns 86.4a–c with $k_a=10k_b$. If the intermediate I is in fact the desired product, it is important to predict when its concentration is greatest; see Example 86.1.

Example 86.1 Analysing consecutive reactions

Suppose that in an industrial batch process a substance A produces the desired compound I which goes on to decay to a worthless product C, each step of the reaction being first-order. At what time will I be present in greatest concentration?

Method The time dependence of the concentration of I is given by eqn 86.4b. We can find the time $t_{\max}$, at which [I] passes through a maximum, by calculating d[I]/dt and setting the resulting rate equal to zero.

Answer It follows from eqn 86.4b that

$$\frac{\mathrm{d[I]}}{\mathrm{d}t}=-\frac{k_a\left(k_a\mathrm{e}^{-k_a t}-k_b\mathrm{e}^{-k_b t}\right)[\mathrm{A}]_0}{k_b-k_a}$$

This rate is equal to zero when $k_a\mathrm{e}^{-k_a t}=k_b\mathrm{e}^{-k_b t}$. Therefore,

$$t_{\max}=\frac{1}{k_a-k_b}\ln\frac{k_a}{k_b}$$

For a given value of k_a, as k_b increases both the time at which [I] is a maximum and the yield of I decrease.

Self-test 86.2 Develop an expression for the maximum concentration of I and justify the last remark.

Answer: $[\mathrm{I}]_{\max}/[\mathrm{A}]_0=(k_a/k_b)^c$, $c=k_b/(k_b-k_a)$

86.3 The steady-state approximation

One feature of the calculation so far has probably not gone unnoticed: there is a considerable increase in mathematical complexity as soon as the reaction mechanism has more than a couple of steps. A reaction scheme involving many steps is nearly always unsolvable analytically, and alternative methods of solution are necessary. One approach is to integrate the rate laws numerically. An alternative approach, which continues to be widely used because it leads to convenient expressions and more readily digestible results, is to make an approximation.

The **steady-state approximation** (which is also widely called the **quasi-steady-state approximation**, QSSA, to distinguish it from a true steady state) assumes that, after an initial **induction period**, an interval during which the concentrations of intermediates, I, rise from zero, and during the major part of the reaction, the rates of change of concentrations of all reaction intermediates are negligibly small (Fig. 86.2):

$$\frac{\mathrm{d[I]}}{\mathrm{d}t}\approx 0 \qquad (86.5)$$

Steady-state approximation

This approximation greatly simplifies the discussion of reaction schemes. For example, when we apply the approximation to the

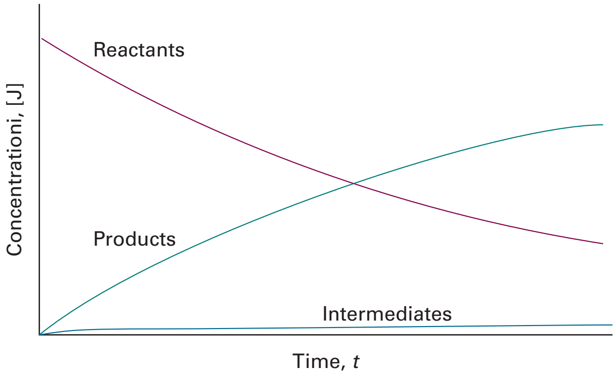

Figure 86.2 The basis of the steady-state approximation. It is supposed that the concentrations of intermediates remain small and hardly change during most of the course of the reaction.

consecutive first-order mechanism, we set $d[I]/dt=0$ in eqn 86.3b, which then becomes $k_a[A]-k_b[I]=0$. Then

$$[I]=(k_a/k_b)[A] \tag{86.6}$$

For this expression to be consistent with eqn 86.4b, we require $k_a/k_b \ll 1$ (so that, even though [A] does depend on the time, the dependence of [I] on the time is negligible). On substituting this value of [I] into eqn 86.3c, that equation becomes

$$\frac{d[P]}{dt}=k_b[I]\approx k_a[A] \tag{86.7}$$

and we see that P is formed by a first-order decay of A, with a rate constant k_a, the rate constant of the slower step. We can write down the solution of this equation at once by substituting the solution for [A], eqn 86.4a, and integrating:

$$[P]=k_a[A]_0\int_0^t e^{-k_at}\,dt=(1-e^{-k_at})[A]_0 \tag{86.8}$$

This is the same (approximate) result as before, eqn 86.4c (when $k_b \gg k_a$), but much more quickly obtained. Figure 86.3 compares the approximate solutions found here with the exact solutions found earlier: k_b does not have to be very much bigger than k_a for the approach to be reasonably accurate.

Example 86.2 Using the steady-state approximation

Devise the rate law for the decomposition of N_2O_5,

$$2\,N_2O_5(g) \rightarrow 4\,NO_2(g)+O_2(g)$$

on the basis of the following mechanism:

$N_2O_5 \rightarrow NO_2+NO_3$	k_a
$NO_2+NO_3 \rightarrow N_2O_5$	k_a'
$NO_2+NO_3 \rightarrow NO_2+O_2+NO$	k_b
$NO+N_2O_5 \rightarrow NO_2+NO_2+NO_2$	k_c

A note on good practice Note that when writing the equation for an elementary reaction all the species are displayed individually; so we write $A \rightarrow B+B$, for instance, not $A \rightarrow 2B$. Also, addition of the equations for the forward elementary steps must result in the overall balanced chemical equation.

Method First, identify the intermediates and write expressions for their net rates of formation. Then, all net rates of change of the concentrations of intermediates are set equal to zero and the resulting equations are solved algebraically.

Answer The intermediates are NO and NO_3; the net rates of change of their concentrations are

$$\frac{d[NO]}{dt}=k_b[NO_2][NO_3]-k_c[NO][N_2O_5]\approx 0$$
$$\frac{d[NO_3]}{dt}=k_a[N_2O_5]-k_a'[NO_2][NO_3]-k_b[NO_2][NO_3]\approx 0$$

The net rate of change of concentration of N_2O_5 is

$$\frac{d[N_2O_5]}{dt}=-k_a[N_2O_5]+k_a'[NO_2][NO_3]-k_c[NO][N_2O_5]$$

We use

$$k_b[NO_2][NO_3]-k_c[NO][N_2O_5]\approx 0$$

from the first of these rate laws and

$$k_a[N_2O_5]-k_a'[NO_2][NO_3]-k_b[NO_2][NO_3]\approx 0$$

from the second to write

$$[NO]=\frac{k_b[NO_2][NO_3]}{k_c[N_2O_5]} \qquad [NO_3]=\frac{k_a[N_2O_5]}{(k_a'+k_b)[NO_2]}$$

and then substitute these expressions into that for $d[N_2O_5]/dt$ to obtain

$$\frac{d[N_2O_5]}{dt}=-\frac{2k_ak_b[N_2O_5]}{k_a'+k_b}$$

Self-test 86.3 Derive the rate law for the decomposition of ozone in the reaction $2\,O_3(g) \rightarrow 3\,O_2(g)$ on the basis of the (incomplete) mechanism

$O_3 \rightarrow O_2+O$	k_a
$O_2+O \rightarrow O_3$	k_a'
$O+O_3 \rightarrow O_2+O_2$	k_b

Answer: $d[O_3]/dt=-2k_ak_b[O_3]^2/(k_a'[O_2]+k_b[O_3])$

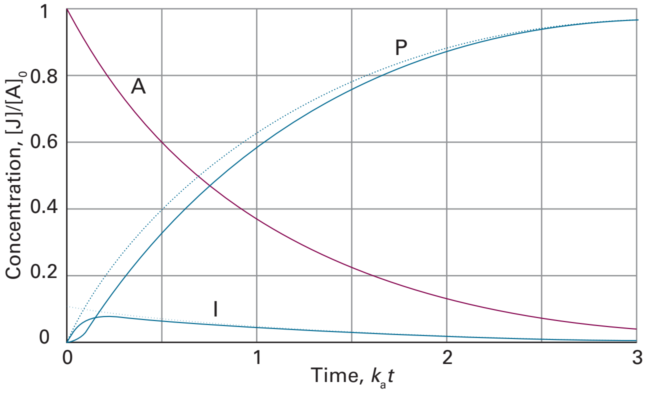

Figure 86.3 A comparison of the exact result for the concentrations of a consecutive reaction and the concentrations obtained by using the steady-state approximation (dotted lines) for $k_b = 20k_a$. (The curve for [A] is unchanged.)

86.4 The rate-determining step

Equation 86.8 shows that when $k_b \gg k_a$ the formation of the final product P depends on only the *smaller* of the two rate constants. That is, the rate of formation of P depends on the rate at which I is formed, not on the rate at which I changes into P. For this reason, the step $A \rightarrow I$ is called the 'rate-determining step' of the reaction. Its existence has been likened to building a six-lane highway up to a single-lane bridge: the traffic flow is governed by the rate of crossing the bridge. Similar remarks apply to more complicated reaction mechanisms, and in general the **rate-determining step** is the slowest step in a mechanism and controls the overall rate of the reaction. However, the rate-determining step is not just the slowest step: it must be slow *and* be a crucial gateway for the formation of products. If a faster reaction can also lead to products, then the slowest step is irrelevant because the slow reaction can then be sidestepped (Fig. 86.4).

The rate law of a reaction that has a rate-determining step can often—but certainly not always—be written down almost by inspection. If the first step in a mechanism is rate-determining, then the rate of the overall reaction is equal to the rate of the first step because all subsequent steps are so fast that once the first intermediate is formed it results immediately in the formation of products. Figure 86.5 shows the reaction profile for a mechanism of this kind in which the slowest step is the one with the highest activation energy. Once over the initial barrier, the intermediates cascade into products. However, a rate-determining step may also stem from the low concentration of a crucial reactant and need not correspond to the step with the highest activation barrier.

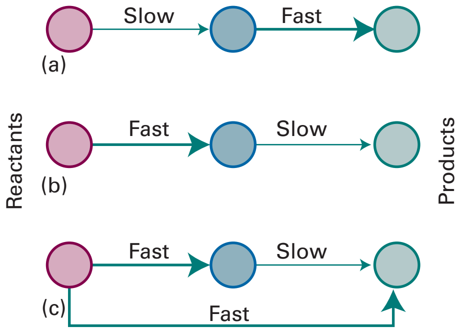

Figure 86.4 In these diagrams of reaction schemes, heavy arrows represent fast steps and light arrows represent slow steps. (a) The first step is rate-determining; (b) the second step is rate-determining; (c) although one step is slow, it is not rate-determining because there is a fast route that circumvents it.

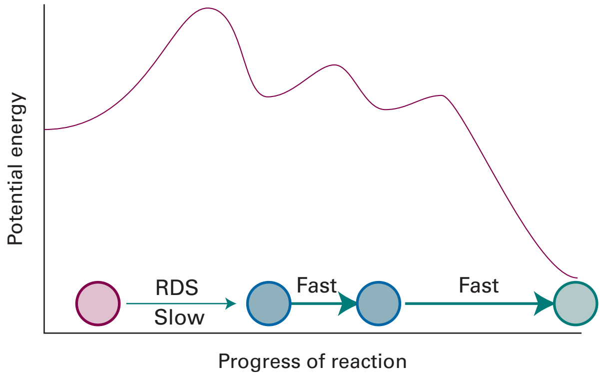

Figure 86.5 The reaction profile for a mechanism in which the first step (RDS) is rate-determining.

Brief illustration 86.2 The rate law of a mechanism with a rate-determining step

The oxidation of NO(g) to NO_2 proceeds by the following mechanism:

$$\begin{array}{ll} NO + NO \rightarrow N_2O_2 & k_a \\ N_2O_2 \rightarrow NO + NO & k_a' \\ N_2O_2 + O_2 \rightarrow NO_2 + NO_2 & k_b \end{array}$$

with rate law (see Self-test 86.4)

$$\frac{d[NO_2]}{dt} = \frac{2k_ak_b[NO]^2[O_2]}{k_a' + k_b[O_2]}$$

When the concentration of O_2 in the reaction mixture is so large that the third step is very fast, so that $[O_2]k_b \gg k_a'$, then the rate law simplifies to

$$\frac{d[NO_2]}{dt} = 2k_a[NO]^2$$

and the formation of N_2O_2 in the first step is rate-determining. We could have written the rate law by inspection of the mechanism, because the rate law for the overall reaction is simply the rate law of that rate-determining step.

Self-test 86.4 Verify that application of the steady-state approximation to the intermediate N_2O_2 results in the rate law.

86.5 Pre-equilibria

From a simple sequence of consecutive reactions we now turn to a slightly more complicated mechanism in which an intermediate I reaches an equilibrium with the reactants A and B:

$$\mathrm{A}+\mathrm{B} \rightleftharpoons \mathrm{I} \rightarrow \mathrm{P} \tag{86.9}$$

Pre-equilibrium

The rate constants are k_a and k_a' for the forward and reverse reactions of the equilibrium and k_b for the final step. This scheme involves a **pre-equilibrium**, in which an intermediate is in equilibrium with the reactants. A pre-equilibrium can arise when the rate of decay of the intermediate back into reactants is much faster than the rate at which it forms products; thus, the condition is possible when $k_a' \gg k_b$ but not when $k_b \gg k_a'$. Because we assume that A, B, and I are in equilibrium, we can write

$$K=\frac{[\mathrm{I}]}{[\mathrm{A}][\mathrm{B}]} \quad \text{with} \quad K=\frac{k_a}{k_a'} \tag{86.10}$$

In writing these equations, we are presuming that the rate of reaction of I to form P is too slow to affect the maintenance of the pre-equilibrium (see the example below). We are also ignoring the fact, as is commonly done, that the standard concentration $c^{\ominus}$ should appear in the expression for K to ensure that it is dimensionless. The rate of formation of P may now be written

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t}=k_b[\mathrm{I}]=k_bK[\mathrm{A}][\mathrm{B}] \tag{86.11}$$

This rate law has the form of a second-order rate law with rate constant that is a combination of the rate constants of the elementary steps:

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t}=k_r[\mathrm{A}][\mathrm{B}] \quad \text{with} \quad k_r=k_bK=\frac{k_ak_b}{k_a'} \tag{86.12}$$

Example 86.3 Analysing a pre-equilibrium

Repeat the pre-equilibrium calculation but without ignoring the fact that I is slowly leaking away as it forms P.

Method Begin by writing the net rates of change of the concentrations of the substances and then invoke the steady-state approximation for the intermediate I. Use the resulting expression to obtain the rate of change of the concentration of P.

Answer The net rates of change of P and I are

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t}=k_b[\mathrm{I}]$$
$$\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t}=k_a[\mathrm{A}][\mathrm{B}]-k_a'[\mathrm{I}]-k_b[\mathrm{I}]\approx 0$$

The second equation solves to

$$[\mathrm{I}]\approx\frac{k_a[\mathrm{A}][\mathrm{B}]}{k_a'+k_b}$$

When we substitute this result into the expression for the rate of formation of P, we obtain

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t}\approx k_r[\mathrm{A}][\mathrm{B}] \quad \text{with} \quad k_r=\frac{k_ak_b}{k_a'+k_b}$$

This expression reduces to that in eqn 86.12 when the rate constant for the decay of I into products is much smaller than that for its decay into reactants, $k_b \ll k_a'$.

Self-test 86.5 Show that the pre-equilibrium mechanism in which $2\,\mathrm{A} \rightleftharpoons \mathrm{I}$ (K) followed by $\mathrm{I}+\mathrm{B} \rightarrow \mathrm{P}$ (k_b) results in an overall third-order reaction.

Answer: $\mathrm{d}[\mathrm{P}]/\mathrm{d}t=k_bK[\mathrm{A}]^2[\mathrm{B}]$

One feature to note is that, although each of the rate constants in eqn 86.12 increases with temperature, that might not be true of k_r itself. Thus, if the rate constant k_a' increases more rapidly than the product k_ak_b increases, then k_r will decrease with increasing temperature and the reaction will go more slowly as the temperature is raised. Mathematically, we would say that the composite reaction had a 'negative activation energy'. For example, suppose that each rate constant in eqn 86.12 exhibits an Arrhenius temperature dependence (Topic 85). It follows from the Arrhenius equation (eqn 85.4, $k_r=A\mathrm{e}^{-E_a/RT}$) that

$$k_r=\frac{\left(A_a\mathrm{e}^{-E_{a,a}/RT}\right)\left(A_b\mathrm{e}^{-E_{a,b}/RT}\right)}{A_{a'}\mathrm{e}^{-E_{a,a'}/RT}}=\frac{A_aA_b}{A_{a'}}\mathrm{e}^{-\left(E_{a,a}+E_{a,b}-E_{a,a'}\right)/RT}$$

where we have used the relations: $\mathrm{e}^{x+y}=\mathrm{e}^x\mathrm{e}^y$ and $\mathrm{e}^{x-y}=\mathrm{e}^x/\mathrm{e}^y$. The effective activation energy of the reaction is therefore

$$E_a=E_{a,a}+E_{a,b}-E_{a,a'} \tag{86.13}$$

This activation energy is positive if $E_{a,a}+E_{a,b}>E_{a,a'}$ (Fig. 86.6a) but negative if $E_{a,a'}>E_{a,a}+E_{a,b}$ (Fig. 86.6b). An important

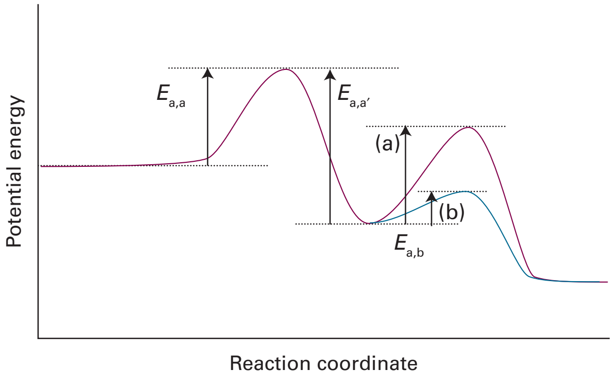

Figure 86.6 For a reaction with a pre-equilibrium, there are three activation energies to take into account: two referring to the reversible steps of the pre-equilibrium and one for the final step. The relative magnitudes of the activation energies determine whether the overall activation energy is (a) positive or (b) negative.

consequence of this discussion is that we have to be very cautious about making predictions about the effect of temperature on reactions that are the outcome of several steps.

86.6 Kinetic and thermodynamic control of reactions

In some cases reactants can give rise to a variety of products, as in nitrations of mono-substituted benzene, when various proportions of the *ortho*-, *meta*-, and *para*-substituted products are obtained, depending on the directing power of the original substituent. Suppose two products, P_1 and P_2, are produced by the following competing reactions:

$$A+B \rightarrow P_1 \qquad v(P_1)=k_{r,1}[A][B]$$
$$A+B \rightarrow P_2 \qquad v(P_2)=k_{r,2}[A][B]$$

The relative proportion in which the two products have been produced at a given stage of the reaction (before it has reached equilibrium) is given by the ratio of the two rates, and therefore of the two rate constants:

$$\frac{[P_2]}{[P_1]}=\frac{k_{r,2}}{k_{r,1}} \qquad \text{Kinetic control} \qquad (86.14)$$

This ratio represents the **kinetic control** over the proportions of products, and is a common feature of the reactions encountered in organic chemistry where reactants are chosen that facilitate pathways favouring the formation of a desired product. If a reaction is allowed to reach equilibrium, then the proportion of products is determined by thermodynamic rather than kinetic considerations, and the ratio of concentrations is controlled by considerations of the standard Gibbs energies of all the reactants and products.

Brief illustration 86.3 The outcome of kinetic control

Consider two products formed from reactant R in reactions for which (a) product P_1 is thermodynamically more stable than product P_2, and (b) the activation energy E_a for the reaction leading to P_2 is greater than that leading to P_1. It follows from eqn 86.14 and the Arrhenius equation ($k_r = Ae^{-E_a/RT}$, eqn 85.4) that the ratio of products is

$$\frac{[P_2]}{[P_1]}=\frac{k_2}{k_1}=\frac{A_2e^{-E_{a,2}/RT}}{A_1e^{-E_{a,1}/RT}}=\frac{A_2}{A_1}e^{-(E_{a,2}-E_{a,1})/RT}=\frac{A_2}{A_1}e^{-\Delta E_a/RT}$$

Because $\Delta E_a = E_{a,2} - E_{a,1} > 0$, as T increases

- the term $\Delta E_a/RT$ decreases, and
- the term $e^{-\Delta E_a/RT}$ increases.

Consequently, the ratio $[P_2]/[P_1]$ increases with increasing temperature before equilibrium is reached.

Self-test 86.6 Consider the reactions from *Brief illustration* 86.3. Derive an expression for the ratio $[P_2]/[P_1]$ when the reaction is under thermodynamic control. State your assumptions.

Answer: $[P_2]/[P_1]=e^{-(\Delta_r G_2^{\ominus}-\Delta_r G_1^{\ominus})/RT}$, assuming that activities can be replaced by concentrations

Checklist of concepts

☐ 1. The **mechanism** of reaction is the sequence of elementary steps involved in a reaction.
☐ 2. The **molecularity** of an elementary reaction is the number of molecules coming together to react.
☐ 3. An elementary unimolecular reaction has first-order kinetics; an elementary bimolecular reaction has second-order kinetics.
☐ 4. The **rate-determining step** is the slowest step in a reaction mechanism that controls the rate of the overall reaction.
☐ 5. In the **steady-state approximation**, it is assumed that the concentrations of all reaction intermediates remain constant and small throughout the reaction.
☐ 6. **Pre-equilibrium** is a state in which an intermediate is in equilibrium with the reactants and which arises

when the rates of formation of the intermediate and its decay back into reactants are much faster than its rate of formation of products.

☐ 7. Provided a reaction has not reached equilibrium, the products of competing reactions are controlled by kinetics.

Checklist of equations

Property	Equation	Comment	Equation number
Unimolecular reaction	$\mathrm{d}[\mathrm{A}]/\mathrm{d}t=-k_\mathrm{r}[\mathrm{A}]$	$\mathrm{A}\rightarrow\mathrm{P}$	86.1
Bimolecular reaction	$\mathrm{d}[\mathrm{A}]/\mathrm{d}t=-k_\mathrm{r}[\mathrm{A}][\mathrm{B}]$	$\mathrm{A}+\mathrm{B}\rightarrow\mathrm{P}$	86.2
Consecutive reactions	$[\mathrm{A}]=[\mathrm{A}]_0\mathrm{e}^{-k_\mathrm{a}t}$ $[\mathrm{I}]=(k_\mathrm{a}/(k_\mathrm{b}-k_\mathrm{a}))(\mathrm{e}^{-k_\mathrm{a}t}-\mathrm{e}^{-k_\mathrm{b}t})[\mathrm{A}]_0$ $[\mathrm{P}]=\{(1+(k_\mathrm{a}\mathrm{e}^{-k_\mathrm{b}t}-k_\mathrm{b}\mathrm{e}^{-k_\mathrm{a}t})/(k_\mathrm{b}-k_\mathrm{a}))\}[\mathrm{A}]_0$	$\mathrm{A}\xrightarrow{k_\mathrm{a}}\mathrm{I}\xrightarrow{k_\mathrm{b}}\mathrm{P}$	86.4
Steady-state approximation	$\mathrm{d}[\mathrm{I}]/\mathrm{d}t\approx 0$	I is an intermediate	86.5

Focus 17 on Chemical kinetics

Topic 82 Reaction rates

Discussion question

82.1 Distinguish between zeroth-order, first-order, second-order, and pseudofirst-order reactions and illustrate how reaction orders may change under different circumstances.

Exercises

82.1(a) Predict how the total pressure varies during the gas-phase reaction $2\ \mathrm{ICl(g)} + \mathrm{H_2(g)} \rightarrow \mathrm{I_2(g)} + 2\ \mathrm{HCl(g)}$ in a constant-volume container.
82.1(b) Predict how the total pressure varies during the gas-phase reaction $\mathrm{N_2(g)} + 3\ \mathrm{H_2(g)} \rightarrow 2\ \mathrm{NH_3(g)}$ in a constant-volume container.

82.2(a) The rate of the reaction $\mathrm{A} + 2\ \mathrm{B} \rightarrow 3\ \mathrm{C} + \mathrm{D}$ was reported as 2.7 mol dm^{-3} s^{-1}. State the rates of formation and consumption of the participants.
82.2(b) The rate of the reaction $\mathrm{A} + 3\ \mathrm{B} \rightarrow \mathrm{C} + 2\ \mathrm{D}$ was reported as 2.7 mol dm^{-3} s^{-1}. State the rates of formation and consumption of the participants.

82.3(a) The rate of formation of C in the reaction $2\ \mathrm{A} + \mathrm{B} \rightarrow 2\ \mathrm{C} + 3\ \mathrm{D}$ is 2.7 mol dm^{-3} s^{-1}. State the reaction rate, and the rates of formation or consumption of A, B, and D.
82.3(b) The rate of consumption of B in the reaction $\mathrm{A} + 3\ \mathrm{B} \rightarrow \mathrm{C} + 2\ \mathrm{D}$ is 2.7 mol dm^{-3} s^{-1}. State the reaction rate, and the rates of formation or consumption of A, C, and D.

82.4(a) The rate law for the reaction in Exercise 82.2(a) was found to be $v = k_r[\mathrm{A}][\mathrm{B}]$. What are the units of k_r? Express the rate law in terms of the rates of formation and consumption of (a) A, (b) C.
82.4(b) The rate law for the reaction in Exercise 82.2(b) was found to be $v = k_r[\mathrm{A}][\mathrm{B}]^2$. What are the units of k_r? Express the rate law in terms of the rates of formation and consumption of (a) A, (b) C.

82.5(a) The rate law for the reaction in Exercise 82.3(a) was reported as $\mathrm{d}[\mathrm{C}]/\mathrm{d}t = k_r[\mathrm{A}][\mathrm{B}][\mathrm{C}]$. Express the rate law in terms of the reaction rate v; what are the units for k_r in each case?
82.5(b) The rate law for the reaction in Exercise 82.3(b) was reported as $\mathrm{d}[\mathrm{C}]/\mathrm{d}t = k_r[\mathrm{A}][\mathrm{B}][\mathrm{C}]^{-1}$. Express the rate law in terms of the reaction rate v; what are the units for k_r in each case?

82.6(a) If the rate laws are expressed with (a) concentrations in moles per decimetre cubed, (b) pressures in kilopascals, what are the units of the second-order and third-order rate constants?
82.6(b) If the rate laws are expressed with (a) concentrations in molecules per metre cubed, (b) pressures in pascals, what are the units of the second-order and third-order rate constants?

Problem

82.1 At 400 K, the rate of decomposition of a gaseous compound initially at a pressure of 12.6 kPa was 9.71 Pa s^{-1} when 10.0 per cent had reacted, and 7.67 Pa s^{-1} when 20.0 per cent had reacted. Determine the order of the reaction.

Topic 83 Integrated rate laws

Discussion question

83.1 Describe the main features, including advantages and disadvantages, of the following experimental methods for determining the rate law of a reaction: the isolation method, the method of initial rates, and fitting data to integrated rate law expressions.

Exercises

83.1(a) At 518 °C, the half-life for the decomposition of a sample of gaseous acetaldehyde (ethanal) initially at 363 Torr was 410 s. When the pressure was 169 Torr, the half-life was 880 s. Determine the order of the reaction.

83.1(b) At 400 K, the half-life for the decomposition of a sample of a gaseous compound initially at 55.5 kPa was 340 s. When the pressure was 28.9 kPa, the half-life was 178 s. Determine the order of the reaction.

83.2(a) The rate constant for the first-order decomposition of N_2O_5 in the reaction $2\,N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$ is $k_r = 3.38\times10^{-5}\ s^{-1}$ at 25 °C. What is the half-life of N_2O_5? What will be the pressure, initially 500 Torr, (i) 50 s, (ii) 20 min after initiation of the reaction?

83.2(b) The rate constant for the first-order decomposition of a compound A in the reaction $2\,A \rightarrow P$ is $k_r = 3.56\times10^{-7}\ s^{-1}$ at 25 °C. What is the half-life of A? What will be the pressure, initially 33.0 kPa, (i) 50 s, (ii) 20 min after initiation of the reaction?

83.3(a) The second-order rate constant for the reaction $CH_3COOC_2H_5(aq) + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + CH_3CH_2OH(aq)$ is $0.11\ dm^3\ mol^{-1}\ s^{-1}$. What is the concentration of ester ($CH_3COOC_2H_5$) after (a) 20 s, (b) 15 min when ethyl acetate is added to sodium hydroxide so that the initial concentrations are $[NaOH] = 0.060\ mol\ dm^{-3}$ and $[CH_3COOC_2H_5] = 0.110\ mol\ dm^{-3}$?

83.3(b) The second-order rate constant for the reaction $A + 2\,B \rightarrow C + D$ is $0.34\ dm^3\ mol^{-1}\ s^{-1}$. What is the concentration of C after (a) 20 s, (b) 15 min when the reactants are mixed with initial concentrations of $[A] = 0.027$ mol dm^{-1} and $[B] = 0.130\ mol\ dm^{-3}$?

83.4(a) A reaction $2\,A \rightarrow P$ has a second-order rate law with $k_r = 4.30\times10^{-4}$ dm^3 mol^{-1} s^{-1}. Calculate the time required for the concentration of A to change from 0.210 mol dm^{-3} to 0.010 mol dm^{-3}.

83.4(b) A reaction $2\,A \rightarrow P$ has a third-order rate law with $k_r = 6.50\times10^{-4}$ dm^6 mol^{-2} s^{-1}. Calculate the time required for the concentration of A to change from 0.067 mol dm^{-3} to 0.015 mol dm^{-3}.

Problems

83.1 For a first-order reaction of the form $A \rightarrow nB$ (with n possibly fractional), the concentration of the product varies with time as $[B] = n[B]_0(1 - e^{-k_r t})$. Plot the time dependence of [A] and [B] for the cases $n = \frac{1}{2}$, 1, and 2.

83.2 For a second-order reaction of the form $A \rightarrow nB$ (with n possibly fractional), the concentration of the product varies with time as $[B] = nk_r t[A]_0^2/(1 + k_r t[A]_0)$. Plot the time dependence of [A] and [B] for the cases $n = \frac{1}{2}$, 1, and 2.

83.3 The data below apply to the formation of urea from ammonium cyanate, $NH_4CNO \rightarrow NH_2CONH_2$. Initially 22.9 g of ammonium cyanate was dissolved in enough water to prepare 1.00 dm^3 of solution. Determine the order of the reaction, the rate constant, and the mass of ammonium cyanate left after 300 min.

t/min	0	20.0	50.0	65.0	150
m(urea)/g	0	7.0	12.1	13.8	17.7

83.4 The data below apply to the reaction, $(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$. Determine the order of the reaction, the rate constant, and the molar concentration of $(CH_3)_3CBr$ after 43.8 h.

t/h	0	3.15	6.20	10.00	18.30	30.80
$[(CH_3)_3CBr]/(10^{-2}\ mol\ dm^{-3})$	10.39	8.96	7.76	6.39	3.53	2.07

83.5 The thermal decomposition of an organic nitrile produced the following data:

$t/(10^3\ s)$	0	2.00	4.00	6.00	8.00	10.00	12.00	∞
[nitrile]/(mol dm^{-3})	1.50	1.26	1.07	0.92	0.81	0.72	0.65	0.40

Determine the order of the reaction and the rate constant.

83.6 A second-order reaction of the type $A + 2\,B \rightarrow P$ was carried out in a solution that was initially 0.050 mol dm^{-3} in A and 0.030 mol dm^{-3} in B. After 1.0 h the concentration of A had fallen to 0.010 mol dm^{-3}. (a) Calculate the rate constant. (b) What is the half-life of the reactants?

83.7‡ The oxidation of HSO_3^- by O_2 in aqueous solution is a reaction of importance to the processes of acid rain formation and flue gas desulfurization. R.E. Connick, et al. (*Inorg. Chem.* **34**, 4543 (1995)) report that the reaction $2\,HSO_3^- + O_2 \rightarrow 2\,SO_4^{2-} + 2\,H^+$ follows the rate law $v = k_r[HSO_3^-]^2[H^+]^2$. Given pH = 5.6 and an oxygen molar concentration of 2.4×10^{-4} mol dm^{-3} (both presumed constant), an initial HSO_3^- molar concentration of 5×10^{-5} mol dm^{-3}, and a rate constant of 3.6×10^6 dm^9 mol^{-3} s^{-1}, what is the initial rate of reaction? How long would it take for HSO_3^- to reach half its initial concentration?

83.8 *Pharmacokinetics* is the study of the rates of absorption and elimination of drugs by organisms. In most cases, elimination is slower than absorption and is a more important determinant of availability of a drug for binding to its target. A drug can be eliminated by many mechanisms, such as metabolism in the liver, intestine, or kidney followed by excretion of breakdown products through urine or faeces. As an example of pharmacokinetic analysis, consider the elimination of beta adrenergic blocking agents (beta blockers), drugs used in the treatment of hypertension. After intravenous administration of a beta blocker, the blood plasma of a patient was analysed for remaining drug and the data are shown below, where c is the drug concentration measured at a time t after the injection.

(a) Is removal of the drug a first- or second-order process? (b) Calculate the rate constant and half-life of the process. *Comment*: An essential aspect of drug development is the optimization of the half-life of elimination, which needs to be long enough to allow the drug to find and act on its target organ but not so long that harmful side-effects become important.

t/min	30	60	120	150	240	360	480
c/(ng cm^{-3})	699	622	413	292	152	60	24

83.9 The following data have been obtained for the decomposition of $N_2O_5(g)$ at 67 °C according to the reaction $2\,N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$. Determine the order of the reaction, the rate constant, and the half-life. It is not necessary to obtain the result graphically; you may do a calculation using estimates of the rates of change of concentration.

t/min	0	1	2	3	4	5
$[N_2O_5]/(mol\ dm^{-3})$	1.000	0.705	0.497	0.349	0.246	0.173

83.10 The gas-phase decomposition of acetic acid at 1189 K proceeds by way of two parallel reactions:

(1) $CH_3COOH \rightarrow CH_4 + CO_2$ $\quad k_1 = 3.74\ s^{-1}$

(2) $CH_3COOH \rightarrow CH_2CO + H_2O$ $\quad k_2 = 4.65\ s^{-1}$

What is the maximum percentage yield of the ketene CH_2CO obtainable at this temperature?

83.11 Sucrose is readily hydrolysed to glucose and fructose in acidic solution. The hydrolysis is often monitored by measuring the angle of rotation of plane-polarized light passing through the solution. From the angle of rotation the concentration of sucrose can be determined. An experiment on the hydrolysis of sucrose in 0.50 M HCl(aq) produced the following data:

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‡ These problems were supplied by Charles Trapp and Carmen Giunta.

t/min	0	14	39	60	80	110	140	170	210
[sucrose]/ (mol dm^{-3})	0.316	0.300	0.274	0.256	0.238	0.211	0.190	0.170	0.146

Determine the rate constant of the reaction and the half-life of a sucrose molecule.

83.12 The composition of the liquid-phase reaction $2\,A \rightarrow B$ was followed by a spectrophotometric method with the following results:

t/min	0	10	20	30	40	∞
[B]/(mol dm^{-3})	0	0.089	0.153	0.200	0.230	0.312

Determine the order of the reaction and its rate constant.

83.13 The ClO radical decays rapidly by way of the reaction $2\,ClO \rightarrow Cl_2 + O_2$. The following data have been obtained:

t/ ms	0.12	0.62	0.96	1.60	3.20	4.00	5.75
[ClO]/(10^{-6} mol dm^{-3})	8.49	8.09	7.10	5.79	5.20	4.77	3.95

Determine the rate constant of the reaction and the half-life of a ClO radical.

83.14 Cyclopropane isomerizes into propene when heated to 500 °C in the gas phase. The extent of conversion for various initial pressures has been followed by gas chromatography by allowing the reaction to proceed for a time with various initial pressures:

p_0/Torr	200	200	400	400	600	600
t/s	100	200	100	200	100	200
p/Torr	186	173	373	347	559	520

where p_0 is the initial pressure and p is the final pressure of cyclopropane. What is the order and rate constant for the reaction under these conditions?

83.15 The addition of hydrogen halides to alkenes has played a fundamental role in the investigation of organic reaction mechanisms. In one study (M.J. Haugh and D.R. Dalton, *J. Amer. Chem. Soc.* **97**, 5674 (1975)), high pressures of hydrogen chloride (up to 25 atm) and propene (up to 5 atm) were examined over a range of temperatures and the amount of 2-chloropropane formed was determined by NMR. Show that if the reaction $A + B \rightarrow P$ proceeds for a short time δt, the concentration of product follows $[P]/[A] = k_r[A]^{m-1}[B]^n\delta t$ if the reaction is mth-order in A and nth-order in B. In a series of runs the ratio of [chloropropane] to [propene] was independent of [propene] but the ratio of [chloropropane] to [HCl] for constant amounts of propene depended on [HCl]. For $\delta t \approx 100\,h$ (which is short on the timescale of the reaction) the latter ratio rose from zero to 0.05, 0.03, 0.01 for $p(HCl) = 10$ atm, 7.5 atm, 5.0 atm. What are the orders of the reaction with respect to each reactant?

83.16 Show that $t_{1/2}$ is given by eqn 83.6 for a reaction that is nth-order in A. Then deduce an expression for the time it takes for the concentration of a substance to fall to one-third the initial value in an nth-order reaction.

83.17 Derive an integrated expression for a second-order rate law $v = k_r[A][B]$ for a reaction of stoichiometry $2\,A + 3\,B \rightarrow P$.

83.18 Derive the integrated form of a third-order rate law $v = k_r[A]^2[B]$ in which the stoichiometry is $2\,A + B \rightarrow P$ and the reactants are initially present in (a) their stoichiometric proportions, (b) with B present initially in twice the amount.

83.19 Show that the ratio $t_{1/2}/t_{3/4}$, where $t_{1/2}$ is the half-life and $t_{3/4}$ is the time for the concentration of A to decrease to $\frac{3}{4}$ of its initial value (implying that $t_{3/4} < t_{1/2}$), can be written as a function of n alone, and can therefore be used as a rapid assessment of the order of a reaction.

Topic 84 Reactions approaching equilibrium

Discussion question

84.1 Describe the strategy of a temperature-jump experiment. What parameters of a reaction are accessible using this technique?

Exercises

84.1(a) The equilibrium $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ at 25 °C is subjected to a temperature jump which slightly increases the concentration of $NH_4^+(aq)$ and $OH^-(aq)$. The measured relaxation time is 7.61 ns. The equilibrium constant for the system is 1.78×10^{-5} at 25 °C, and the equilibrium concentration of $NH_3(aq)$ is 0.15 mol dm^{-3}. Calculate the rate constants for the forward and reverse steps.

84.1(b) The equilibrium $A \rightleftharpoons B + C$ at 25 °C is subjected to a temperature jump which slightly increases the concentrations of B and C. The measured relaxation time is 3.0 μs. The equilibrium constant for the system is 2.0×10^{-16} at 25 °C, and the equilibrium concentrations of B and C at 25 °C are both 2.0×10^{-4} mol dm^{-3}. Calculate the rate constants for the forward and reverse steps.

Problems

84.1 Show by differentiation that eqn 84.4 is a solution of eqn 84.3.

84.2 Set up the rate equations and plot the corresponding graphs for the approach to an equilibrium of the form $A \rightleftharpoons 2\,B$.

84.3 The equilibrium $A \rightleftharpoons B$ is first-order in both directions. Derive an expression for the concentration of A as a function of time when the initial molar concentrations of A and B are $[A]_0$ and $[B]_0$. What is the final composition of the system?

84.4 Show that eqn 84.8 is an expression for the overall equilibrium constant in terms of the rate constants for the intermediate steps of a reaction mechanism. To facilitate the task, begin with a mechanism containing three steps, and then argue that your expression may be generalized for any number of steps.

84.5 Consider the dimerization $2\,A \rightleftharpoons A_2$, with forward rate constant k_a and backward rate constant k_a'. (a) Derive the following expression for the relaxation time in terms of the total concentration of protein, $[A]_{tot} = [A] + 2[A_2]$:

$$\frac{1}{\tau^2} = k_a'^2 + 8k_a k_a'[A]_{tot}$$

(b) Describe the computational procedures that lead to the determination of the rate constants k_a and k_a' from measurements of τ for different values of $[A]_{tot}$. (c) Use the data provided below and the procedure you outlined in part (b) to calculate the rate constants k_a and k_a', and the equilibrium constant K for formation of hydrogen-bonded dimers of 2-pyridone.

$[P]/(\text{mol dm}^{-3})$	0.500	0.352	0.251	0.151	0.101
τ/ns	2.3	2.7	3.3	4.0	5.3

84.6 Consider the dimerization $2\,A \rightleftharpoons A_2$ with forward rate constant k_r and backward rate constant k_r'. Show that the relaxation time is

$$\tau = \frac{1}{k_r' + 4k_r[A]_{eq}}$$

Topic 85 The Arrhenius equation

Discussion question

85.1 Define the terms in and discuss the generality of the expression $\ln k_r = \ln A - E_a/RT$.

Exercises

85.1(a) The rate constant for the decomposition of a certain substance is $3.80 \times 10^{-3}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ at 35 °C and $2.67 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ at 50 °C. Evaluate the Arrhenius parameters of the reaction.

85.1(b) The rate constant for the decomposition of a certain substance is $2.25 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ at 29 °C and $4.01 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ at 37 °C. Evaluate the Arrhenius parameters of the reaction.

85.2(a) The rate of a chemical reaction is found to triple when the temperature is raised from 24 °C to 49 °C. Determine the activation energy.

85.2(b) The rate of a chemical reaction is found to double when the temperature is raised from 25 °C to 35 °C. Determine the activation energy.

Problems

85.1 Show that the definition of E_a given in eqn 85.3 reduces to eqn 85.1 for a temperature-independent activation energy.

85.2 A first-order decomposition reaction is observed to have the following rate constants at the indicated temperatures. Estimate the activation energy.

$k_r/(10^{-3}\ \text{s}^{-1})$	2.46	45.1	576
θ/°C	0	20.0	40.0

85.3 The second-order rate constants for the reaction of oxygen atoms with aromatic hydrocarbons have been measured (R. Atkinson and J.N. Pitts, *J. Phys. Chem.* **79**, 295 (1975)). In the reaction with benzene the rate constants are $1.44 \times 10^7\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ at 300.3 K, $3.03 \times 10^7\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ at 341.2 K, and $6.9 \times 10^7\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ at 392.2 K. Find the pre-exponential factor and activation energy of the reaction.

85.4‡ P.W. Seakins, et al. (*J. Phys. Chem.* **96**, 9847 (1992)) measured the forward and reverse rate constants for the gas-phase reaction $C_2H_5(g) + HBr(g) \rightarrow C_2H_6(g) + Br(g)$ and used their findings to compute thermodynamic parameters for C_2H_5. The reaction is bimolecular in both directions with Arrhenius parameters $A = 1.0 \times 10^9\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$, $E_a = -4.2$ kJ mol^{-1} for the forward reaction and $A = 1.4 \times 10^{11}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$, $E_a = 53.3$ kJ mol^{-1} for the reverse reaction. Compute $\Delta_f H^\ominus, S_m^\ominus$, and $\Delta_f G^\ominus$ of C_2H_5 at 298 K.

85.5‡ Methane is a by-product of a number of natural processes (such as digestion of cellulose in ruminant animals, anaerobic decomposition of organic waste matter), and industrial processes (such as food production and fossil fuel use). Reaction with the hydroxyl radical OH is the main path by which CH_4 is removed from the lower atmosphere. T. Gierczak, et al. (*J. Phys. Chem. A* **101**, 3125 (1997)) measured the rate constants for the elementary bimolecular gas-phase reaction of methane with the hydroxyl radical over a range of temperatures of importance to atmospheric chemistry. Deduce the Arrhenius parameters A and E_a from the following measurements:

T/K	295	223	218	213	206	200	195
$k_r/(10^6\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$	3.55	0.494	0.452	0.379	0.295	0.241	0.217

85.6‡ As we saw in Problem 85.5, reaction with the hydroxyl radical OH is the main path by which CH_4, a by-product of many natural and industrial processes, is removed from the lower atmosphere. T. Gierczak, et al. (*J. Phys. Chem. A* **101**, 3125 (1997)) measured the rate constants for the bimolecular gas-phase reaction $CH_4(g) + OH(g) \rightarrow CH_3(g) + H_2O(g)$ and found $A = 1.13 \times 10^9\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ and $E_a = 14.1$ kJ mol^{-1} for the Arrhenius parameters. (a) Estimate the rate of consumption of CH_4. Take the average OH concentration to be 1.5×10^{-21} mol dm^{-3}, that of CH_4 to be 4.0×10^{-8} mol dm^{-3}, and the temperature to be −10 °C. (b) Estimate the global annual mass of CH_4 consumed by this reaction (which is slightly less than the amount introduced to the atmosphere) given an effective volume for the Earth's lower atmosphere of 4×10^{21} dm^3.

Topic 86 Reaction mechanisms

Discussion questions

86.1 Distinguish reaction order and molecularity.

86.2 Assess the validity of the following statement: the rate-determining step is the slowest step in a reaction mechanism.

86.3 Distinguish between a pre-equilibrium approximation and a steady-state approximation.

86.4 Distinguish between kinetic and thermodynamic control of a reaction. Suggest criteria for expecting one rather than the other.

86.5 Is it possible for the activation energy of a reaction to be negative? Explain your conclusion and provide a molecular interpretation.

Exercises

86.1(a) The reaction mechanism for the decomposition of A_2,

$$\begin{aligned}&A_2 \rightleftharpoons A+A\ \text{(fast)}\\ &A+B \rightarrow P\ \text{(slow)}\end{aligned}$$

involves an intermediate, A. Deduce the rate law for the reaction in two ways by (i) assuming a pre-equilibrium and (ii) making a steady-state approximation.

86.1(b) The reaction mechanism for renaturation of a double helix from its strands A and B,

$$\begin{aligned}&A+B \rightleftharpoons \text{unstable helix (fast)}\\ &\text{Unstable helix} \rightarrow \text{stable double helix (slow)}\end{aligned}$$

involves an intermediate. Deduce the rate law for the reaction in two ways by (i) assuming a pre-equilibrium and (ii) making a steady-state approximation.

86.2(a) The mechanism of a composite reaction consists of a fast pre-equilibrium step with forward and reverse activation energies of 25 kJ mol^{-1} and 38 kJ mol^{-1}, respectively, followed by an elementary step of activation energy 10 kJ mol^{-1}. What is the activation energy of the composite reaction?

86.2(b) The mechanism of a composite reaction consists of a fast pre-equilibrium step with forward and reverse activation energies of 27 kJ mol^{-1} and 35 kJ mol^{-1}, respectively, followed by an elementary step of activation energy 15 kJ mol^{-1}. What is the activation energy of the composite reaction?

Problems

86.1 Use mathematical software or spreadsheet to examine the time dependence of [I] in the reaction mechanism $A \rightarrow I \rightarrow P$ (k_a, k_b). In all of the following calculations, use $[A]_0 = 1\ \text{mol dm}^{-3}$ and a time range of 0 to 5 s. (a) Plot [I] against t for $k_a = 10\ \text{s}^{-1}$ and $k_b = 1\ \text{s}^{-1}$. (b) Increase the ratio k_b/k_a steadily by decreasing the value of k_a and examine the plot of [I] against t at each turn. What approximation about $\text{d}[I]/\text{d}t$ becomes increasingly valid?

86.2 Use mathematical software or a spreadsheet to investigate the effects on [A], [I], [P], and $t_{\max}$ of decreasing the ratio k_a/k_b from 10 (as in Fig. 86.1) to 0.01. Compare your results with those shown in Fig. 86.3.

86.3 Set up the rate equations for the reaction mechanism

$$A \underset{k_a'}{\overset{k_a}{\rightleftarrows}} B \underset{k_b'}{\overset{k_b}{\rightleftarrows}} C$$

Show that the mechanism is equivalent to

$$A \underset{k_r'}{\overset{k_r}{\rightleftarrows}} C$$

under specified circumstances.

86.4 Derive an equation for the steady state rate of the sequence of reactions $A \rightleftarrows B \rightleftarrows C \rightleftarrows D$, with [A] maintained at a fixed value and the product D removed as soon as it is formed.

86.5 Show that the following mechanism can account for the rate law of the reaction in Problem 83.15:

$HCl + HCl \rightleftharpoons (HCl)_2$	K_1
$HCl + CH_3CH{=}CH_2 \rightleftharpoons \text{complex}$	K_2
$(HCl)_2 + \text{complex} \rightarrow CH_3CHClCH_3 + HCl + HCl$	k_r (slow)

What further tests could you apply to verify this mechanism?

86.6 Polypeptides are polymers of amino acids. Suppose that a long polypeptide chain can undergo a transition from a helical conformation to a random coil. Consider a mechanism for a helix–coil transition that begins in the middle of the chain:

$$\begin{aligned}&hhhh\ldots \rightleftarrows hchh\ldots\\ &hchh\ldots \rightleftarrows hcch\ldots\end{aligned}$$

in which h and c label, respectively, an amino acid in a helical or coil part of the chain. The first conversion from h to c, also called a nucleation step, is relatively slow, so neither step may be rate-determining. (a) Set up the rate equations for this mechanism. (b) Apply the steady-state approximation and show that, under these circumstances, the mechanism is equivalent to $hhhh\ldots \rightleftarrows cccc\ldots$.

Integrated activities

F17.1‡ J. Czarnowski and H.J. Schuhmacher (*Chem. Phys. Lett.* **17**, 235 (1972)) suggested the following mechanism for the thermal decomposition of F_2O in the reaction $2\,F_2O(g) \rightarrow 2\,F_2(g) + O_2(g)$:

(1) $F_2O + F_2O \rightarrow F + OF + F_2O$	k_a
(2) $F + F_2O \rightarrow F_2 + OF$	k_b
(3) $OF + OF \rightarrow O_2 + F + F$	k_c
(4) $F + F + F_2O \rightarrow F_2 + F_2O$	k_d

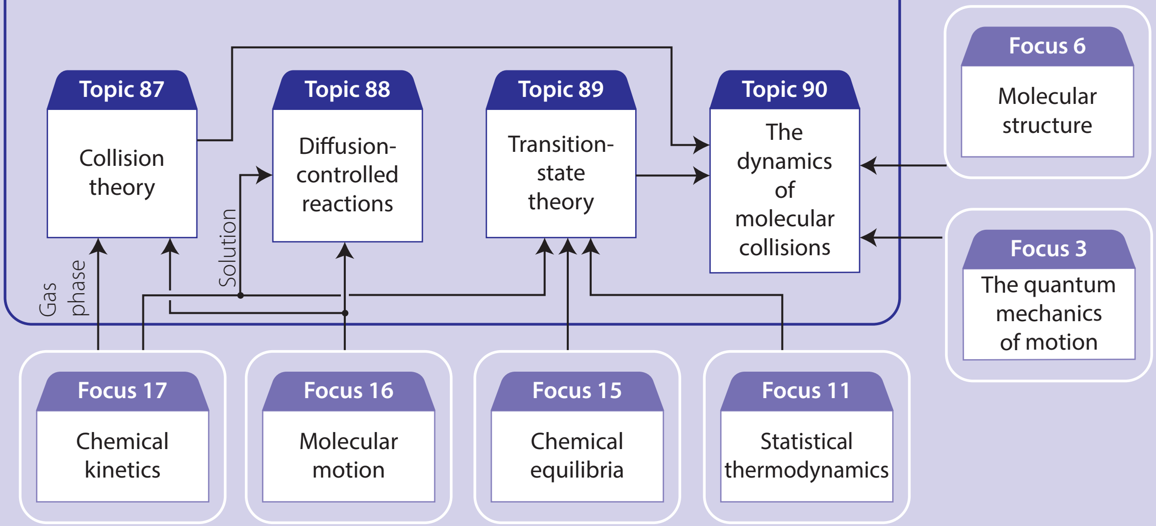
(a) Using the steady-state approximation, show that this mechanism is consistent with the experimental rate law $-d[F_2O]/dt = k_r[F_2O]^2 + k_r'[F_2O]^{3/2}$. (b) The experimentally determined Arrhenius parameters in the range 501–583 K are $A = 7.8 \times 10^{13}$ dm^3 mol^{-1} s^{-1}, $E_a/R = 1.935 \times 10^4$ K for k_r; and $A = 2.3 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, $E_a/R = 1.691 \times 10^4$ K for k_r'. At 540 K, $\Delta_f H^\ominus(F_2O) = +24.41$ kJ mol^{-1}, $D(F\text{–}F) = 160.6$ kJ mol^{-1}, and $D(O\text{–}O) = 498.2$ kJ mol^{-1}. Estimate the bond dissociation energies of the first and second F–O bonds in F_2O and the Arrhenius activation energy of reaction 2.

F17.2 Two groups of protons have $\delta = 4.0$ and $\delta = 5.2$ and are interconverted by a conformational change of a fluxional molecule. In a 60 MHz NMR spectrometer the spectrum collapsed into a single line at 280 K but at 300 MHz the collapse did not occur until the temperature had been raised to 300 K. What is the activation energy of the interconversion?

F17.3 Conventional equilibrium considerations do not apply when a reaction is being driven by light absorption. Thus the steady-state concentration of products and reactants might differ significantly from equilibrium values. For instance, suppose the reaction $A \rightarrow B$ is driven by light absorption, and that its rate is I_a, but that the reverse reaction $B \rightarrow A$ is bimolecular and second-order with a rate $k_r[B]^2$. What is the stationary-state concentration of B? Why does this 'photostationary state' differ from the equilibrium state?

F17.4 The photochemical chlorination of chloroform in the gas phase has been found to follow the rate law $d[CCl_4]/dt = k_r[Cl_2]^{1/2}I_a^{1/2}$. Devise a mechanism that leads to this rate law when the chlorine pressure is high.

FOCUS 18 ON Reaction dynamics



As well as its interest in structure, chemistry is concerned with change. In this group of Topics we consider a variety of models of how chemical reactions take place. The focus is on the calculation, or at least the interpretation, of the magnitude of the rate constant of a reaction, as introduced in *Chemical kinetics*, and particularly its temperature dependence as expressed by the Arrhenius equation described there.

The simplest model of bimolecular elementary reactions in the gas phase is collision theory (**Topic 87**), in which it is supposed that a reaction occurs when two reactant molecules collide with sufficient energy and in an appropriate relative orientation. This simple model can be elaborated by assessing the way in which the energy of the collision is dispersed over the molecules and then congregates in one particular bond.

In solution we are confronted with a different type of problem, for there are now two principal components to the rate of reaction (**Topic 88**). One is the rate at which two reactants diffuse through the solvent and finally encounter; the other is the rate at which, once they are together, they acquire sufficient energy to react. When the former process is dominant, elaborations of the diffusion equation introduced in *Molecular motion* enable us to relate the rate to the diffusional characteristics of the solution.

Reactions in both types of fluid medium are brought together in a theory that supposes that the reactants form a cluster of atoms when they encounter one another that can be treated as being in equilibrium with the reactants. This 'transition-state theory' (**Topic 89**) draws on the concepts of *Statistical thermodynamics* and *Chemical equilibria* to relate the rate constant to the supposed structure adopted by the cluster of atoms.

Underlying all these discussions is the quantum mechanical process of reactants moving through space (in states described in *The quantum mechanics of motion*) and exchanging partners. Some headway with this immensely intricate problem has been made by advances in computational chemistry, as outlined in *Molecular structure*, and the analysis of motion over potential energy surfaces (**Topic 90**).

TOPIC 87

Collision theory

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➤ Why do you need to know this material?

A major component of chemistry is the study of the mechanisms of chemical reactions. One of the earliest approaches, which continues to give insight into the details of mechanisms, is collision theory.

➤ What is the key idea?

According to collision theory, in a bimolecular gas-phase reaction, a reaction takes place on the collision of reactants provided their relative kinetic energy exceeds a threshold value and certain steric requirements are fulfilled.

➤ What do you need to know already?

This Topic draws on the kinetic theory of gases (Topic 78). You should also be familiar with the Arrhenius equation for the temperature dependence of the rate constant (Topic 85).

We consider the following gas-phase bimolecular elementary reaction with rate constant k_r:

$$\mathrm{A}+\mathrm{B}\rightarrow\mathrm{P}\quad v=k_r[\mathrm{A}][\mathrm{B}] \tag{87.1}$$

where A and B denote reactants and P products. We can anticipate the general form of the expression for k_r by considering the physical requirements for reaction. To build a model of the reaction rate we can expect that it will be proportional to the rate of collisions, and therefore

- proportional to the mean speed of the molecules, $v_{\text{mean}} \propto (T/M)^{1/2}$ (eqn 78.7 of Topic 78), where M is the molar mass of the molecules and T is the temperature;
- proportional to their collision cross-section, σ (Topic 78), the 'target area' the molecules present in a collision;
- proportional to the number densities of A and B, $\mathcal{N}_\mathrm{A}=N_\mathrm{A}[\mathrm{A}]$ and $\mathcal{N}_\mathrm{B}=N_\mathrm{A}[\mathrm{B}]$, where N_A is Avogadro's constant.

That is, we expect

$$v\propto\sigma(T/M)^{1/2}\mathcal{N}_A\mathcal{N}_B\propto\sigma(T/M)^{1/2}[\mathrm{A}][\mathrm{B}]$$

However, a collision will be successful only if the kinetic energy exceeds a minimum value, which we denote E'. This requirement suggests in addition that

- the rate should also be proportional to a Boltzmann factor of the form $\mathrm{e}^{-E'/RT}$ representing the fraction of collisions with at least the minimum required energy E'.

Therefore,

$$v\propto\sigma(T/M)^{1/2}\mathrm{e}^{-E'/RT}[\mathrm{A}][\mathrm{B}]$$

We can now anticipate, by writing the reaction rate in the form given in eqn 87.1, that

$$k_r\propto\sigma(T/M)^{1/2}\mathrm{e}^{-E'/RT}$$

At this point, we begin to recognize the form of the Arrhenius equation ($k_r=A\mathrm{e}^{-E_a/RT}$, eqn 85.4) and identify the minimum kinetic energy E' with the activation energy E_a of the reaction. This identification, however, should not be regarded as precise, since collision theory is only a rudimentary model of chemical reactivity.

Finally, we should note that

- not every collision will lead to reaction even if the energy requirement is satisfied, because the reactants may need to collide in a certain relative orientation.

This 'steric requirement' suggests that a further factor, P, should be introduced, and that

$$k_r \propto P\sigma(T/M)^{1/2}\mathrm{e}^{-E'/RT} \tag{87.2}$$

As we shall see in detail below, this expression has the form predicted by collision theory. It reflects three aspects of a successful collision:

$$k_r \propto \overbrace{P}^{\text{Steric requirement}} \quad \overbrace{\sigma(T/M)^{1/2}}^{\text{Encounter rate}} \quad \overbrace{\mathrm{e}^{-E'/RT}}^{\text{Minimum energy requirement}}$$

87.1 Collision rates in gases

We have anticipated that the reaction rate, and hence k_r, depends on the frequency with which molecules collide. The **collision density**, Z_{AB}, is the number of (A,B) collisions in a region of the sample in an interval of time, divided by the volume of the region and the duration of the interval. The frequency of collisions of a single molecule in a gas was calculated in Topic 78 (eqn 78.10, $z=\sigma v_{rel}\mathcal{N}_A$). As shown in the following *Justification*, that result can be adapted to deduce that

$$Z_{AB}=\sigma\left(\frac{8kT}{\pi\mu}\right)^{1/2} N_A^2[\mathrm{A}][\mathrm{B}] \tag{87.3a}$$

Kinetic-molecular theory Collision density

where σ is the collision cross-section (Fig. 87.1),

$$\sigma=\pi d^2 \qquad d=\tfrac{1}{2}(d_A+d_B) \tag{87.3b}$$

Collision cross-section

d_A and d_B are the diameters of A and B, respectively, and μ is the reduced mass,

$$\mu=\frac{m_A m_B}{m_A+m_B} \tag{87.3c}$$

Reduced mass

For like molecules, $\mu=\frac{1}{2}m_A$, and at a molar concentration [A],

$$Z_{AA}=\frac{1}{2}\sigma\left(\frac{16kT}{\pi m_A}\right)^{1/2} N_A^2[\mathrm{A}]^2=\sigma\left(\frac{4kT}{\pi m_A}\right)^{1/2} N_A^2[\mathrm{A}]^2 \tag{87.3d}$$

The factor of $\frac{1}{2}$ is included to avoid double-counting of collisions in this instance. The molar concentration of a perfect gas is $[\mathrm{A}]=n/V=p/RT$.

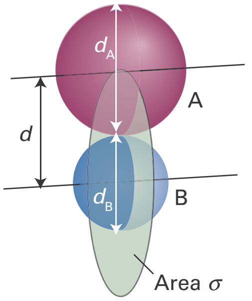

Figure 87.1 The collision cross-section for two molecules can be regarded as the area within which the projectile molecule (A) must enter around the target molecule (B) in order for a collision to occur. If the diameters of the two molecules are d_A and d_B, the radius of the target area is $d=½(d_A+d_B)$ and the cross-section is πd^2.

Brief illustration 87.1 Collision density

Collision densities may be very large. For example, in nitrogen at 25 °C and 1.0 bar, when $[\mathrm{N_2}]\approx 40\,\mathrm{mol\,m^{-3}}$, with $\sigma=0.43\,\mathrm{nm^2}$ (Table 78.1) and $m_{\mathrm{N_2}}=28.02m_u$, the collision density is

$$\begin{aligned}Z_{\mathrm{N_2N_2}}&=(4.3\times10^{-19}\,\mathrm{m^2})\\&\quad\times\left(\frac{4\times(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}{\pi\times28.02\times(1.661\times10^{-27}\,\mathrm{kg})}\right)^{1/2}\\&\quad\times(6.022\times10^{23}\,\mathrm{mol^{-1}})^2\times(40\,\mathrm{mol\,m^{-3}})^2\\&=8.4\times10^{34}\,\mathrm{m^{-3}\,s^{-1}}\end{aligned}$$

Self-test 87.1 Calculate the collision density in molecular hydrogen under the same conditions. (See Table 78.1 for σ.)

Answer: $Z_{\mathrm{H_2H_2}}=2.0\times10^{35}\,\mathrm{m^{-3}\,s^{-1}}$

Justification 87.1 The collision density

It follows from Topic 78 that the collision frequency, z, for a single A molecule of mass m_A in a gas of other A molecules is $z=\sigma v_{rel}\mathcal{N}_A$, where $\mathcal{N}_A$ is the number density of A molecules and v_{rel} is their relative mean speed. As indicated in Topic 78, $v_{rel}=2^{1/2}v_{mean}$ with $v_{mean}=(8kT/\pi m)^{1/2}$. For future convenience, it is sensible to introduce $\mu=\frac{1}{2}m$ (for like molecules of mass m), and then to write $v_{rel}=(8kT/\pi\mu)^{1/2}$. This expression also applies to the mean relative speed of dissimilar molecules, provided that μ is interpreted as the reduced mass.

The total collision density is the collision frequency multiplied by the number density of A molecules:

$$Z_{AA}=\frac{1}{2}z\mathcal{N}_A=\frac{1}{2}\sigma v_{rel}\mathcal{N}_A^2$$

The factor of $\frac{1}{2}$ has been introduced to avoid double-counting of the collisions (so one A molecule colliding with another A molecule is counted as one collision regardless of their actual identities). For collisions of A and B molecules present at number densities $\mathcal{N}_A$ and $\mathcal{N}_B$, the collision density is

$$Z_{AB} = \sigma v_{\rm rel}\mathcal{N}_{\rm A}\mathcal{N}_{\rm B}$$

The factor of $\frac{1}{2}$ has been discarded because now we are considering an A molecule colliding with any of the B molecules as a collision. The number density of a species J is $\mathcal{N}_J = N_A[J]$, where [J] is their molar concentration and N_A is Avogadro's constant. Equation 87.3 then follows.

87.2 The energy requirement

According to collision theory, the rate of change in the number density, $\mathcal{N}_A$, of A molecules is the product of the collision density and the probability that a collision occurs with sufficient energy. The latter condition can be incorporated by writing the collision cross-section σ as a function of the kinetic energy ε of approach of the two colliding species, and setting the cross-section, $\sigma(\varepsilon)$, equal to zero if the kinetic energy of approach is below a certain threshold value, ε_a. Later, we shall identify $N_A\varepsilon_a$ as E_a, the (molar) activation energy of the reaction. Then, for a collision between A and B with a specific relative speed of approach $s_{\rm rel}$ (not, at this stage, the mean value, $v_{\rm rel}$),

$$\frac{{\rm d}\mathcal{N}_{\rm A}}{{\rm d}t} = -\sigma(\varepsilon)s_{\rm rel}\mathcal{N}_{\rm A}\mathcal{N}_{\rm B} \tag{87.4a}$$

or, in terms of molar concentrations,

$$\frac{{\rm d}[{\rm A}]}{{\rm d}t} = -\sigma(\varepsilon)s_{\rm rel}N_{\rm A}[{\rm A}][{\rm B}] \tag{87.4b}$$

The kinetic energy associated with the relative motion of the two particles takes the form $\varepsilon = \frac{1}{2}\mu s_{\rm rel}^2$ when the centre-of-mass coordinates are separated from the internal coordinates of each particle. Therefore the relative speed is given by $s_{\rm rel} = (2\varepsilon/\mu)^{1/2}$. At this point we recognize that a wide range of approach energies ε is present in a sample, so we should average the expression just derived over a Boltzmann distribution of energies $f(\varepsilon)$, and write (see *Mathematical background* 7 for a discussion of averages)

$$\frac{{\rm d}[{\rm A}]}{{\rm d}t} = -\left\{\int_0^\infty \sigma(\varepsilon)s_{\rm rel}f(\varepsilon){\rm d}\varepsilon\right\}N_{\rm A}[{\rm A}][{\rm B}] \tag{87.5}$$

and hence recognize the rate constant as

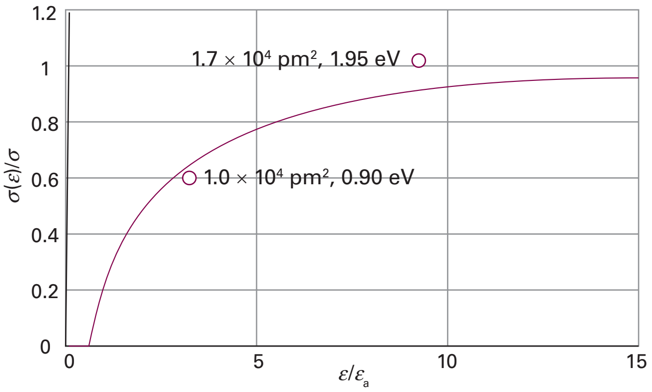

Figure 87.2 The variation of the reactive cross-section with energy, as expressed by eqn 87.7. The data points are from experiments on the reaction $\rm H + D_2 \rightarrow HD + D$ (K. Tsukiyama, et al., *J. Chem. Phys.* **84**, 1934 (1986)).

$$k_{\rm r} = N_{\rm A}\int_0^\infty \sigma(\varepsilon)s_{\rm rel}f(\varepsilon){\rm d}\varepsilon \tag{87.6}$$

Rate constant

Now suppose that the reactive collision cross-section is zero below ε_a. We show in the following *Justification* that, above ε_a, $\sigma(\varepsilon)$ varies as

$$\sigma(\varepsilon) = \left(1 - \frac{\varepsilon_{\rm a}}{\varepsilon}\right)\sigma \tag{87.7}$$

Energy dependence of σ

with the energy independent σ given by eqn 87.3b. This form of the energy dependence for $\sigma(\varepsilon)$ is broadly consistent with experimental determinations of the reaction between H and D_2 as determined by molecular beam measurements of the kind described in Topic 90 (Fig. 87.2).

Justification 87.2 The collision cross-section

Consider two colliding molecules A and B with relative speed $s_{\rm rel}$ and relative kinetic energy $\varepsilon = \frac{1}{2}\mu s_{\rm rel}^2$ (Fig 87.3). Intuitively we expect that a head-on collision between A and B will be most effective in bringing about a chemical reaction. Therefore, $s_{\rm rel,A-B}$, the magnitude of the relative velocity component parallel to an axis that contains the vector connecting the centres of A and B, must be large. From trigonometry and the definitions of the distances a and d, and the angle θ given in Fig 87.3, it follows that

$$s_{\rm rel,A-B} = s_{\rm rel}\cos\theta = s_{\rm rel}\left(\frac{d^2 - a^2}{d^2}\right)^{1/2}$$

We assume that only the kinetic energy associated with the head-on component of the collision, $\varepsilon_{\rm A-B}$, can lead to a

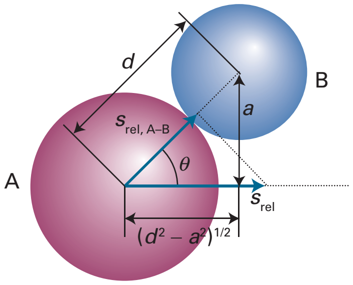

Figure 87.3 The parameters used in the calculation of the dependence of the collision cross-section on the relative kinetic energy of two molecules A and B.

chemical reaction. After squaring both sides of this equation and multiplying by $\frac{1}{2}\mu$, it follows that

$$\varepsilon_{\text{A–B}}=\varepsilon\times\frac{d^2-a^2}{d^2}$$

The existence of an energy threshold, ε_a, for the formation of products implies that there is a maximum value of a, $a_{\max}$, above which reaction does not occur. Setting $a=a_{\max}$ and $\varepsilon_{\text{A–B}}=\varepsilon_a$ gives

$$a_{\max}^2=\left(1-\frac{\varepsilon_a}{\varepsilon}\right)d^2$$

Substitution of $\sigma(\varepsilon)$ for $\pi a_{\max}^2$ and σ for πd^2 in the equation above gives eqn 87.7. Note that the equation can be used only when $\varepsilon>\varepsilon_a$.

With the energy dependence of the collision cross-section established, we can evaluate the integral in eqn 87.6. In the following *Justification* we show that

$$k_r=\sigma N_A v_{\text{rel}}e^{-E_a/RT} \qquad \textit{Collision theory} \quad \text{Rate constant} \qquad (87.8)$$

Justification 87.3 The rate constant

The Maxwell–Boltzmann distribution of molecular speeds is eqn 78.4 of Topic 78:

$$f(v)\mathrm{d}v=4\pi\left(\frac{\mu}{2\pi kT}\right)^{3/2}v^2e^{-\mu v^2/2kT}\mathrm{d}v$$

(We have replaced M/R by μ/k.) This expression may be expressed in terms of the kinetic energy, ε, by writing $\varepsilon=\frac{1}{2}\mu v^2$; then $\mathrm{d}v=\mathrm{d}\varepsilon/(2\mu\varepsilon)^{1/2}$, when it becomes

$$\begin{aligned}f(v)\mathrm{d}v&=4\pi\left(\frac{\mu}{2\pi kT}\right)^{3/2}\left(\frac{2\varepsilon}{\mu}\right)e^{-\varepsilon/kT}\frac{\mathrm{d}\varepsilon}{(2\mu\varepsilon)^{1/2}}\\&=2\pi\left(\frac{1}{\pi kT}\right)^{3/2}\varepsilon^{1/2}e^{-\varepsilon/kT}\mathrm{d}\varepsilon=f(\varepsilon)\mathrm{d}\varepsilon\end{aligned}$$

The integral we need to evaluate is therefore

$$\begin{aligned}\int_0^\infty\sigma(\varepsilon)\overbrace{s_{\text{rel}}}^{(2\varepsilon/\mu)^{1/2}}f(\varepsilon)\mathrm{d}\varepsilon&=2\pi\left(\frac{1}{\pi kT}\right)^{3/2}\int_0^\infty\sigma(\varepsilon)\left(\frac{2\varepsilon}{\mu}\right)^{1/2}\varepsilon^{1/2}e^{-\varepsilon/kT}\mathrm{d}\varepsilon\\&=\left(\frac{8}{\pi\mu kT}\right)^{1/2}\left(\frac{1}{kT}\right)\int_0^\infty\varepsilon\sigma(\varepsilon)e^{-\varepsilon/kT}\mathrm{d}\varepsilon\end{aligned}$$

To proceed, we introduce the approximation for $\sigma(\varepsilon)$ in eqn 87.7 and evaluate

$$\int_0^\infty\varepsilon\sigma(\varepsilon)e^{-\varepsilon/kT}\mathrm{d}\varepsilon=\sigma\int_{\varepsilon_a}^\infty\varepsilon\left(1-\frac{\varepsilon_a}{\varepsilon}\right)e^{-\varepsilon/kT}\mathrm{d}\varepsilon=\sigma(kT)^2e^{-\varepsilon_a/kT}$$

We have made use of the fact that $\sigma=0$ for $\varepsilon<\varepsilon_a$. It follows that

$$\int_0^\infty\sigma(\varepsilon)s_{\text{rel}}f(\varepsilon)\mathrm{d}\varepsilon=\sigma\left(\frac{8kT}{\pi\mu}\right)^{1/2}e^{-\varepsilon_a/kT}$$

as in eqn 87.8 (with $\varepsilon_a/kT=E_a/RT$).

Equation 87.8 has the Arrhenius form $k_r=Ae^{-E_a/RT}$ provided the exponential temperature dependence dominates the weak square-root temperature dependence of the pre-exponential factor A. It follows that we can identify (within the constraints of collision theory) the activation energy, E_a, with the minimum kinetic energy along the line of approach that is needed for reaction, and that the pre-exponential factor is a measure of the rate at which collisions occur in the gas.

The simplest procedure for calculating k_r is to use for σ the values obtained for non-reactive collisions (for example, typically those obtained from viscosity measurements) or from tables of molecular radii. If the collision cross-sections of A and B are $\sigma_A=\pi d_A^2$ and $\sigma_B=\pi d_B^2$, then an approximate value of the AB cross-section can be estimated from $\sigma=\pi d^2$, with $d=\frac{1}{2}(d_A+d_B)$. That is,

$$\sigma\approx\frac{1}{4}(\sigma_A^{1/2}+\sigma_B^{1/2})^2$$

Brief illustration 87.2 The rate constant

To estimate the rate constant for the reaction $H_2+C_2H_4\rightarrow C_2H_6$ at 628 K we first calculate the reduced mass using $m(H_2)=2.016m_u$ and $m(C_2H_4)=28.05m_u$. A straightforward calculation gives $\mu=3.123\times10^{-27}$ kg. It then follows that

$$\begin{aligned}\left(\frac{8kT}{\pi\mu}\right)^{1/2}&=\left(\frac{8\times(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(628\,\mathrm{K})}{\pi\times(3.123\times10^{-27}\,\mathrm{kg})}\right)^{1/2}\\&=2.65\ldots\,\mathrm{km\,s^{-1}}\end{aligned}$$

From Table 78.1, $\sigma(H_2)=0.27\,nm^2$ and $\sigma(C_2H_4)=0.64\,nm^2$, giving $\sigma(H_2,C_2H_4)\approx 0.44\,nm^2$. The activation energy is large: 180 kJ mol⁻¹. Therefore,

$$\begin{aligned}k_r &= (4.4\times10^{-19}\,\mathrm{m^2})\times(2.65\ldots\times10^3\,\mathrm{m\,s^{-1}})\times(6.022\times10^{23}\,\mathrm{mol^{-1}})\\ &\quad\times e^{-(1.80\times10^5\,\mathrm{J\,mol^{-1}})/(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(628\,\mathrm{K})}\\ &= \overbrace{7.04\ldots\times10^8\,\mathrm{m^3\,mol^{-1}\,s^{-1}}}^{A}\times e^{-34.4\ldots} = 7.5\times10^{-7}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}\end{aligned}$$

or $7.5\times10^{-4}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$.

Self-test 87.2 Evaluate the rate constant for the reaction $NO+Cl_2\rightarrow NOCl+Cl$ at 298 K from $\sigma(NO)=0.42\,nm^2$ and $\sigma(Cl_2)=0.93\,nm^2$ and an activation energy of 85 kJ mol⁻¹ .

Answer: $2.7\times10^{-4}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$

87.3 The steric requirement

Table 87.1 compares some values of the pre-exponential factor calculated from the collisional data in Table 78.1 with values obtained from Arrhenius plots. One of the reactions shows fair agreement between theory and experiment, but for others there are major discrepancies. In some cases the experimental values are orders of magnitude smaller than those calculated, which suggests that the collision energy is not the only criterion for reaction and that some other feature, such as the relative orientation of the colliding species, is important. Moreover, one reaction in the table has a pre-exponential factor larger than theory, which seems to indicate that the reaction occurs more quickly than the particles collide!

The disagreement between experiment and theory can be accommodated by introducing a **steric factor**, P, and expressing the **reactive cross-section**, σ^*, as a multiple of the collision cross-section, $\sigma^*=P\sigma$ (Fig. 87.4). Then the rate constant becomes

$$k_r = P\sigma N_A\left(\frac{8kT}{\pi\mu}\right)^{1/2} e^{-E_a/RT} \tag{87.9}$$

Table 87.1* Arrhenius parameters for gas-phase reactions

	$A/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})$			
	Experiment	Theory	$E_a/(\mathrm{kJ\,mol^{-1}})$	P
$2\,NOCl\rightarrow 2\,NO+Cl_2$	9.4×10^9	5.9×10^{10}	102	0.16
$2\,ClO\rightarrow Cl_2+O_2$	6.3×10^7	2.5×10^{10}	0	2.5×10^{-3}
$H_2+C_2H_4\rightarrow C_2H_6$	1.24×10^6	7.4×10^{11}	180	1.7×10^{-6}
$K+Br_2\rightarrow KBr+Br$	1.0×10^{12}	2.1×10^{11}	0	4.8

* More values are given in the *Resource section*.

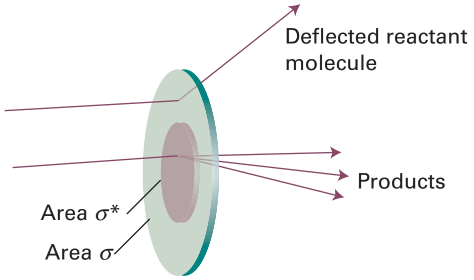

Figure 87.4 The collision cross-section is the target area that results in simple deflection of the projectile molecule; the reactive cross-section is the corresponding area for chemical change to occur on collision.

This expression has the form we anticipated in eqn 87.2. The steric factor is normally found to be several orders of magnitude smaller than 1.

Brief illustration 87.3 The steric factor

It is found experimentally that the pre-exponential factor for the reaction $H_2+C_2H_4\rightarrow C_2H_6$ at 628 K is $1.24\times10^6\,\mathrm{dm^3\,mol^{-3}\,s^{-1}}$. In *Brief illustration* 87.2 we calculated the result that can be expressed as $A=7.04\ldots\times10^{11}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. It follows that the steric factor for this reaction is

$$P=\frac{A_{\text{experimental}}}{A_{\text{calculated}}}=\frac{1.24\times10^6\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}}{7.04\ldots\times10^{11}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}}\approx 1.8\times10^{-6}$$

The very small value of P is one reason why catalysts are needed to bring this reaction about at a reasonable rate. As a general guide, the more complex the reactant molecules, the smaller the value of P.

Self-test 87.3 It is found for the reaction $NO+Cl_2\rightarrow NOCl+Cl$ that $A=4.0\times10^9\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ at 298 K. Estimate the P factor for the reaction (see the preceding Self-test).

Answer: 0.019

An example of a reaction for which it is possible to estimate the steric factor is $K+Br_2\rightarrow KBr+Br$, with the experimental value $P=4.8$. In this reaction, the distance of approach at which reaction occurs appears to be considerably larger than the distance needed for deflection of the path of the approaching molecules in a non-reactive collision. It has been proposed that the reaction proceeds by a **harpoon mechanism**. This brilliant name is based on a model of the reaction which pictures the K atom as approaching a Br_2 molecule, and when the two are close enough an electron (the harpoon) flips across from K to Br_2. In place of two neutral particles there are now two ions, so there is a Coulombic attraction between them: this attraction is the line on the harpoon. Under its influence the ions move together (the line is wound in), the reaction takes place, and KBr+Br emerge. The harpoon extends the cross-section for the reactive encounter, and the reaction rate is significantly underestimated by taking for the collision cross-section the value for simple mechanical contact between K and Br_2.

Example 87.1 illustrates two points about steric factors. First, the concept of a steric factor is not wholly useless because in some cases, such as unimolecular gas-phase reactions (Topic 91), its numerical value can be estimated. Second, and more pessimistically, most reactions are much more complex than $K+Br_2$, and we cannot expect to obtain P so easily.

Example 87.1 Estimating a steric factor

Estimate the value of P for the harpoon mechanism by calculating the distance at which it becomes energetically favourable for the electron to leap from K to Br_2. Take the sum of the radii of the reactants (treating them as spherical) to be 400 pm.

Method Begin by identifying all the contributions to the energy of interaction between the colliding species. There are three contributions to the energy of the process $K+Br_2 \rightarrow K^+ + Br_2^-$. The first is the ionization energy, I, of K. The second is the electron affinity, E_{ea}, of Br_2. The third is the Coulombic interaction energy between the ions when they have been formed: when their separation is R, this energy is $-e^2/4\pi\varepsilon_0 R$. The electron flips across when the sum of these three contributions changes from positive to negative (that is, when the sum is zero) and becomes energetically favourable.

Answer The net change in energy when the transfer occurs at a separation R is

$$E = I - E_{ea} - \frac{e^2}{4\pi\varepsilon_0 R}$$

The ionization energy I is larger than E_{ea}, so E becomes negative only when R has decreased to less than some critical value R^* given by

$$R^* = \frac{e^2}{4\pi\varepsilon_0 (I - E_{ea})}$$

When the particles are at this separation, the harpoon shoots across from K to Br_2, so we can identify the reactive cross-section as $\sigma^* = \pi R^{*2}$. This value of σ^* implies that the steric factor is

$$P = \frac{\sigma^*}{\sigma} = \frac{R^{*2}}{d^2} = \left(\frac{e^2}{4\pi\varepsilon_0 d(I - E_{ea})}\right)^2$$

where $d = R(K) + R(Br_2)$, the sum of the radii of the spherical reactants. With $I = 420\,kJ\,mol^{-1}$ (corresponding to 7.0×10^{-19} J), $E_{ea} \approx 250\,kJ\,mol^{-1}$ (corresponding to 4.2×10^{-19} J), and $d = 400$ pm, we find $P = 4.2$, in good agreement with the experimental value (4.8).

Self-test 87.4 Estimate the value of P for the harpoon reaction between Na and Cl_2 for which $d \approx 350$ pm; take $E_{ea} \approx 230\,kJ\,mol^{-1}$.

Answer: 2.2

Checklist of concepts

☐ 1. In **collision theory**, it is supposed that the rate is proportional to the collision frequency, a steric factor, and the fraction of collisions that occur with at least the kinetic energy E_a along their lines of centres.

☐ 2. The **collision density** is the number of collisions in a region of the sample in an interval of time divided by the volume of the region and the duration of the interval.

☐ 3. The **activation energy** is the minimum kinetic energy along the line of approach of reactant molecules that is required for reaction.

☐ 4. The **steric factor** is an adjustment that takes into account the orientational requirements for a successful collision.

Checklist of equations

Property	Equation	Comment	Equation number
Collision density	$Z_{AB} = \sigma(8kT/\pi\mu)^{1/2} N_A^2[A][B]$	Unlike molecules, KMT (kinetic-molecular theory)	87.3a
	$Z_{AA} = \sigma(4kT/\pi m_A)^{1/2} N_A^2[A]^2$	Like molecules, KMT	87.3d
Energy dependence of σ	$\sigma(\varepsilon) = (1 - \varepsilon_a/\varepsilon)\sigma$	$\sigma = 0$ for $\varepsilon < \varepsilon_a$	87.7
Rate constant	$k_r = P\sigma N_A(8kT/\pi\mu)^{1/2} e^{-E_a/RT}$	KMT, collision theory	87.8

TOPIC 88

Diffusion-controlled reactions

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➤ Why do you need to know this material?

Most chemical reactions take place in solution, and it is important to understand what controls their rates and how those rates can be modified.

➤ What is the key idea?

There are two limiting types of chemical reaction in solution: diffusion control and activation control.

➤ What do you need to know already?

This Topic makes use of the steady-state approximation (Topic 86) and draws on the formulation and solution of the diffusion equation (Topic 81). At one point it uses the Stokes–Einstein relation (Topic 80).

To consider reactions in solution we have to imagine processes that are entirely different from those in gases. No longer are there collisions of molecules hurtling together; now there is the jostling of one molecule through a dense but mobile collection of molecules making up the fluid environment.

88.1 Reaction in solution

Encounters between reactants in solution occur in a very different manner from encounters in gases. The encounters of reactant molecules dissolved in solvent are considerably less frequent than in a gas. However, because a molecule also migrates only slowly away from a location, two reactant molecules that encounter each other stay near each other for much longer than in a gas. This lingering of one molecule near another on account of the hindering presence of solvent molecules is called the **cage effect**. Such an **encounter pair** may accumulate enough energy to react even though it does not have enough energy to do so when it first forms. The activation energy of a reaction is a much more complicated quantity in solution than in a gas because the encounter pair is surrounded by solvent and we need to consider the energy of the entire local assembly of reactant and solvent molecules.

(a) Classes of reaction

The complicated overall process can be divided into simpler parts by setting up a simple kinetic scheme. We suppose that the rate of formation of an encounter pair AB is first-order in each of the reactants A and B:

$$\mathrm{A}+\mathrm{B}\rightarrow\mathrm{AB}\quad v=k_\mathrm{d}[\mathrm{A}][\mathrm{B}]$$

As we shall see, k_d (where the d signifies diffusion) is determined by the diffusional characteristics of A and B. The encounter pair can break up without reaction or it can go on to form products P. If we suppose that both processes are pseudofirst-order reactions (with the solvent perhaps playing a role), then we can write

$$\mathrm{AB}\rightarrow\mathrm{A}+\mathrm{B}\quad v=k_\mathrm{d}'[\mathrm{AB}]$$

and

$$\mathrm{AB}\rightarrow\mathrm{P}\quad v=k_\mathrm{a}[\mathrm{AB}]$$

The concentration of AB can now be found from the equation for the net rate of change of concentration of AB:

$$\frac{\mathrm{d}[\mathrm{AB}]}{\mathrm{d}t}=k_\mathrm{d}[\mathrm{A}][\mathrm{B}]-k_\mathrm{d}'[\mathrm{AB}]-k_\mathrm{a}[\mathrm{AB}]=0$$

where we have applied the steady-state approximation (Topic 86). This expression solves to

$$[\mathrm{AB}]=\frac{k_\mathrm{d}[\mathrm{A}][\mathrm{B}]}{k_\mathrm{a}+k_\mathrm{d}'}$$

The rate of formation of products is therefore

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t}=k_\mathrm{a}[\mathrm{AB}]=k_\mathrm{r}[\mathrm{A}][\mathrm{B}] \qquad k_\mathrm{r}=\frac{k_\mathrm{a}k_\mathrm{d}}{k_\mathrm{a}+k_\mathrm{d}'} \tag{88.1}$$

Two limits can now be distinguished. If the rate of separation of the unreacted encounter pair is much slower than the rate at which it forms products, then $k_\mathrm{d}' \ll k_\mathrm{a}$ and the effective rate constant is

$$k_\mathrm{r}=\frac{k_\mathrm{a}k_\mathrm{d}}{k_\mathrm{a}}=k_\mathrm{d} \qquad \text{Diffusion-controlled limit} \tag{88.2a}$$

In this **diffusion-controlled limit**, the rate of reaction is governed by the rate at which the reactant molecules diffuse through the solvent. Because the combination of radicals involves very little activation energy, radical and atom recombination reactions are often diffusion-controlled. An **activation-controlled reaction** arises when a substantial activation energy is involved in the reaction $\mathrm{AB}\rightarrow\mathrm{P}$. Then $k_\mathrm{a} \ll k_\mathrm{d}'$ and

$$k_\mathrm{r}=\frac{k_\mathrm{a}k_\mathrm{d}}{k_\mathrm{d}'}=k_\mathrm{a}K \qquad \text{Activation-controlled limit} \tag{88.2b}$$

where K is the equilibrium constant for $\mathrm{A}+\mathrm{B}\rightleftharpoons\mathrm{AB}$. In this limit, the reaction proceeds at the rate at which energy accumulates in the encounter pair from the surrounding solvent. Some experimental data are given in Table 88.1.

Table 88.1* Arrhenius parameters for reactions in solution

	$A/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})$	$E_\mathrm{a}/(\mathrm{kJ\,mol^{-1}})$
$(\mathrm{CH_3})_3\mathrm{CCl}$ solvolysis		
in water	7.1×10^{16}	100
in ethanol	3.0×10^{13}	112
in chloroform	1.4×10^{4}	45
$\mathrm{CH_3CH_2Br}+\mathrm{OH^-}$ in ethanol	4.3×10^{11}	90

* More values are given in the *Resource section*.

(b) Diffusion and reaction

The rate of a diffusion-controlled reaction is calculated by considering the rate at which the reactants diffuse together. As shown in the following *Justification*, the rate constant for a reaction in which the two molecules react if they come within a distance R^* of one another is

$$k_\mathrm{d}=4\pi R^* D N_\mathrm{A} \tag{88.3}$$

where D is the sum of the diffusion coefficients of the two reactant species in the solution.

Brief illustration 88.1 Diffusion control 1

The order of magnitude of R^* is 10^{-7} m (100 nm) and that of D for a species in water is $10^{-9}\,\mathrm{m^2\,s^{-1}}$. It follows from eqn 88.3 that

$$k_\mathrm{d}\approx 4\pi\times(10^{-7}\,\mathrm{m})\times(10^{-9}\,\mathrm{m^2\,s^{-1}})\times(6.022\times10^{23})\approx10^{9}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$$

which corresponds to $10^{12}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. An indication that a reaction is diffusion-controlled is that its rate constant is of the order of $10^{12}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$.

Self-test 88.1 Estimate the rate constant for a diffusion-controlled reaction in benzene ($D\approx2\times10^{-9}\,\mathrm{m^2\,s^{-1}}$), taking $R^*\approx100$ nm.

Answer: $1.5\times10^{12}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$

Justification 88.1 Solution of the radial diffusion equation

The general form of the diffusion equation (Topic 81) corresponding to motion in three dimensions is $D_\mathrm{B}\nabla^2[\mathrm{B}](\boldsymbol{r},t)=\partial[\mathrm{B}](\boldsymbol{r},t)/\partial t$; therefore, the concentration of B when the system has reached a steady state ($\partial[\mathrm{B}](\boldsymbol{r},t)/\partial t=0$) satisfies $\nabla^2[\mathrm{B}](\boldsymbol{r})=0$, with the concentration of B now depending only on location, not time. For a spherically symmetrical system, ∇^2 can be replaced by radial derivatives alone (see Table 6.1), so the equation satisfied by $[\mathrm{B}](r)$, as $[\mathrm{B}](r)$ can now be written, is

$$\frac{\mathrm{d}^2[\mathrm{B}](r)}{\mathrm{d}r^2}+\frac{2}{r}\frac{\mathrm{d}[\mathrm{B}](r)}{\mathrm{d}r}=0$$

The general solution of this equation is

$$[\mathrm{B}](r)=a+\frac{b}{r}$$

as may be verified by substitution. We need two boundary conditions to pin down the values of the two constants (a and b). One condition is that $[\mathrm{B}](r)$ has its bulk value [B] as $r\rightarrow\infty$.

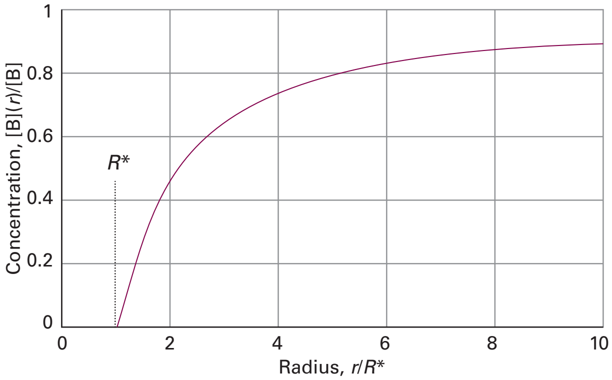

Figure 88.1 The concentration profile for reaction in solution when a molecule B diffuses towards another reactant molecule and reacts if it reaches R^*.

The second condition is that the concentration of B is zero at $r = R^*$, the distance at which reaction occurs. It follows that $a = [\mathrm{B}]$ and $b = -R^*[\mathrm{B}]$, and hence that (for $r \geq R^*$)

$$[\mathrm{B}](r) = \left(1 - \frac{R^*}{r}\right)[\mathrm{B}] \qquad (88.4)$$

Figure 88.1 illustrates the variation of concentration expressed by this equation.

The rate of reaction is the (molar) flux, J, of the reactant B towards A, multiplied by the area of the spherical surface of radius R^*:

$$\text{Rate of reaction} = 4\pi R^{*2} J$$

From Fick's first law (eqn 79.3 of Topic 79, written in the form $J = -D\partial[\mathrm{J}]/\partial x$), the flux of B towards A is proportional to the concentration gradient, so, at a radius R^*,

$$J = D_\mathrm{B}\left(\frac{\mathrm{d}[\mathrm{B}](r)}{\mathrm{d}r}\right)_{r=R^*} = \frac{D_\mathrm{B}[\mathrm{B}]}{R^*}$$

(A sign change has been introduced because we are interested in the flux towards decreasing values of r.) It follows that

$$\text{Rate of reaction} = 4\pi R^* D_\mathrm{B}[\mathrm{B}]$$

The rate of the diffusion-controlled reaction is equal to the average flow of B molecules to all the A molecules in the sample. If the bulk concentration of A is [A], the number of A molecules in the sample of volume V is $N_\mathrm{A}[\mathrm{A}]V$; the global flow of all B to all A is therefore $4\pi R^* D_\mathrm{B} N_\mathrm{A}[\mathrm{A}][\mathrm{B}]V$. Because it is unrealistic to suppose that all A molecules are stationary, we replace D_B by the sum of the diffusion coefficients of the two species and write $D = D_\mathrm{A} + D_\mathrm{B}$. Then the rate of change of concentration of AB is

$$\frac{\mathrm{d}[\mathrm{AB}]}{\mathrm{d}t} = 4\pi R^* D N_\mathrm{A}[\mathrm{A}][\mathrm{B}]$$

Hence, the diffusion-controlled rate constant is as given in eqn 88.3.

We can take eqn 88.3 further by incorporating the Stokes–Einstein equation (eqn 80.19 of Topic 80, $D_\mathrm{J} = kT/6\pi\eta R_\mathrm{J}$) relating the diffusion constant and the hydrodynamic radius R_A and R_B of each molecule in a medium of viscosity η. As this relation is approximate, little extra error is introduced if we write $R_\mathrm{A} = R_\mathrm{B} = \frac{1}{2}R^*$, which leads to

$$k_\mathrm{d} = \frac{8RT}{3\eta} \qquad \text{Diffusion-controlled rate constant} \qquad (88.5)$$

(The R in this equation is the gas constant.) The radii have cancelled because, although the diffusion constants are smaller when the radii are large, the reactive collision radius is larger and the particles need travel a shorter distance to meet. In this approximation, the rate constant is independent of the identities of the reactants, and depends only on the temperature and the viscosity of the solvent.

Brief illustration 88.2 Diffusion control 2

The rate constant for the recombination of I atoms in hexane at 298 K, when the viscosity of the solvent is 0.326 cP (with $1\,\mathrm{P} = 10^{-1}\,\mathrm{kg\,m^{-1}\,s^{-1}}$), is

$$k_\mathrm{d} = \frac{8 \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})}{3 \times (3.26 \times 10^{-4}\,\mathrm{kg\,m^{-1}\,s^{-1}})} = 2.0 \times 10^{7}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$$

where we have used $1\,\mathrm{J} = 1\,\mathrm{kg\,m^2\,s^{-2}}$. Because $1\,\mathrm{m^3} = 10^3\,\mathrm{dm^3}$, this result corresponds to $2.0 \times 10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. The experimental value is $1.3 \times 10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, so the agreement is very good considering the approximations involved.

Self-test 88.2 Evaluate a typical rate constant for a reaction taking place in ethanol at 20 °C, for which the viscosity is 1.06 cP.

Answer: $6.1 \times 10^{9}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$

88.2 The material-balance equation

The diffusion of reactants plays an important role in many chemical processes, such as the diffusion of $\mathrm{O_2}$ molecules into red blood corpuscles and the diffusion of a gas towards a catalyst. We can catch a glimpse of the kinds of calculations involved by considering the diffusion equation (Topic 81) generalized to take into account the possibility that the diffusing, convecting molecules are also reacting.

(a) The formulation of the equation

Consider a small volume element in a chemical reactor (or a biological cell). The net rate at which J molecules enter the region by diffusion and convection is given by eqn 81.10 of Topic 81, which we repeat here:

$$\frac{\partial[\mathrm{J}]}{\partial t}=D\frac{\partial^2[\mathrm{J}]}{\partial x^2}-v\frac{\partial[\mathrm{J}]}{\partial x} \qquad \text{Diffusion equation} \tag{88.6}$$

where v is the velocity of flow of J. The net rate of change of molar concentration due to chemical reaction is

$$\frac{\partial[\mathrm{J}]}{\partial t}=-k_{\mathrm{r}}[\mathrm{J}]$$

if we suppose that J disappears by a pseudofirst-order reaction. Therefore, the overall rate of change of the concentration of J is

$$\frac{\partial[\mathrm{J}]}{\partial t}=\overbrace{D\frac{\partial^2[\mathrm{J}]}{\partial x^2}}^{\text{Spread due to non-uniform distribution}}-\overbrace{v\frac{\partial[\mathrm{J}]}{\partial x}}^{\text{Change due to convection}}-\overbrace{k_{\mathrm{r}}[\mathrm{J}]}^{\text{Loss due to reaction}} \qquad \text{Material-balance equation} \tag{88.7}$$

Equation 88.7 is called the **material-balance equation**. If the rate constant is large, then [J] will decline rapidly. However, if the diffusion constant is large, then the decline can be replenished as J diffuses rapidly into the region. The convection term, which may represent the effects of stirring, can sweep material either into or out of the region according to the signs of v and the concentration gradient $\partial[\mathrm{J}]/\partial x$.

(b) Solutions of the equation

The material-balance equation is a second-order partial differential equation and is far from easy to solve in general. Some idea of how it is solved can be obtained by considering the special case in which there is no convective motion (as in an unstirred reaction vessel):

$$\frac{\partial[\mathrm{J}]}{\partial t}=D\frac{\partial^2[\mathrm{J}]}{\partial x^2}-k_{\mathrm{r}}[\mathrm{J}] \tag{88.8}$$

As may be verified by substitution (Problem 88.1), if the solution of this equation in the absence of reaction (that is, for $k_{\mathrm{r}}=0$) is [J], then the solution $[\mathrm{J}]^*$ in the presence of reaction ($k_{\mathrm{r}}>0$) is

$$[\mathrm{J}]^*=[\mathrm{J}]\mathrm{e}^{-k_{\mathrm{r}}t} \qquad \text{Diffusion with reaction} \tag{88.9}$$

An example of a solution of the diffusion equation in the absence of reaction is that given in Topic 81 (eqn 81.11) for a system in which initially a layer of n_0N_{A} molecules is spread over a plane of area A:

$$[\mathrm{J}]=\frac{n_0\mathrm{e}^{-x^2/4Dt}}{A(\pi Dt)^{1/2}} \tag{88.10}$$

When this expression is substituted into eqn 88.9, we obtain the concentration of J as it diffuses away from its initial surface layer and undergoes reaction in the overlying solution (Fig. 88.2).

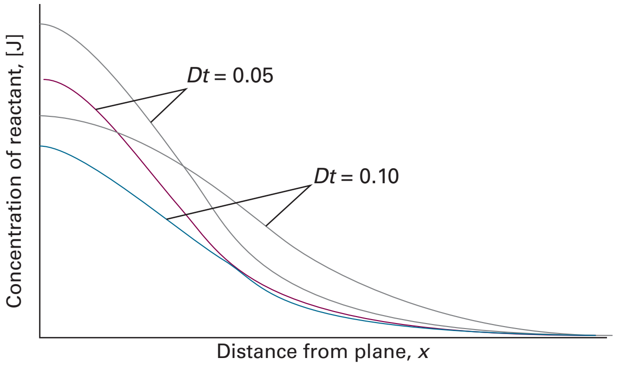

Figure 88.2 The concentration profiles for a diffusing, reacting system (for example, a column of solution) in which one reactant is initially in a layer at $x=0$. In the absence of reaction (grey lines) the concentration profiles are the same as in Fig. 81.3.

Brief illustration 88.3 Reaction with diffusion

Suppose 1.0 g of iodine (3.9 mmol $\mathrm{I_2}$) is spread over a surface of area 5.0 $\mathrm{cm^2}$ under a column of hexane ($D=4.1\times10^{-9}\,\mathrm{m^2\,s^{-1}}$). As it diffuses upwards it reacts with a pseudofirst-order rate constant $k_{\mathrm{r}}=4.0\times10^{-5}\,\mathrm{s^{-1}}$. By substituting these values into

$$[\mathrm{J}]^*=\frac{n_0\mathrm{e}^{-x^2/4Dt-k_{\mathrm{r}}t}}{A(\pi Dt)^{1/2}}$$

we can construct the following table:

$[\mathrm{J}]^*/(\mathrm{mol\,dm^{-3}})$	x		
t	1 mm	5 mm	1 cm
100 s	3.72	0	0
1000 s	1.96	0.45	0.005
10 000 s	0.46	0.40	0.25

Self-test 88.3 What is the value of [J] at 15 000 s at the same three locations?

Answer: 1.02, 0.92, 0.68 mol $\mathrm{dm^{-3}}$

Even this relatively simple example has led to an equation that is difficult to solve, and only in some special cases can the full material-balance equation be solved analytically. Most modern work on reactor design and cell kinetics uses numerical methods to solve the equation, and detailed solutions for realistic environments, such as vessels of different shapes (which influence the boundary conditions on the solutions) and with a variety of inhomogeneously distributed reactants, can be obtained reasonably easily.

Checklist of concepts

☐ 1. A reaction in solution may be **diffusion-controlled** if its rate is controlled by the rate at which reactant molecules encounter each other in solution.

☐ 2. The rate of an **activation-controlled reaction** is controlled by the rate at which the encounter pair accumulates sufficient energy.

☐ 3. The **material-balance equation** relates the overall rate of change of the concentration of a species to its rates of diffusion, convection and reaction.

☐ 4. The **cage effect**, the lingering of one reactant molecule near another due to the hindering presence of solvent molecules, results in the formation of an **encounter pair** of reactant molecules.

Checklist of equations

Property	Equation	Comment	Equation number
Diffusion-controlled limit	$k_r = k_d$	$v = k_d[A][B]$ for the encounter rate	88.2a
Activation-controlled limit	$k_r = k_a K$	K for $A+B \rightleftharpoons AB$, k_a for the decomposition of AB to P	88.2b
Diffusion-controlled rate constant	$k_d = 4\pi R^* D N_A$	$D = D_A + D_B$	88.3
	$k_d = 8RT/3\eta$	Assumes Stokes–Einstein relation	88.5
Material-balance equation	$\partial[J]/\partial t = D\partial^2[J]/\partial x^2 - v\partial[J]/\partial x - k_r[J]$	Pseudofirst-order reaction	88.7

TOPIC 89

Transition-state theory

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➤ Why do you need to know this material?

Transition-state theory provides a way to relate the rate constant of reactions to models of the cluster of atoms whose formation is proposed when reactants come together. It provides a link between information about the structures of reactants and the rate constant for their reaction.

➤ What is the key idea?

Reactants come together to form an activated complex that decays into products.

➤ What do you need to know already?

This Topic makes use of two strands: one is the relation between equilibrium constants and partition functions (Topic 74); the other is the relation between equilibrium constants and thermodynamic functions, such as the Gibbs energy, enthalpy, and entropy of reaction (Topic 73). You need to be aware of the Arrhenius equation for the temperature dependence of the rate constant (Topic 85).

In **transition-state theory** (which is also widely referred to as *activated-complex theory*), the notion of the transition state is used in conjunction with concepts of statistical thermodynamics to provide a more detailed calculation of rate constants than that presented by collision theory (Topic 87). Transition-state theory has the advantage that a quantity corresponding to the steric factor appears automatically, and P does not need to be grafted on to an equation as an afterthought; it is an attempt to identify the principal features governing the size of a rate constant in terms of a model of the events that take place during the reaction. There are several approaches to the calculation of rate constants by transition-state theory; here we present the simplest one.

89.1 The Eyring equation

In the course of a chemical reaction that begins with a collision between molecules of A and molecules of B, the potential energy of the system typically changes in the manner shown in Fig. 89.1. Although the illustration displays an exothermic reaction, a potential barrier is also common for endothermic reactions. As the reaction event proceeds, A and B come into contact, distort, and begin to exchange or discard atoms.

(a) The formulation of the equation

The **reaction coordinate** is a representation of the atomic displacements, such as changes in interatomic distances and bond angles, that are directly involved in the formation of products from reactants. The potential energy rises to a maximum and

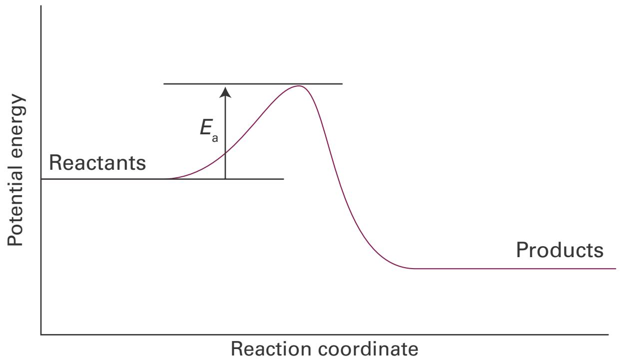

Figure 89.1 A potential energy profile for an exothermic reaction. The height of the barrier between the reactants and products is the activation energy of the reaction.

the cluster of atoms that corresponds to the region close to the maximum is called the **activated complex**. After the maximum, the potential energy falls as the atoms rearrange in the cluster and reaches a value characteristic of the products. The climax of the reaction is at the peak of the potential energy, which can be identified with the activation energy E_a; however, as in collision theory, this identification should be regarded as approximate. Here two reactant molecules have come to such a degree of closeness and distortion that a small further distortion will send them in the direction of products. This crucial configuration is called the **transition state** of the reaction. Although some molecules entering the transition state might revert to reactants, if they pass through this configuration then it is inevitable that products will emerge from the encounter. (This point is developed in more detail in the discussion of potential energy surfaces in Topic 90.)

A note on good practice The terms *activated complex* and *transition state* are often used as synonyms; however, it is best to preserve the distinction, with the former referring to the cluster of atoms and the latter to their critical configuration.

Transition-state theory pictures a reaction between A and B as proceeding through the formation of an activated complex, $C^{\ddagger}$, in a rapid pre-equilibrium (Fig. 89.2):

$$A+B \rightleftharpoons C^{\ddagger} \qquad K^{\ddagger}=\frac{p_{C^{\ddagger}}p^{\ominus}}{p_A p_B} \tag{89.1}$$

where we have replaced the activity of each species by $p/p^{\ominus}$. When we express the partial pressures, p_J, in terms of the molar concentrations, [J], by using $p_J=RT[J]$, the concentration of activated complex is related to the (dimensionless) equilibrium constant by

$$[C^{\ddagger}]=\frac{RT}{p^{\ominus}}K^{\ddagger}[A][B] \tag{89.2}$$

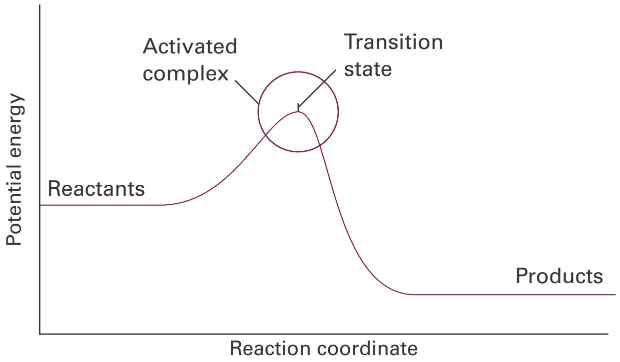

Figure 89.2 A reaction profile (for an exothermic reaction). The horizontal axis is the reaction coordinate, and the vertical axis is potential energy. The activated complex is the region near the potential maximum, and the transition state corresponds to the maximum itself.

The activated complex falls apart by unimolecular decay into products, *P*, with a rate constant $k^{\ddagger}$:

$$C^{\ddagger} \rightarrow P \quad v=k^{\ddagger}[C^{\ddagger}] \tag{89.3}$$

It follows that

$$v=k_r[A][B] \quad k_r=\frac{RT}{p^{\ominus}}k^{\ddagger}K^{\ddagger} \tag{89.4}$$

Our task is to calculate the unimolecular rate constant $k^{\ddagger}$ and the equilibrium constant $K^{\ddagger}$.

(b) The rate of decay of the activated complex

An activated complex can form products if it passes through the transition state. As the reactant molecules approach the activated complex region, some bonds are forming and shortening while others are lengthening and breaking; therefore, along the reaction coordinate, there is a vibration-like motion of the atoms in the activated complex. If this motion occurs with a frequency $\nu^{\ddagger}$, then the frequency with which the cluster of atoms forming the complex approaches the transition state is also $\nu^{\ddagger}$. However, it is possible that not every oscillation along the reaction coordinate takes the complex through the transition state. For instance, the centrifugal effect of rotations might also be an important contribution to the break-up of the complex, and in some cases the complex might be rotating too slowly, or rotating rapidly but about the wrong axis. Therefore, we suppose that the rate of passage of the complex through the transition state is proportional to the vibrational frequency along the reaction coordinate, and write

$$k^{\ddagger}=\kappa\nu^{\ddagger} \tag{89.5}$$

where κ (kappa) is the **transmission coefficient**. In the absence of information to the contrary, κ is assumed to be about 1.

Brief illustration 89.1 The decay rate

Typical molecular vibration wavenumbers of small molecules (Topic 44) occur at wavenumbers of the order of $10^3\,\mathrm{cm^{-1}}$ (C–H bends, for example, occur in the range 1340–$1465\,\mathrm{cm^{-1}}$) and therefore at frequencies of the order of 10^{13} Hz. If we suppose that the loosely bound cluster vibrates at one or two orders of magnitude lower frequency, then $\nu^{\ddagger}\approx 10^{11}-10^{12}$ Hz. These figures suggest that $k^{\ddagger}\approx 10^{11}-10^{12}\,\mathrm{s^{-1}}$, with κ perhaps reducing that value further.

Self-test 89.1 Estimate the change in $\nu^{\ddagger}$ that would occur if ^{1}H is replaced by ^{2}H in a C—H group at the site of reaction. Assume that the C atom is immobile.

Answer: $\nu^{\ddagger}\rightarrow\nu^{\ddagger}/2^{1/2}$

(c) The concentration of the activated complex

Topic 74 explains how to calculate equilibrium constants from structural data. Equation 74.4 of that Topic (K in terms of the standard molar partition functions $q_J^{\ominus}$) can be used directly, which in this case gives

$$K^{\ddagger}=\frac{N_{\mathrm{A}}q_{\mathrm{C}^{\ddagger}}^{\ominus}}{q_{\mathrm{A}}^{\ominus}q_{\mathrm{B}}^{\ominus}}\mathrm{e}^{-\Delta E_0/RT} \tag{89.6}$$

with

$$\Delta E_0=E_0(\mathrm{C}^{\ddagger})-E_0(\mathrm{A})-E_0(\mathrm{B}) \tag{89.7}$$

Note that the units of N_{A} and the $q_J^{\ominus}$ are $\mathrm{mol^{-1}}$, so $K^{\ddagger}$ is dimensionless (as is appropriate for an equilibrium constant).

In the final step of this part of the calculation, we focus attention on the partition function of the activated complex. We have already assumed that a vibration of the activated complex $\mathrm{C}^{\ddagger}$ tips it through the transition state. The partition function for this vibration is (see eqn 52.15 of Topic 52, which is essentially the following)

$$q=\frac{1}{1-\mathrm{e}^{-h\nu^{\ddagger}/kT}}$$

where $\nu^{\ddagger}$ is its frequency (the same frequency that determines $k^{\ddagger}$). This frequency is much lower than for an ordinary molecular vibration because the oscillation corresponds to the complex falling apart (Fig. 89.3), so the force constant is very low.

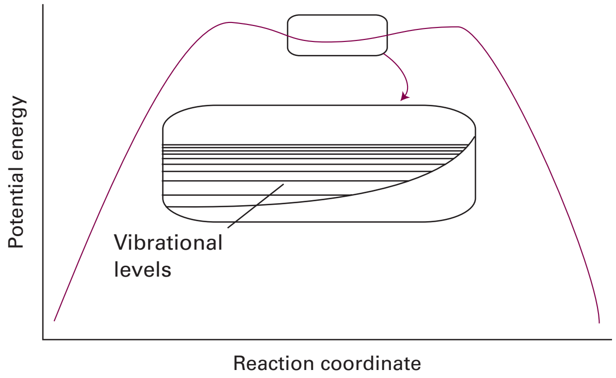

Figure 89.3 In an elementary depiction of the activated complex close to the transition state, there is a broad, shallow dip in the potential energy surface along the reaction coordinate. The complex vibrates harmonically and almost classically in this well. However, this depiction is an oversimplification, for in many cases there is no dip at the top of the barrier, and the curvature of the potential energy, and therefore the force constant, is negative. Formally, the vibrational frequency is then imaginary. We ignore this problem here.

Therefore, provided that $h\nu^{\ddagger}/kT\ll 1$, the exponential may be expanded and the partition function reduces to

$$q=\frac{1}{1-\left(1-h\nu^{\ddagger}/kT+\cdots\right)}\approx\frac{kT}{h\nu^{\ddagger}}$$

We can therefore write

$$q_{\mathrm{C}^{\ddagger}}^{\ominus}=\frac{kT}{h\nu^{\ddagger}}\bar{q}_{\mathrm{C}^{\ddagger}} \tag{89.8}$$

where $\bar{q}_{\mathrm{C}^{\ddagger}}$ denotes the partition function for all the other modes of the complex. The constant $K^{\ddagger}$ is therefore

$$K^{\ddagger}=\frac{kT}{h\nu^{\ddagger}}\bar{K}^{\ddagger}\qquad \bar{K}^{\ddagger}=\frac{N_{\mathrm{A}}\bar{q}_{\mathrm{C}^{\ddagger}}^{\ominus}}{q_{\mathrm{A}}^{\ominus}q_{\mathrm{B}}^{\ominus}}\mathrm{e}^{-\Delta E_0/RT} \tag{89.9}$$

with $\bar{K}^{\ddagger}$ a kind of equilibrium constant, but with one vibrational mode of $\mathrm{C}^{\ddagger}$ discarded.

Brief illustration 89.2 The discarded mode

Consider the case of two structureless particles A and B colliding to give an activated complex that resembles a diatomic molecule. The activated complex is a diatomic cluster. It has one vibrational mode, but that mode corresponds to motion along the reaction coordinate and therefore does not appear in $\bar{q}^{\ominus}_{C^\ddagger}$. It follows that the standard molar partition function of the activated complex has only rotational and translational contributions.

Self-test 89.2 Which mode would be discarded for a reaction in which the activated complex is modelled as a linear triatomic cluster?

Answer: Antisymmetric stretch

(d) The rate constant

We can now combine all the parts of the calculation into

$$k_r = \frac{RT}{p^{\ominus}} k^\ddagger \bar{K}^\ddagger = \kappa \nu^\ddagger \frac{kT}{h\nu^\ddagger}\frac{RT}{p^{\ominus}}\bar{K}^\ddagger$$

At this stage the unknown frequencies $\nu^\ddagger$ (in blue) cancel, and, after writing $\bar{K}_c^\ddagger = (RT/p^{\ominus})\bar{K}^\ddagger$, we obtain the **Eyring equation**:

$$k_r = \kappa \frac{kT}{h}\bar{K}_c^\ddagger \qquad \text{Eyring equation} \tag{89.10}$$

The factor $\bar{K}_c^\ddagger$ is given by eqn 89.9 and the definition $\bar{K}_c^\ddagger = (RT/p^{\ominus})\bar{K}^\ddagger$ in terms of the partition functions of A, B, and C‡, so in principle we now have an explicit expression for the second-order rate constant for a bimolecular reaction in terms of the molecular parameters for the reactants and the activated complex, and the quantity κ.

The partition functions for the reactants can normally be calculated quite readily using either spectroscopic information about their energy levels or the approximate expressions set out in Topic 52. The difficulty with the Eyring equation, however, lies in the calculation of the partition function of the activated complex: C‡ is difficult to investigate spectroscopically (but see the following section), and in general we need to make assumptions about its size, shape, and structure. We shall illustrate what is involved in one simple but significant case.

Example 89.1 Analysing the collision of structureless particles

Consider the case of two structureless (and different) particles A and B colliding to give an activated complex that resembles a diatomic molecule, and deduce an expression for the rate constant of the reaction A + B → Products.

Method Because the reactants J = A, B are structureless 'atoms', the only contributions to their partition functions are the translational terms. The activated complex is a diatomic cluster of mass $m_{C^\ddagger} = m_A + m_B$ and moment of inertia I. It has one vibrational mode but, as explained in *Brief illustration* 89.2, that mode corresponds to motion along the reaction coordinate. It follows that the standard molar partition function of the activated complex has only rotational and translational contributions. Expressions for the relevant partition functions are given by eqns 52.10 and 52.13 of Topic 52 (and are repeated below).

Answer The translational partition functions are

$$q_J^{\ominus} = \frac{V_m^{\ominus}}{\Lambda_J^3} \qquad \Lambda_J = \frac{h}{(2\pi m_J kT)^{1/2}} \qquad V_m^{\ominus} = \frac{RT}{p^{\ominus}}$$

with J = A, B, and C‡, and with $m_{C^\ddagger} = m_A + m_B$. The expression for the partition function of the activated complex is

$$\bar{q}^{\ominus}_{C^\ddagger} = \overbrace{\frac{2IkT}{\hbar^2}}^{q^R}\,\overbrace{\frac{V_m^{\ominus}}{\Lambda_{C^\ddagger}^3}}^{q^T}$$

where we have used the high-temperature form of the rotational partition function (Topic 52). By substituting these expressions into the Eyring equation, we find that the rate constant is

$$\begin{aligned} k_r &= \kappa \frac{kT}{h}\frac{RT}{p^{\ominus}}\left(\frac{N_A \Lambda_A^3 \Lambda_B^3}{\Lambda_{C^\ddagger}^3 V_m^{\ominus}}\right)\frac{2IkT}{\hbar^2}e^{-\Delta E_0/RT} \\ &= \kappa \frac{kT}{h} N_A \left(\frac{\Lambda_A \Lambda_B}{\Lambda_{C^\ddagger}}\right)^3 \frac{2IkT}{\hbar^2}e^{-\Delta E_0/RT} \end{aligned}$$

The moment of inertia of a diatomic molecule of bond length r is μr^2, where $\mu = m_A m_B/(m_A + m_B)$ is the effective mass, so after introducing the expressions for the thermal wavelengths and cancelling common terms, we find (Problem 89.3)

$$k_r = \kappa N_A \left(\frac{8kT}{\pi\mu}\right)^{1/2} \pi r^2 e^{-\Delta E_0/RT}$$

Finally, by identifying $\kappa\pi r^2$ as the reactive cross-section σ^*, we arrive at precisely the same expression as that obtained from simple collision theory (eqn 87.9):

$$k_r = N_A \left(\frac{8kT}{\pi\mu}\right)^{1/2} \sigma^* e^{-\Delta E_0/RT}$$

Self-test 89.3 What additional factors would be present if the reaction were AB + C → Products through a linear activated complex?

Answer: Rotation and vibration of AB, bends and symmetric stretch of the activated complex

(e) Observation and manipulation of the activated complex

The development of femtosecond pulsed lasers (Topic 46) has made it possible to make observations on species that have such short lifetimes that in a number of respects they resemble an activated complex, which often survive for only a few picoseconds. In a typical experiment designed to detect an activated complex, a femtosecond laser pulse is used to excite a molecule to a dissociative state, and then the system is exposed to a second femtosecond pulse at an interval after the dissociating pulse. The frequency of the second pulse is set at an absorption of one of the free fragmentation products, so its absorption is a measure of the abundance of the dissociation product. For example, when ICN is dissociated by the first pulse, the emergence of CN from the photoactivated state can be monitored by watching the growth of the free CN absorption (or, more commonly, its laser-induced fluorescence). In this way it has been found that the CN signal remains zero until the fragments have separated by about 600 pm, which takes about 205 fs.

Some sense of the progress that has been made in the study of the intimate mechanism of chemical reactions can be obtained by considering the decay of the ion pair Na^+I^-. As shown in Fig. 89.4, excitation of the ionic species with a femtosecond laser pulse forms an excited state that corresponds to a covalently bonded NaI molecule. The system can be described with two potential energy surfaces, one largely 'ionic' and another 'covalent', which cross at an internuclear separation of 693 pm. A short laser pulse is composed of a wide range of frequencies, which excite many vibrational states of NaI simultaneously. Consequently, the electronically excited complex exists as a superposition of states, or a localized wavepacket, which oscillates between the 'covalent' and 'ionic' potential energy surfaces, as shown in Fig. 89.4. The complex can also dissociate, shown as movement of the wavepacket toward very long internuclear separation along the dissociative surface. However, not every outward-going swing leads to dissociation because there is a chance that the I atom can be harpooned again, in which case it fails to make good its escape. The dynamics of the system is probed by a second laser pulse with a frequency that corresponds to the absorption frequency of the free Na product or to the frequency at which Na absorbs when it is a part of the complex. The latter frequency depends on the Na···I distance, so an absorption (in practice, a laser-induced fluorescence) is obtained each time the wavepacket returns to that separation.

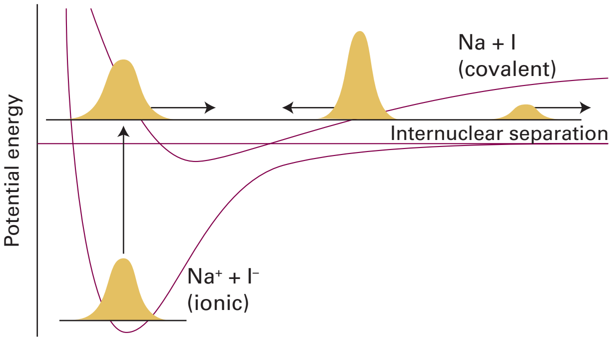

Figure 89.4 Excitation of the ion pair Na^+I^- forms an excited state with covalent character. Also shown is migration between a 'covalent' surface (upper curve) and an 'ionic' surface (lower curve) of the wavepacket formed by laser excitation.

Brief illustration 89.3 Femtosecond analysis

A typical set of results is shown in Fig. 89.5. The bound Na absorption intensity shows up as a series of pulses that recur in about 1 ps, showing that the wavepacket oscillates with about that period. The decline in intensity shows the rate at which the complex can dissociate as the two atoms swing away from each other. The free Na absorption also grows in an oscillating manner, showing the periodicity of wavepacket oscillation, each swing of which gives it a chance to dissociate. The precise period of the oscillation in NaI is 1.25 ps. The complex survives for about ten oscillations. In contrast, although the oscillation frequency of NaBr is similar, it barely survives one oscillation.

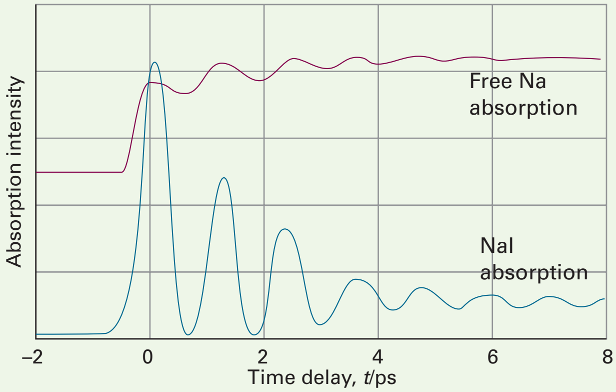

Figure 89.5 Femtosecond spectroscopic results for the reaction in which sodium iodide separates into Na and I. The lower curve is the absorption of the electronically excited complex and the upper curve is the absorption of free Na atoms. (Adapted from A.H. Zewail, *Science* **242**, 1645 (1988).)

Self-test 89.4 Confirm the assumption in transition-state theory that the vibrational frequency of the dissociative mode of the activated complex is very low by calculating the vibrational wavenumber corresponding to the 1.25 ps period of oscillation in NaI.

Answer: $27\,\mathrm{cm}^{-1}$

Femtosecond spectroscopy has also been used to examine analogues of the activated complex involved in bimolecular reactions. Thus, a molecular beam can be used to produce a van der Waals molecule (Topic 90), such as IH···OCO. The HI bond can be dissociated by a femtosecond pulse, and the H atom is ejected towards the O atom of the neighbouring CO_2 molecule to form HOCO. Hence, the van der Waals molecule is a source of a species that resembles the activated complex of the reaction

$$\mathrm{H} + \mathrm{CO_2} \rightarrow [\mathrm{HOCO}]^{\ddagger} \rightarrow \mathrm{HO} + \mathrm{CO}$$

The probe pulse is tuned to the OH radical, which enables the evolution of $[\mathrm{HOCO}]^{\ddagger}$ to be studied in real time.

The techniques used for the spectroscopic detection of transition states can also be used to control the outcome of a chemical reaction by direct manipulation of the transition state. Consider the reaction $\mathrm{I_2}+\mathrm{Xe}\rightarrow\mathrm{XeI}^*+\mathrm{I}$, which occurs by a harpoon mechanism with a transition state denoted as $[\mathrm{Xe}^+\cdots\mathrm{I}^-\cdots\mathrm{I}]$. The reaction can be initiated by exciting I_2 to an electronic state at least 52 460 $\mathrm{cm^{-1}}$ above the ground state and then followed by measuring the time dependence of the chemiluminescence of XeI^*. To exert control over the yield of the product, a pair of femtosecond pulses can be used to induce the reaction. The first pulse excites the I_2 molecule to a low-energy and unreactive electronic state. We already know that excitation by a femtosecond pulse generates a wavepacket that can be treated as a particle travelling across the potential energy surface. In this case, the wavepacket does not have enough energy to react, but excitation by another laser pulse with the appropriate wavelength can provide the necessary additional energy. It follows that activated complexes with different geometries can be prepared by varying the time delay between the two pulses, as the partially localized wavepacket will be at different locations on the potential energy surface as it evolves after being formed by the first pulse. Because the reaction occurs by the harpoon mechanism, the product yield expected to be optimal if the second pulse is applied when the wavepacket is at a point where the $\mathrm{Xe}\cdots\mathrm{I_2}$ distance is just right for electron transfer from Xe to I_2 to occur. This type of control of the $\mathrm{I_2}+\mathrm{Xe}$ reaction has been demonstrated.

89.2 Thermodynamic aspects

The statistical thermodynamic version of transition-state theory rapidly runs into difficulties because only in some cases is anything known about the structure of the activated complex. However, the concepts that it introduces, principally that of an equilibrium between the reactants and the activated complex, have motivated a more general, empirical approach in which the activation process is expressed in terms of thermodynamic functions.

(a) Activation parameters

If we accept that $\bar{K}^{\ddagger}$ is an equilibrium constant (despite one mode of $C^{\ddagger}$ having been discarded), we can express it in terms of a **Gibbs energy of activation**, $\Delta^{\ddagger}G$, through the definition

$$\Delta^{\ddagger}G = -RT\ln\bar{K}^{\ddagger} \qquad (89.11)$$

Definition Gibbs energy of activation

All the $\Delta^{\ddagger}X$ in this section are *standard* thermodynamic quantities, $\Delta^{\ddagger}X^{\ominus}$, but we shall omit the standard state sign to avoid overburdening the notation. Then the rate constant becomes

$$k_r = \kappa\frac{kT}{h}\frac{RT}{p^{\ominus}}\mathrm{e}^{-\Delta^{\ddagger}G/RT} \qquad (89.12)$$

Because $G=H-TS$, the Gibbs energy of activation can be divided into an **entropy of activation**, $\Delta^{\ddagger}S$, and an **enthalpy of activation**, $\Delta^{\ddagger}H$, by writing

$$\Delta^{\ddagger}G = \Delta^{\ddagger}H - T\Delta^{\ddagger}S \qquad (89.13)$$

Definition Entropy and enthalpy of activation

When eqn 89.13 is used in eqn 89.12 and κ is absorbed into the entropy term, we obtain

$$k_r = B\mathrm{e}^{\Delta^{\ddagger}S/R}\mathrm{e}^{-\Delta^{\ddagger}H/RT} \qquad B = \frac{kT}{h}\frac{RT}{p^{\ominus}} \qquad (89.14)$$

The formal definition of activation energy (eqn 85.3 of Topic 85, $E_a = RT^2(\mathrm{d}\ln k_r/\mathrm{d}T)$) then gives $E_a = \Delta^{\ddagger}H + 2RT$, so[1]

$$k_r = \mathrm{e}^2B\mathrm{e}^{\Delta^{\ddagger}S/R}\mathrm{e}^{-E_a/RT} \qquad (89.15a)$$

from which it follows that the Arrhenius factor A can be identified as

$$A = \mathrm{e}^2B\mathrm{e}^{\Delta^{\ddagger}S/R} \qquad (89.15b)$$

Transition-state theory A-factor

The entropy of activation is negative because throughout the system reactant species are combining to form reactive pairs. However, if there is a reduction in entropy below what would be expected for the simple encounter of A and B, then the Arrhenius factor A will be smaller than that expected on the basis of simple collision theory. Indeed, we can identify that *additional* reduction in entropy, $\Delta^{\ddagger}S_{\mathrm{steric}}$, as the origin of the steric factor of collision theory, and write

$$P = \mathrm{e}^{\Delta^{\ddagger}S_{\mathrm{steric}}/R} \qquad (89.15c)$$

Transition-state theory P-factor

---

[1] For reactions of the type $\mathrm{A}+\mathrm{B}\rightarrow\mathrm{P}$ in the gas phase, $E_a = \Delta^{\ddagger}H + 2RT$. For such reactions in solution, $E_a = \Delta^{\ddagger}H + RT$.

Thus, the more complex the steric requirements of the encounter, the more negative the value of $\Delta^{\ddagger}S_{\text{steric}}$, and the smaller the value of P.

Brief illustration 89.4 Activation parameters

The reaction of propylxanthate ion in acetic acid buffer solutions can be represented by the equation $A^- + H^+ \rightarrow P$. Near 30 °C, $A = 2.05\times10^{13}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$. To evaluate the entropy of activation at 30 °C we first note that because the reaction is in solution the e^2 of eqn 89.15 should be replaced by e (see footnote 1 on the previous page), and then use eqn 89.15b in the form

$$\Delta^{\ddagger}S = R\ln\frac{A}{eB} \quad \text{with } B = \frac{kT}{h}\frac{RT}{p^{\ominus}} = 1.592\times10^{14}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

Therefore,

$$\begin{aligned}\Delta^{\ddagger}S &= R\ln\frac{2.05\times10^{13}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}{e\times\left(1.592\times10^{14}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}\right)} = R\ln 0.047\ldots\\ &= -25.4\ \text{J K}^{-1}\ \text{mol}^{-1}\end{aligned}$$

Self-test 89.5 The reaction $A^- + H^+ \rightarrow P$ in solution has $A = 6.92\times10^{12}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$. Evaluate the entropy of activation at 25 °C.

Answer: $-34.1\ \text{J K}^{-1}\,\text{mol}^{-1}$

Gibbs energies, enthalpies, entropies, volumes, and heat capacities of activation are widely used to report experimental reaction rates, especially for organic reactions in solution. They are encountered when relationships between equilibrium constants and rates of reaction are explored using **correlation analysis**, in which ln K (which is equal to $-\Delta_r G^{\ominus}/RT$) is plotted against ln k_r (which is proportional to $-\Delta^{\ddagger}G/RT$). In many cases the correlation is linear, signifying that, as the reaction becomes thermodynamically more favourable, its rate constant increases (Fig. 89.6). This linear correlation is the origin of the alternative name **linear free energy relation** (LFER).

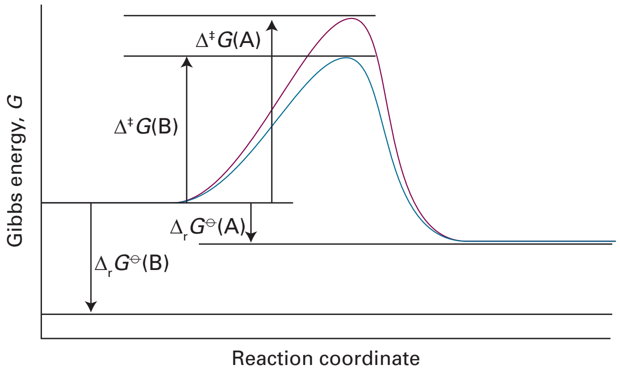

Figure 89.6 For a related pair of reactions (denoted A and B), the reaction with the larger (more negative) standard reaction Gibbs energy (B) has a lower activation barrier and therefore larger rate constant. This approximate linear correlation between $\Delta^{\ddagger}G$ and $\Delta_r G^{\ominus}$ is the origin of linear free energy relations.

(b) Reactions between ions

The thermodynamic version of transition-state theory simplifies the discussion of reactions in solution. The statistical thermodynamic theory is very complicated to apply because the solvent plays a role in the activated complex. In the thermodynamic approach we combine the rate law

$$\frac{d[P]}{dt} = k^{\ddagger}[C^{\ddagger}]$$

with the thermodynamic equilibrium constant

$$K = \frac{a_{C^\ddagger}}{a_A a_B} = K_\gamma\frac{[C^{\ddagger}]c^{\ominus}}{[A][B]} \qquad K_\gamma = \frac{\gamma_{C^\ddagger}}{\gamma_A\gamma_B}$$

Then

$$\frac{d[P]}{dt} = k_r[A][B] \qquad k_r = \frac{k^{\ddagger}K}{K_\gamma c^{\ominus}} \tag{89.16a}$$

If k_r° is the rate constant when the activity coefficients are 1 (that is, $k_r^{\circ} = k^{\ddagger}K/c^{\ominus}$), we can write

$$k_r = \frac{k_r^{\circ}}{K_\gamma} \qquad \log k_r = \log k_r^{\circ} - \log K_\gamma \tag{89.16b}$$

At low concentrations the activity coefficients can be expressed in terms of the ionic strength, I, of the solution by using the Debye–Hückel limiting law (Topic 72, particularly eqn 72.26, $\log\gamma_\pm = -A|z_+z_-|I^{1/2}$). However, we need the expressions for the individual ions rather than the mean value, and so write $\log\gamma_J = -Az_J^2 I^{1/2}$ and

$$\log\gamma_A = -Az_A^2 I^{1/2} \qquad \log\gamma_B = -Az_B^2 I^{1/2} \tag{89.17a}$$

with $A = 0.509$ in aqueous solution at 298 K and z_A and z_B the charge numbers of A and B, respectively. Because the activated complex forms from reaction of one of the ions of A with one of the ions of B, the charge number of the activated complex is $z_A + z_B$, where z_J is positive for cations and negative for anions. Therefore

$$\log\gamma_{C^\ddagger} = -A(z_A + z_B)^2 I^{1/2} \tag{89.17b}$$

Inserting these relations into eqn 89.16b results in

$$\begin{aligned}\log k_\mathrm{r} &= \log k_\mathrm{r}^\circ - A\{z_\mathrm{A}^2 + z_\mathrm{B}^2 - (z_\mathrm{A}+z_\mathrm{B})^2\}I^{1/2} \\ &= \log k_\mathrm{r}^\circ + 2Az_\mathrm{A}z_\mathrm{B}I^{1/2}\end{aligned} \qquad (89.18)$$

Equation 89.18 expresses the **kinetic salt effect**, the variation of the rate constant of a reaction between ions with the ionic strength of the solution (Fig. 89.7). If the reactant ions have the same sign (as in a reaction between cations or between anions), then increasing the ionic strength by the addition of inert ions increases the rate constant. The formation of a single, highly charged ionic complex from two less highly charged ions is favoured by a high ionic strength because the new ion has a denser ionic atmosphere and interacts with that atmosphere more strongly. Conversely, ions of opposite charge react more slowly in solutions of high ionic strength. Now the charges cancel and the complex has a less favourable interaction with its atmosphere than the separated ions.

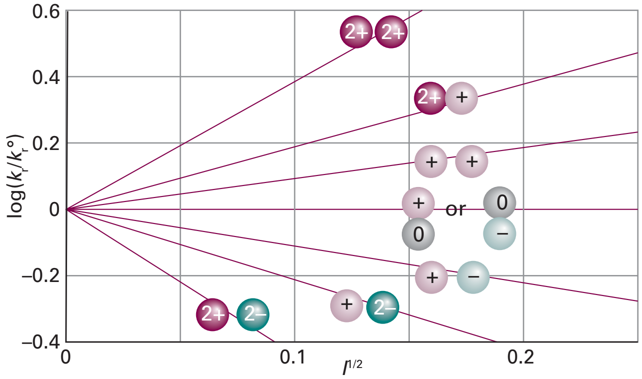

Figure 89.7 Experimental tests of the kinetic salt effect for reactions in water at 298 K. The ion types are shown as spheres, and the slopes of the lines are those given by the Debye–Hückel limiting law and eqn 89.18.

Example 89.2 Analysing the kinetic salt effect

The rate constant for the base (OH⁻) hydrolysis of $[\mathrm{CoBr(NH_3)_5}]^{2+}$ varies with ionic strength as tabulated below. What can be deduced about the charge of the activated complex in the rate-determining stage? We cannot assume without more evidence that it is a bimolecular process with an activated complex of charge +1.

I	0.0050	0.0100	0.0150	0.0200	0.0250	0.0300
$k_\mathrm{r}/k_\mathrm{r}^\circ$	0.718	0.631	0.562	0.515	0.475	0.447

Method According to eqn 89.18, a plot of $\log(k_\mathrm{r}/k_\mathrm{r}^\circ)$ against $I^{1/2}$ will have a slope of $1.02z_\mathrm{A}z_\mathrm{B}$, from which we can infer the charges of the ions involved in the formation of the activated complex.

Answer Form the following table:

I	0.0050	0.0100	0.0150	0.0200	0.0250	0.0300
$I^{1/2}$	0.071	0.100	0.122	0.141	0.158	0.173
$\log(k_\mathrm{r}/k_\mathrm{r}^\circ)$	−0.14	−0.20	−0.25	−0.29	−0.32	−0.35

These points are plotted in Fig. 89.8. The slope of the (least-squares) straight line is −2.04, indicating that $z_\mathrm{A}z_\mathrm{B} = -2$. Because $z_\mathrm{A} = -1$ for the OH⁻ ion, if that ion is involved in the formation of the activated complex, then the charge number of the second ion is +2. This analysis suggests that the pentaamminebromidocobalt(III) cation, $[\mathrm{CoBr(NH_3)_5}]^{2+}$, participates in the formation of the activated complex and that the charge of the activated complex is −1+2=+1. Although we do not pursue the point here, you should be aware that the rate constant is also influenced by the relative permittivity of the medium.

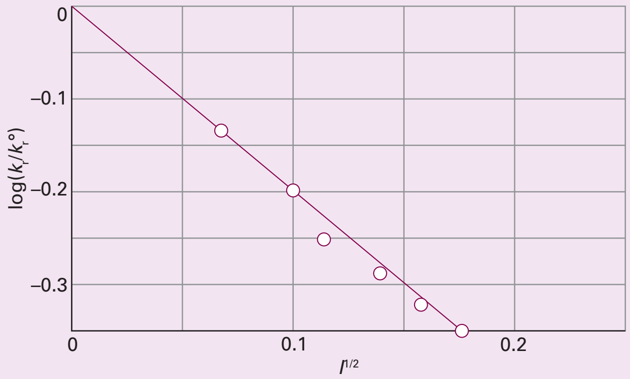

Figure 89.8 The experimental ionic strength dependence of the rate constant of a hydrolysis reaction: the slope gives information about the charge types involved in the activated complex of the rate-determining step. See Example 89.2.

Self-test 89.6 An ion of charge number +1 is known to be involved in the activated complex of a reaction. Deduce the charge number of the other ion from the following data:

I	0.0050	0.0100	0.0150	0.0200	0.0250	0.0300
$k_\mathrm{r}/k_\mathrm{r}^\circ$	0.930	0.902	0.884	0.867	0.853	0.841

Answer: −1

Checklist of concepts

☐ **1.** In transition-state theory, it is supposed that an **activated complex** is in equilibrium with the reactants.

☐ **2.** The rate at which the activated complex forms products depends on the rate at which it passes through a **transition state**.

☐ **3.** The rate constant may be parameterized in terms of the **Gibbs energy**, **entropy**, and **enthalpy of activation**.

☐ **4.** The **kinetic salt effect** is the effect of an added inert salt on the rate of a reaction between ions.

Checklist of equations

Property	Equation	Comment	Equation number
'Equilibrium constant' for activated complex formation	$\bar{K}^{\ddagger}=(N_{\rm A}\bar{q}^{\ominus}_{{\rm C}^{\ddagger}}/q^{\ominus}_{\rm A}q^{\ominus}_{\rm B})\,{\rm e}^{-\Delta E_0/RT}$	Assume equilibrium; one vibrational mode of C‡ discarded	89.9
Eyring equation	$k_{\rm r}=\kappa(kT/h)\bar{K}_{\rm c}{}^{\ddagger}$	Transition-state theory	89.10
Gibbs energy of activation	$\Delta^{\ddagger}G=-RT\ln\bar{K}^{\ddagger}$	Definition	89.11
Enthalpy and entropy of activation	$\Delta^{\ddagger}G=\Delta^{\ddagger}H-T\Delta^{\ddagger}S$	Definition	89.13
Parameterization	$k_{\rm r}={\rm e}^{n}B{\rm e}^{\Delta^{\ddagger}S/R}{\rm e}^{-E_{\rm a}/RT}$	$n=2$ for gas-phase reactions; $n=1$ for solution	89.15a
A-factor	$A={\rm e}^{n}B{\rm e}^{\Delta^{\ddagger}S/R}$		89.15b
P-factor	$P={\rm e}^{\Delta^{\ddagger}S_{\rm steric}/R}$		89.15c
Kinetic salt effect	$\log k_{\rm r}=\log k_{\rm r}^{\circ}+2Az_{\rm A}z_{\rm B}I^{1/2}$	Assumes Debye–Hückel limiting law valid	89.18

TOPIC 90

The dynamics of molecular collisions

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➤ Why do you need to know this material?

Chemists are interested in the details of chemical reactions, and there is no more detailed approach than that involved in the study of the dynamics of reactive encounters, when one molecule collides with another and atoms exchange partners.

➤ What is the key idea?

The rates of reactions in the gas phase can be investigated by exploring the trajectories of molecules on potential energy surfaces.

➤ What do you need to know already?

This Topic builds on the concept of rate constant (Topic 82) and in one part of the discussion uses the concept of partition function (Topic 52). The discussion of potential energy surfaces is qualitative, but the underlying calculations are those of self-consistent field theory (Topic 27). You should also be familiar with the concepts of rotational states (Topic 14) and vibrational states (Topic 12).

The investigation of the dynamics of the collisions between reactant molecules is the most detailed level of the examination of the factors that govern the rates of reactions.

90.1 Molecular beams

Molecular beams, which consist of collimated, narrow streams of molecules travelling through an evacuated vessel, allow us to study collisions between molecules in preselected energy states (for example, specific rotational and vibrational states), and can be used to determine the states of the products of a reactive collision. Information of this kind is essential if a full picture of the reaction is to be built, because the rate constant is an average over events in which reactants in different initial states evolve into products in their final states.

(a) Techniques

The basic arrangement for a molecular beam experiment is shown in Fig. 90.1. If the pressure of vapour in the source is increased so that the mean free path of the molecules in the emerging beam is much shorter than the diameter of the pinhole, many collisions take place even outside the source. The net effect of these collisions, which give rise to **hydrodynamic flow**, is to transfer momentum into the direction of the beam. The molecules in the beam then travel with very similar speeds,

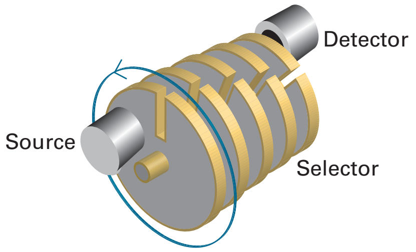

Figure 90.1 The basic arrangement of a molecular beam apparatus. The atoms or molecules emerge from a heated source, and pass through the velocity selector, a rotating series of slotted discs. Molecules emerging from the source travel in a beam towards the rotating slits. Only if the speed of a molecule is such as to carry it along the succession of slits that rotate into its path will it collide with the target gas molecules. The scattering occurs from the target gas molecules (which might form another beam), and the flux of particles entering the detector set at some angle is recorded.

so further downstream few collisions take place between them. This condition is called **molecular flow**. Because the spread in speeds is so small, the molecules are effectively in a state of very low translational temperature (Fig. 90.2). The translational temperature may reach as low as 1 K. Such jets are called **supersonic** because the average speed of the molecules in the jet is much greater than the speed of sound in the jet.

A supersonic jet can be converted into a more parallel **supersonic beam** if it is 'skimmed' in the region of hydrodynamic flow and the excess gas is pumped away. A skimmer consists of a conical nozzle shaped to avoid any supersonic shock waves spreading back into the gas and so increasing the translational temperature (Fig. 90.3). A jet or beam may also be formed by using helium or neon as the principal gas, and injecting molecules of interest into it in the hydrodynamic region of flow.

The low translational temperature of the molecules is reflected in the low rotational and vibrational temperatures of the molecules. In this context, a rotational or vibrational temperature means the temperature that should be used in the Boltzmann distribution to reproduce the observed populations of the states. However, as rotational modes equilibrate more slowly, and vibrational modes equilibrate even more slowly, the rotational and vibrational populations of the species correspond to somewhat higher temperatures, of the order of 10 K for rotation and 100 K for vibrations.

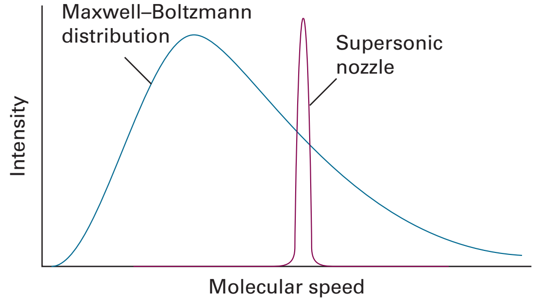

Figure 90.2 The shift in the mean speed and the width of the distribution brought about by use of a supersonic nozzle.

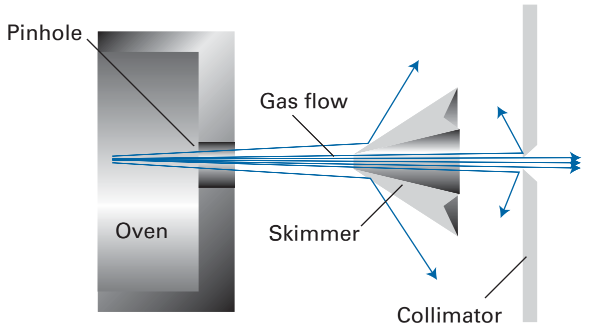

Figure 90.3 A supersonic nozzle skims off some of the molecules of the beam and leads to a beam with well-defined velocity.

The target gas may be either a bulk sample or another molecular beam. The detectors may consist of a chamber fitted with a sensitive pressure gauge, a bolometer (a detector that responds to the incident energy by making use of the temperature dependence of resistance), or an ionization detector, in which the incoming molecule is first ionized and then detected electronically. The state of the scattered molecules may also be determined spectroscopically, and is of interest when the collisions change their vibrational or rotational states.

(b) Experimental results

The primary experimental information from a molecular beam experiment is the fraction of the molecules in the incident beam that are scattered into a particular direction. The fraction is normally expressed in terms of dI, the rate at which molecules are scattered into a cone (described by a solid angle dΩ) that represents the area covered by the 'eye' of the detector (Fig. 90.4). This rate is reported as the **differential scattering cross-section**, σ_d, the constant of proportionality between the value of dI and the intensity, I, of the incident beam, the number density of target molecules, $\mathcal{N}$, and the infinitesimal path length, dx, through the sample:

$$\mathrm{d}I = \sigma_\mathrm{d} I \mathcal{N} \mathrm{d}x \tag{90.1}$$

Rate of molecular scattering in terms of the differential scattering cross-section

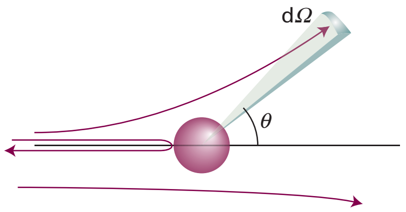

Figure 90.4 The definition of the solid angle, dΩ, for scattering.

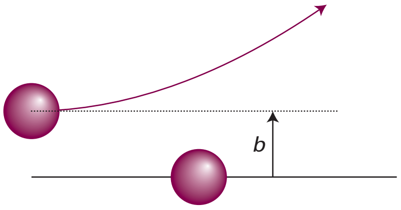

Figure 90.5 The definition of the impact parameter, b, as the perpendicular separation of the initial paths of the particles.

The value of σ_d (which has the dimensions of area) depends on the **impact parameter**, b, the initial perpendicular separation of the paths of the colliding molecules (Fig. 90.5), and the details of the intermolecular potential.

Brief illustration 90.1 The role of the impact parameter

The role of the impact parameter is most easily seen by considering the impact of two hard spheres (Fig. 90.6). If $b=0$, the lighter projectile is on a trajectory that leads to a head-on collision, so the only scattering intensity is detected when the detector is at $\theta=\pi$. When the impact parameter is so great that the spheres do not make contact ($b>R_A+R_B$), there is no scattering and the scattering cross-section is zero at all angles except $\theta=0$. Glancing blows, with $0<b<R_A+R_B$, lead to scattering intensity in cones around the forward direction.

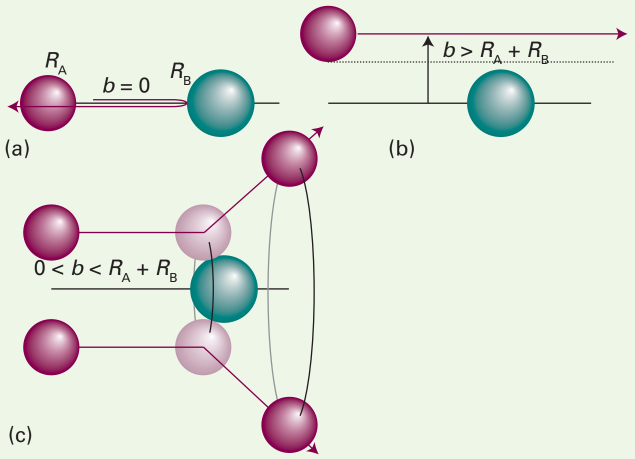

Figure 90.6 Three typical cases for the collisions of two hard spheres: (a) $b=0$, giving backward scattering; (b) $b>R_A+R_B$, giving forward scattering; (c) $0<b<R_A+R_B$, leading to scattering into one direction on a ring of possibilities. (The target molecule is taken to be so heavy that it remains virtually stationary.)

Self-test 90.1 What is the scattering angle for identical hard spheres of radius R when $b=R$?

Answer: 45°

The scattering pattern of real molecules, which are not hard spheres, depends on the details of the intermolecular potential, including the anisotropy (the dependence on relative orientation) that is present when the molecules are not spherical. The scattering also depends on the relative speed of approach of the two particles: a very fast particle might pass through the interaction region without much deflection, whereas a slower one on the same path might be temporarily captured and undergo considerable deflection (Fig. 90.7). The variation of the scattering cross-section with the relative speed of approach should therefore give information about the strength and range of the intermolecular potential.

A further point is that the outcome of collisions is determined by quantum, not classical, mechanics. The wave nature of the particles can be taken into account, at least to some extent, by drawing all classical trajectories that take the projectile particle from source to detector, and then considering the effects of interference between them.

Two quantum mechanical effects are of great importance. A particle with a certain impact parameter might approach the attractive region of the potential in such a way that the particle is deflected towards the repulsive core (Fig. 90.8), which then repels it out through the attractive region to continue its flight in the forward direction. Some molecules, however, also travel in the forward direction because they have impact parameters so large that they are undeflected. The wavefunctions of the

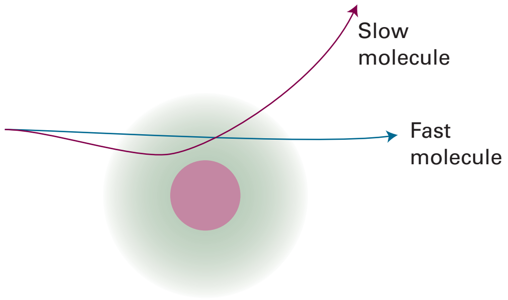

Figure 90.7 The extent of scattering may depend on the relative speed of approach as well as the impact parameter. The dark central zone represents the repulsive core; the fuzzy outer zone represents the long-range attractive potential.

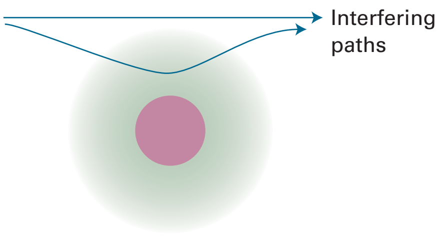

Figure 90.8 Two paths leading to the same destination will interfere quantum mechanically; in this case they give rise to quantum oscillations in the forward direction.

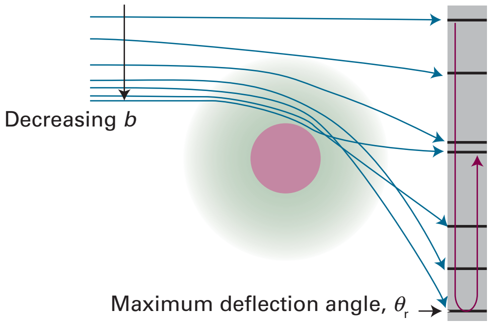

Figure 90.9 The interference of paths leading to rainbow scattering. The rainbow angle, θ_r, is the maximum scattering angle reached as b is decreased. Interference between the numerous paths at that angle modifies the scattering intensity markedly.

particles that take the two types of path interfere, and the intensity in the forward direction is modified. The effect is called **quantum oscillation**. The same phenomenon accounts for the optical 'glory effect', in which a bright halo can sometimes be seen surrounding an illuminated object. (The coloured rings around the shadow of an aircraft cast on clouds by the Sun, and often seen in flight, are an example of an optical glory.)

The second quantum effect we need consider is the observation of a strongly enhanced scattering in a non-forward direction. This effect is called **rainbow scattering** because the same mechanism accounts for the appearance of an optical rainbow. The origin of the phenomenon is illustrated in Fig. 90.9. As the impact parameter decreases, there comes a stage at which the scattering angle passes through a maximum and the interference between the paths results in a strongly scattered beam. The **rainbow angle**, θ_r, is the angle for which $d\theta/db = 0$ and the scattering is strong.

Another phenomenon that can occur in certain beams is the capturing of one species by another. The vibrational temperature in supersonic beams is so low that **van der Waals molecules** may be formed, which are complexes of the form AB in which A and B are held together by van der Waals forces or hydrogen bonds. Large numbers of such molecules have been studied spectroscopically, including ArHCl, $(HCl)_2$, $ArCO_2$, and $(H_2O)_2$. More recently, van der Waals clusters of water molecules have been pursued as far as $(H_2O)_6$. The study of their spectroscopic properties gives detailed information about the intermolecular potentials involved.

90.2 Reactive collisions

Detailed experimental information about the intimate processes that occur during reactive encounters comes from molecular beams, especially **crossed molecular beams** (Fig. 90.10). The detector for the products of the collision of two beams can be moved to different angles, so the angular distribution of the products can be determined. Because the molecules in the incoming beams can be prepared with different energies (for example, with different translational energies by using rotating sectors and supersonic nozzles, with different vibrational energies by using selective excitation with lasers, and with different orientations by using electric fields), it is possible to study the dependence of the success of collisions on these variables and to study how they affect the properties of the emerging product molecules.

(a) Probes of reactive collisions

One method for examining the energy distribution in the products is **infrared chemiluminescence**, in which vibrationally excited molecules emit infrared radiation as they return to their ground states. By studying the intensities of the infrared emission spectrum, the populations of the vibrational states of the products may be determined (Fig. 90.11). Another method makes use of **laser-induced fluorescence**. In this technique, a laser is used to excite a product molecule from a specific vibration–rotation level; the intensity of the fluorescence from the upper state is monitored and interpreted in terms of the population of the initial vibration–rotation state of the product.

When the molecules being studied do not fluoresce efficiently, versions of Raman spectroscopy (Topic 40) can be used to monitor the progress of reaction. **Multiphoton ionization** (MPI) techniques are also good alternatives for the study of weakly fluorescing molecules. In MPI, the absorption by a molecule of several photons from one or more pulsed lasers results in ionization if the total photon energy is greater than the ionization energy of the molecule.

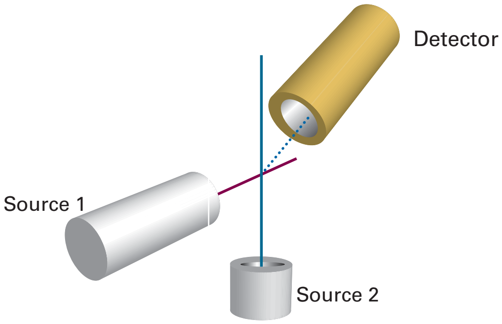

Figure 90.10 In a crossed-beam experiment, state-selected molecules are generated in two separate sources, and are directed perpendicular to one another. The detector responds to molecules (which may be product molecules if a chemical reaction occurs) scattered into a chosen direction.

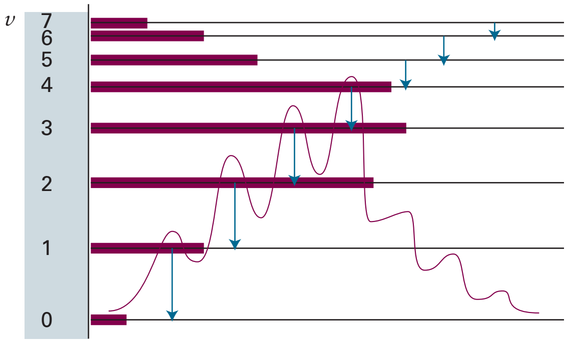

Figure 90.11 Infrared chemiluminescence from CO produced in the reaction O + CS → CO + S arises from the non-equilibrium populations of the vibrational states of CO and the radiative relaxation to equilibrium.

The angular distribution of products can be determined by **reaction product imaging**. In this technique, product ions are accelerated by an electric field towards a phosphorescent screen and the light emitted from specific spots where the ions struck the screen is imaged by a charge-coupled device (CCD). An important variant of MPI is **resonant multiphoton ionization** (REMPI), in which one or more photons promote a molecule to an electronically excited state and then additional photons are used to generate ions from the excited state. The power of REMPI lies in the fact that the experimenter can choose which reactant or product to study by tuning the laser frequency to the electronic absorption band of a specific molecule.

(b) State-to-state reaction dynamics

The concept of collision cross-section is introduced in connection with collision theory in Topic 87, where it is shown that the second-order rate constant, k_r, can be expressed as a Boltzmann-weighted average of the reactive cross-section and the relative speed of approach of the colliding reactant molecules, $s_{\rm rel}$. We shall write eqn 87.6 of that Topic ($k_r = N_A \int_0^\infty \sigma(\varepsilon) s_{\rm rel} f(\varepsilon)\mathrm{d}\varepsilon$) as

$$k_r = \langle \sigma s_{\rm rel} \rangle N_A \qquad (90.2)$$

where the angle brackets denote a Boltzmann average. Molecular beam studies provide a more sophisticated version of this quantity, for they provide the **state-to-state cross-section**, $\sigma_{nn'}$, and hence the **state-to-state rate constant**, $k_{nn'}$, for the reactive transition from initial state n of the reactants to final state n' of the products:

$$k_{nn'} = \langle \sigma_{nn'} s_{\rm rel} \rangle N_A \qquad \text{State-to-state rate constant} \qquad (90.3)$$

The rate constant k_r is the sum of the state-to-state rate constants over all final states (because a reaction is successful whatever the final state of the products) and over a Boltzmann-weighted sum of initial states (because the reactants are initially present with a characteristic distribution of populations at a temperature T):

$$k_r = \sum_{n,n'} k_{nn'}(T) f_n(T) \qquad (90.4)$$

where $f_n(T)$ is the Boltzmann factor at a temperature T. It follows that if we can determine or calculate the state-to-state cross-sections for a wide range of approach speeds and initial and final states, then we have a route to the calculation of the rate constant for the reaction.

Brief illustration 90.2 The state-to-state rate constant

Suppose a harmonic oscillator collides with another oscillator of the same effective mass and force constant. Assume the state-to-state rate constant for the excitation of the latter's vibration is $k_{vv'} = k_r^\circ \delta_{vv'}$ for all the states v and v', where $\delta_{vv'}$ is the Kronecker delta: $\delta_{vv'} = 1$ when $v = v'$ and 0 otherwise. It follows that an excitation can flow only from any level to the same level of the second oscillator. At a temperature T, when $f_v(T) = \mathrm{e}^{-vh\nu/kT}/q$, where q is the molecular vibrational partition function (Topic 52, $q = 1/(1-\mathrm{e}^{-h\nu/kT})$), the overall rate constant is

$$k_r = \frac{k_r^\circ}{q} \sum_{v,v'} \delta_{vv'} \mathrm{e}^{-vh\nu/kT} = \frac{k_r^\circ}{q} \overbrace{\sum_{v'} \mathrm{e}^{-v'h\nu/kT}}^{q} = k_r^\circ$$

Self-test 90.2 Now suppose that $k_{vv'} = k_r^\circ \delta_{vv'} \mathrm{e}^{-\lambda v}$, implying that the transfer becomes less efficient as the vibrational quantum number increases. Evaluate k_r.

Answer: $k_r = k_r^\circ (1-\mathrm{e}^{-h\mathrm{n}/kT})/(1-\mathrm{e}^{-(\lambda + h\mathrm{n}/kT)})$

90.3 Potential energy surfaces

One of the most important concepts for discussing beam results and calculating the state-to-state collision cross-section is the **potential energy surface** of a reaction, the potential energy as a function of the relative positions of all the atoms taking part in the reaction. Potential energy surfaces may be constructed from experimental data and from results of quantum chemical calculations (Topics 27–30). The theoretical method requires the systematic calculation of the energies of the system in a large number of geometrical arrangements. Special computational techniques, such as those described in Topics 29–30, are used to take into account electron correlation, which arises from instantaneous interactions between electrons as they move closer to and farther from each other in a molecule or molecular cluster. Techniques that incorporate electron correlation accurately are very time-consuming and, consequently, only reactions between relatively simple particles, such as the reactions $H+H_2 \rightarrow H_2+H$ and $H+H_2O \rightarrow OH+H_2$, currently are amenable to this type of theoretical treatment. An alternative is to use semi-empirical methods, in which results of calculations and experimental parameters are used to construct the potential energy surface.

To illustrate the features of a potential energy surface, consider the collision between an H atom and an H_2 molecule. Detailed calculations show that the approach of an atom H_A along the H_B–H_C axis requires less energy for reaction than any other approach, so initially we confine our attention to a collinear approach. Two parameters are required to define the nuclear separations: one is the H_A–H_B separation, R_{AB}, and the other is the H_B–H_C separation, R_{BC}.

At the start of the encounter R_{AB} is infinite and R_{BC} is the H_2 equilibrium bond length. At the end of a successful reactive encounter R_{AB} is equal to the equilibrium bond length and R_{BC} is infinite. The total energy of the three-atom system depends on their relative separations, and can be found by doing an electronic structure calculation. The plot of the total energy of the system against R_{AB} and R_{BC} gives the potential energy surface of this collinear reaction (Fig. 90.12). This surface is normally depicted as a contour diagram (Fig. 90.13).

When R_{AB} is very large, the variation in potential energy represented by the surface as R_{BC} changes is that of an isolated H_2 molecule as its bond length is altered. A section through the surface at $R_{AB}=\infty$, for example, is the same as the H_2 bonding potential energy curve. At the edge of the diagram where R_{BC} is very large, a section through the surface is the molecular potential energy curve of an isolated H_AH_B molecule.

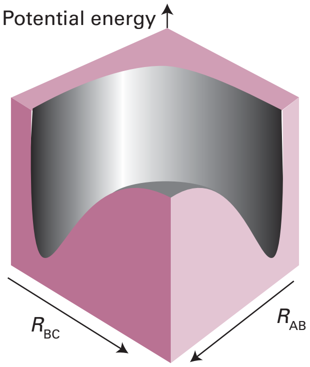

Figure 90.12 The potential energy surface for the $H+H_2 \rightarrow H_2+H$ reaction when the atoms are constrained to be collinear.

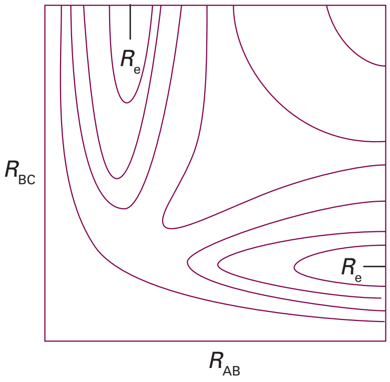

Figure 90.13 The contour diagram (with contours of equal potential energy) corresponding to the surface in Fig. 90.12. R_e marks the equilibrium bond length of an H_2 molecule (strictly, it relates to the arrangement when the third atom is at infinity).

Brief illustration 90.3 A potential energy surface

The bimolecular reaction $H+O_2 \rightarrow OH+O$ plays an important role in combustion processes. The reaction can be characterized in terms of the HO_2 potential energy surface and the two distances for collinear approach, R_{HO_A} and $R_{O_AO_B}$. When R_{HO_A} is very large, the variation of the HO_2 potential energy with $R_{O_AO_B}$ is that of an isolated dioxygen molecule as its bond length is changed. Similarly, when $R_{O_AO_B}$ is very large, a section through the potential energy surface is the molecular potential energy curve of an isolated OH radical.

Self-test 90.3 Repeat the analysis for $H+OD \rightarrow OH+D$.

Answer: R_{HO} at infinity: OD potential energy curve; R_{OD} at infinity: OH potential energy curve

The actual path of the atoms in the course of the encounter depends on their total energy, the sum of their kinetic and potential energies. However, we can obtain an initial idea of the paths available to the system for paths that correspond to least potential energy. For example, consider the changes in potential energy as H_A approaches H_BH_C. If the H_B–H_C bond length is constant during the initial approach of H_A, then the potential energy of the H_3 cluster rises along the path marked A in Fig. 90.14. We see that the potential energy reaches a high value as H_A is pushed into the molecule and then decreases sharply as H_C breaks off and separates to a great distance. An alternative reaction path can be imagined (B) in which the H_B–H_C bond length increases while H_A is still far away. Both paths, although feasible if the molecules have sufficient initial kinetic energy, take the three atoms to regions of high potential energy in the course of the encounter.

The path of least potential energy is the one marked C, corresponding to R_{BC} lengthening as H_A approaches and begins to

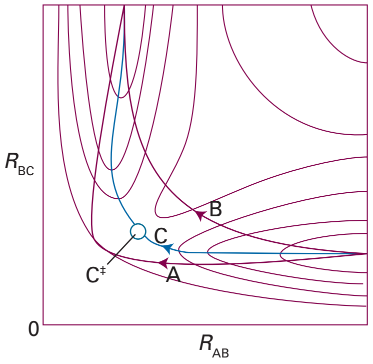

Figure 90.14 Various trajectories through the potential energy surface shown in Fig. 90.13. Path A corresponds to a route in which R_{BC} is held constant as H_A approaches; path B corresponds to a route in which R_{BC} lengthens at an early stage during the approach of H_A; path C is the route along the floor of the potential valley.

form a bond with H_B. The H_B–H_C bond relaxes at the demand of the incoming atom, and the potential energy climbs only as far as the saddle-shaped region of the surface, to the **saddle point** marked $C^\ddagger$. The encounter of least potential energy is one in which the atoms take route C up the floor of the valley, through the saddle point, and down the floor of the other valley as H_C recedes and the new H_A–H_B bond achieves its equilibrium length. This path is the reaction coordinate.

We can now make contact with the transition-state theory of reaction rates (Topic 89). In terms of trajectories on potential surfaces with a total energy close to the saddle-point energy, the transition state can be identified with a critical geometry such that every trajectory that goes through this geometry goes on to react (Fig. 90.15). Most trajectories on potential energy surfaces do not go directly over the saddle point and therefore, to result in a reaction, they require a total energy significantly higher than the saddle-point energy. As a result, the experimentally determined activation energy is often much higher than the calculated saddle-point energy.

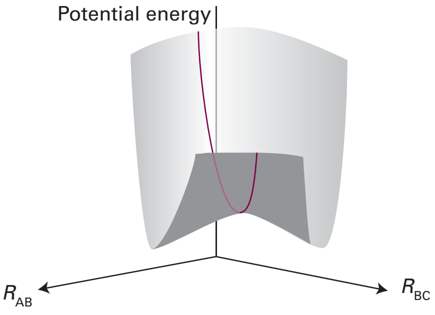

Figure 90.15 The transition state is a set of configurations (here, marked by the line across the saddle point) through which successful reactive trajectories must pass.

90.4 Some results from experiments and calculations

To travel successfully from reactants to products, classically the incoming molecules must possess enough kinetic energy to be able to climb to the saddle point of the potential surface. We proceed with this classical argument, although quantum mechanical tunnelling can also play an important role in reactivity, particularly in hydrogen atom or electron transfer reactions. Therefore, the shape of the surface can be explored experimentally by changing the relative speed of approach (by selecting the beam velocity) and the degree of vibrational excitation and observing whether reaction occurs and whether the products emerge in a vibrationally excited state (Fig. 90.16). For example, one question that can be answered is whether it is better to smash the reactants together with a lot of translational kinetic energy or to ensure instead that they approach in

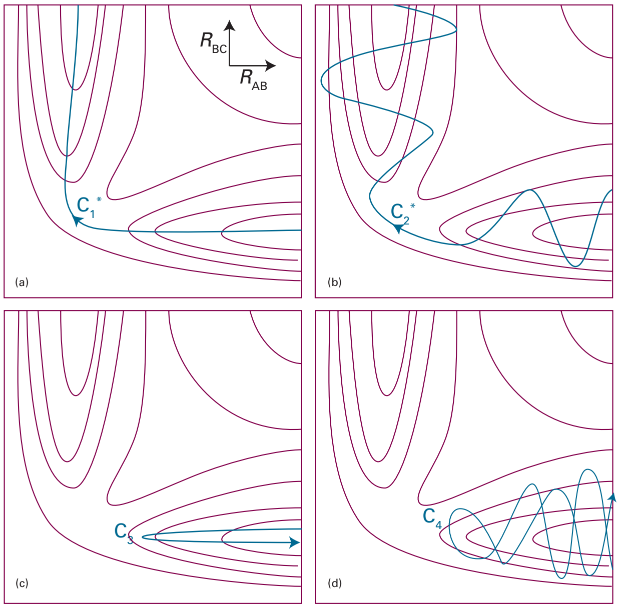

Figure 90.16 Some successful (*) and unsuccessful encounters. (a) C_1^* corresponds to the path along the foot of the valley; (b) C_2^* corresponds to an approach of A to a vibrating BC molecule, and the formation of a vibrating AB molecule as C departs. (c) C_3 corresponds to A approaching a non-vibrating BC molecule, but with insufficient translational kinetic energy; (d) C_4 corresponds to A approaching a vibrating BC molecule, but still the energy, and the phase of the vibration, is insufficient for reaction.

highly excited vibrational states. Thus, is trajectory C_2^*, where the H_BH_C molecule is initially vibrationally excited, more efficient at leading to reaction than the trajectory C_1^*, in which the total energy is the same but reactants have a high translational kinetic energy?

(a) The direction of attack and separation

Figure 90.17 shows the results of a calculation of the potential energy as an H atom approaches an H_2 molecule from different angles, the H_2 bond being allowed to relax to the optimum length in each case. The potential barrier is least for collinear attack, as we assumed earlier. (But we must be aware that other lines of attack are feasible and contribute to the overall rate.) In contrast, Fig. 90.18 shows the potential energy changes that occur as a Cl atom approaches an HI molecule. The lowest barrier occurs for approaches within a cone of half-angle 30° surrounding the H atom. The relevance of this result to the calculation of the steric factor of collision theory should be noted: not every collision is successful, because not every one lies within the reactive cone.

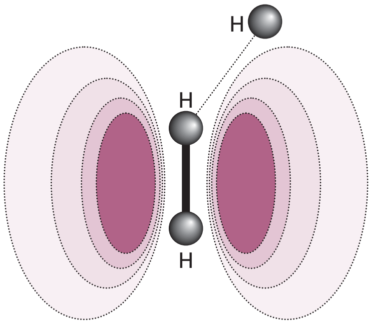

Figure 90.17 An indication of how the anisotropy of the potential energy changes as H approaches H_2 with different angles of attack. The collinear attack has the lowest potential barrier to reaction. The surface indicates the potential energy profile along the reaction coordinate for each configuration.

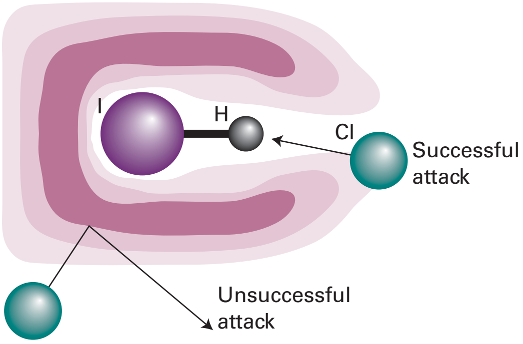

Figure 90.18 The potential energy barrier for the approach of Cl to HI. In this case, successful encounters occur only when Cl approaches within a cone surrounding the H atom.

If the collision is sticky, so that when the reactants collide they orbit around each other, the products can be expected to emerge in random directions because all memory of the approach direction has been lost. A rotation takes about 1 ps, so if the collision is over in less than that time the complex will not have had time to rotate and the products will be thrown off in a specific direction.

Brief illustration 90.4 The angular product distribution

The collision of K with CH_3I leads to formation of KI and CH_3 only if the molecules approach each other very closely. In this mechanism, K effectively bumps into a brick wall, and the KI product bounces out in the backward direction. The detection of this anisotropy in the angular distribution of products gives an indication of the distance and orientation of approach needed for reaction, as well as showing that the event is complete in less than 1 ps.

Self-test 90.4 In the collision of K and I_2, most of the products (KI and I) are thrown off in the forward direction (forward and backward directions refer to directions in a centre-of-mass coordinate system with the origin at the centre of mass of the colliding reactants and collision occurring when molecules are at the origin.) How can this product distribution be explained?

Answer: Harpoon mechanism (Topic 87);
transition takes place at long range

(b) Attractive and repulsive surfaces

Some reactions are very sensitive to whether the energy has been pre-digested into a vibrational mode or left as the relative translational kinetic energy of the colliding molecules. For example, if two HI molecules are hurled together with more than twice the activation energy of the reaction, then no reaction occurs if all the energy is translational. For $F + HCl \rightarrow Cl + HF$, for example, the reaction is about five times more efficient when the HCl is in its first vibrational excited state than when, although HCl has the same total energy, it is in its vibrational ground state.

The origin of these requirements can be found by examining the potential energy surface. Figure 90.19 shows an **attractive surface** in which the saddle point occurs early in the reaction coordinate. Figure 90.20 shows a **repulsive surface** in which the saddle point occurs late. A surface that is attractive in one direction is repulsive in the reverse direction.

Consider first the attractive surface. If the original molecule is vibrationally excited, then a collision with an incoming molecule takes the system along C. This path is bottled up in the region of the reactants, and does not take the system to the saddle point. If, however, the same amount of energy is present solely as translational kinetic energy, then the system moves

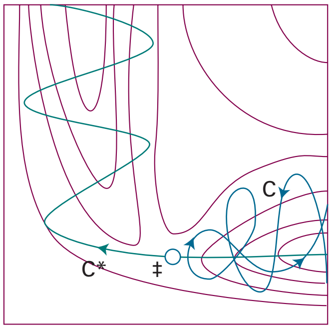

Figure 90.19 An attractive potential energy surface. A successful encounter (C*) involves high translational kinetic energy and results in a vibrationally excited product.

along C* and travels smoothly over the saddle point into products. We can therefore conclude that reactions with attractive potential energy surfaces proceed more efficiently if the energy is in relative translational motion. Moreover, the potential surface shows that once past the saddle point the trajectory runs up the steep wall of the product valley, and then rolls from side to side as it falls to the foot of the valley as the products separate. In other words, the products emerge in a vibrationally excited state.

Now consider the repulsive surface. On trajectory C the collisional energy is largely in translation. As the reactants approach, the potential energy rises. Their path takes them up the opposing face of the valley, and they are reflected back into the reactant region. This path corresponds to an unsuccessful encounter, even though the energy is sufficient for reaction. On C* some of the energy is in the vibration of the reactant molecule and the motion causes the trajectory to weave from side to side up the valley as it approaches the saddle point. This motion may be sufficient to tip the system round the corner to the saddle point and then on to products. In this case, the product molecule is expected to be in an unexcited vibrational state.

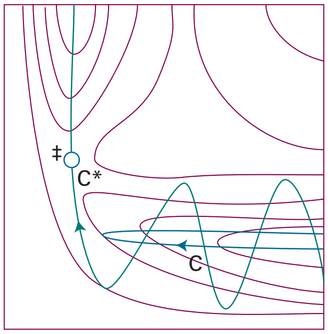

Figure 90.20 A repulsive potential energy surface. A successful encounter (C*) involves initial vibrational excitation and the products have high translational kinetic energy. A reaction that is attractive in one direction is repulsive in the reverse direction.

Reactions with repulsive potential surfaces can therefore be expected to proceed more efficiently if the excess energy is present as vibrations. This is the case with the $H+Cl_2 \rightarrow HCl+Cl$ reaction, for instance.

Brief illustration 90.5 Attractive and repulsive surfaces

The reaction $H+Cl_2 \rightarrow HCl+Cl$ has a repulsive potential surface. Of the following four reactive processes, all at the same total energy,

(1) $H+Cl_2(\nu=0) \rightarrow HCl(\nu'=0)+Cl$
(2) $H+Cl_2(\nu=2) \rightarrow HCl(\nu'=0)+Cl$
(3) $H+Cl_2(\nu=0) \rightarrow HCl(\nu'=2)+Cl$
(4) $H+Cl_2(\nu=2) \rightarrow HCl(\nu'=2)+Cl$

reaction (2) is most probable, with reactants vibrationally excited and products vibrationally unexcited.

Self-test 90.5 Which of the following four reactive processes, all at the same total energy, is most probable?

(1) $HCl(\nu=0)+Cl \rightarrow H+Cl_2(\nu'=0)$
(2) $HCl(\nu=2)+Cl \rightarrow H+Cl_2(\nu'=0)$
(3) $HCl(\nu=0)+Cl \rightarrow H+Cl_2(\nu'=2)$
(4) $HCl(\nu=2)+Cl \rightarrow H+Cl_2(\nu'=2)$

Answer: (3); attractive surface

(c) Classical trajectories

A clear picture of the reaction event can be obtained by using classical mechanics to calculate the trajectories of the atoms taking place in a reaction from a set of initial conditions, such as velocities, relative orientations, and internal energies of the reacting particles. The initial values used for the internal energy reflect the quantization of electronic, vibrational, and rotational energies in molecules but the features of quantum mechanics are not used explicitly in the calculation of the trajectory.

Figure 90.21 shows the result of such a calculation of the positions of the three atoms in the reaction $H+H_2 \rightarrow H_2+H$, the horizontal coordinate now being time and the vertical coordinate the separations. This illustration shows clearly the vibration of the original molecule and the approach of the attacking atom. The reaction itself, the switch of partners, takes place very rapidly and is an example of a **direct-mode process**. The newly formed molecule shakes, but quickly settles down to steady, harmonic vibration as the expelled atom departs. In contrast, Fig. 90.22 shows an example of a **complex-mode process**, in which the activated complex survives for an extended period.

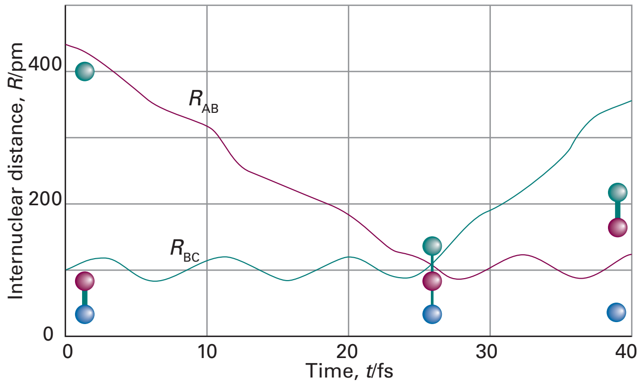

Figure 90.21 The calculated trajectories for a reactive encounter between A and a vibrating BC molecule leading to the formation of a vibrating AB molecule. This direct-mode reaction is between H and H_2 (M. Karplus, et al., *J. Chem. Phys.* **43**, 3258 (1965)).

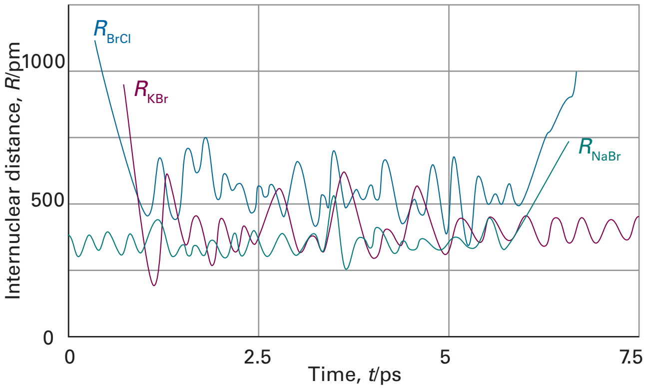

Figure 90.22 An example of the trajectories calculated for a complex-mode reaction, KCl + NaBr → KBr + NaCl, in which the collision cluster has a long lifetime (P. Brumer and M. Karplus, *Faraday Disc. Chem. Soc.* **55**, 80 (1973)).

Brief illustration 90.6 The complex-mode process

The reaction in Fig. 90.22 is the exchange reaction $KCl + NaBr \rightarrow KBr + NaCl$. The tetratomic activated complex survives for about 5 ps, during which time the atoms make about 15 oscillations before dissociating into products.

Self-test 90.6 What is the approximate vibrational frequency of the mode of the activated complex that leads to its dissociation and formation of products?

Answer: 3 THz

(d) Quantum mechanical scattering theory

Classical trajectory calculations do not recognize the fact that the motion of atoms, electrons, and nuclei is governed by quantum mechanics. The concept of trajectory then fades and is replaced by the unfolding of a wavefunction that represents initially the reactants and finally the products.

Complete quantum mechanical calculations of rate constants are very onerous because it is necessary to take into account all the allowed electronic, vibrational, and rotational states populated by each atom and molecule in the system at a given temperature. There are many thermally accessible states, with some transitions between reactant states and product states being allowed but others not allowed. The **cumulative reaction probability**, $\bar{P}(E)$, at a fixed total energy E is written as

$$\bar{P}(E) = \sum_{i,j} P_{ij}(E) \qquad \text{Cumulative reaction probability} \qquad (90.5)$$

where $P_{ij}(E)$ is the state-to-state reaction probability, with i designating the reactant state and j the product state. Although each P_{ij} cannot exceed 1, their sum, $\bar{P}$, can exceed 1. The cumulative reaction probability increases with energy as more reactant and product states become accessible, and the observed rate constant is proportional to a Boltzmann average of $\bar{P}(E)$ at the prevailing temperature. Specifically,

$$k_r(T) = \frac{\int_0^\infty \bar{P}(E) e^{-E/kT} dE}{hQ_R(T)} \qquad \text{Rate constant} \qquad (90.6)$$

where $Q_R(T)$ is the partition function density (the partition function divided by the volume) of the reactants at the temperature T.

The significance of eqn 90.6 is that it provides a direct connection between an experimental quantity, the rate constant, and a theoretical quantity, $\bar{P}(E)$. For instance, if we were developing a version of transition-state theory we might make the following assumptions for the model of the process:

- A product is formed only if an activated complex is formed.
- If the complex is formed in any state, then it will form products.
- A minimum energy is needed for the complex to form.
- The activated complex has a thermal equilibrium distribution of populations corresponding to a temperature T.

The second condition implies that P_{ij} is the state-to-state reaction probability for reactant states i forming complex states j. The third condition implies that $P_{ij}=0$ for E less than a threshold value E_a, the lowest energy state of the complex. It follows that $\bar{P}(E)=0$ for $E<E_a$. As the energy increases above E_a, successive states of the activated complex become accessible and, from the second condition, the cumulative reaction probability increases in steps of 1. To implement this model, it follows that we need to count the number of thermally accessible states of

the complex, $N(E)$, for the available energy, and set $\bar{P}(E)=N(E)$ for $E \geq E_a$. The fourth assumption implies that we can estimate this number by equating it to the molecular partition function of the complex q_c at the prevailing temperature.

Example 90.1 Deriving the collision-theory rate constant

Consider the case of two structureless particles colliding to give an activated complex that resembles a diatomic molecule and derive an expression for the rate constant of the reaction $A+A \rightarrow$ Products.

Method Because the reactant A is a structureless 'atom' of mass m, the only contribution to its partition function is translation. The complex is a diatomic cluster of 'bond length' r, mass $2m$, and moment of inertia $I=\mu r^2=\frac{1}{2}mr^2$. The vibrational mode corresponds to motion along the reaction coordinate, so (as in transition-state theory) does not contribute to q_c. Expressions for the relevant partition functions are given by eqns 52.10 and 52.13 of Topic 52.

Answer Because $\bar{P}(E)=0$ for $E<E_a$ and $\bar{P}(E)=q_c$ for $E \geq E_a$, eqn 90.6 becomes

$$k_r=\frac{q_c}{hQ_R(T)}\int_{E_a}^{\infty} e^{-E/kT}dE=\frac{kTq_c}{hQ_R(T)}e^{-E_a/kT}$$

Only translation contributes to the partition functions of the reactants A+A, and

$$q_r^T=\frac{V}{\Lambda_r^3}=\frac{V(2\pi mkT)^{3/2}}{h^3}$$

The reactant partition function density is therefore

$$Q_R(T)=\frac{(q_r^T)^2}{V}=\left(\frac{(2\pi mkT)^{3/2}V}{h^3}\right)^2\frac{1}{V}=\frac{(2\pi mkT)^3 V}{h^6}$$

The translational and rotational partition functions of the complex A_2 (from eqns 52.10 and 52.13, with symmetry number $\sigma=2$) are

$$q_c^T=\frac{V(2\pi m_{C^\ddagger}kT)^{3/2}}{h^3}=\frac{V(4\pi mkT)^{3/2}}{h^3}$$

$$q_c^R=\frac{4\pi^2kTI}{h^2}\overset{I=\frac{1}{2}mr^2}{=}\frac{2\pi^2mkTr^2}{h^2}$$

It follows that

$$q_c=q_c^T q_c^R=\frac{V(4\pi mkT)^{3/2}}{h^3}\times\frac{2\pi^2mkTr^2}{h^2}$$
$$=\frac{2\pi^2mkTr^2(4\pi mkT)^{3/2}V}{h^5}$$

Therefore

$$k_r=\frac{kT}{h}\times\frac{2\pi^2mkTr^2(4\pi mkT)^{3/2}Vh^6}{h^5(2\pi mkT)^3V}\times e^{-E_a/kT}$$
$$=2\left(\frac{kT}{\pi m}\right)^{1/2}\pi r^2e^{-E_a/kT}$$

which is the same as the result from collision theory (see eqn 87.9) provided we identify the reactive cross-section with πr^2. Note that eqn 87.9 was derived for collisions between two different particles A and B so we need to introduce a factor of $\frac{1}{2}$ into that equation to avoid the double-counting of the collisions between identical particles.

Self-test 90.7 Verify that the result for k_r in Example 90.1 matches the result from transition-state theory (Example 89.1) when the atoms A and B are not identical.

Answer: $k_r=(8kT/\pi\mu)^{1/2}\pi r^2e^{-\Delta E_0/RT}$

Checklist of concepts

☐ 1. A **molecular beam** is a collimated, narrow stream of molecules travelling through an evacuated vessel.

☐ 2. In a molecular beam, the scattering pattern of real molecules depends on quantum mechanical effects and the details of the intermolecular potential.

☐ 3. Two quantum mechanical effects in scattering processes are **quantum oscillations** and **rainbow scattering**.

☐ 4. **van der Waals molecules** are complexes of the form AB in which A and B are held together by van der Waals forces or hydrogen bonds.

☐ 5. Techniques for the study of reactive collisions include **infrared chemiluminescence**, **laser-induced fluorescence**, **multiphoton ionization** (MPI), **reaction product imaging**, and **resonant multiphoton ionization** (REMPI).

☐ 6. A **potential energy surface** maps the potential energy as a function of the relative positions of all the atoms taking part in a reaction.

☐ 7. In an **attractive surface**, the saddle point (the highest point) occurs early on the reaction coordinate.

☐ 8. In a **repulsive surface**, the saddle point occurs late on the reaction coordinate.

Checklist of equations

Property	Equation	Comment	Equation number
Rate of molecular scattering	$\mathrm{d}I=\sigma_\mathrm{d}I\mathcal{N}\mathrm{d}x$	σ_d is the differential scattering cross-section	90.1
Rate constant	$k_\mathrm{r}=\langle\sigma s_\mathrm{rel}\rangle N_\mathrm{A}$		90.2
State-to-state rate constant	$k_{nn'}=\langle\sigma_{nn'}s_\mathrm{rel}\rangle N_\mathrm{A}$		90.3
Overall rate constant	$k_\mathrm{r}=\sum_{n,n'}k_{nn'}(T)f_n(T)$		90.4
Cumulative reaction probability	$\bar{P}(E)=\sum_{i,j}P_{ij}(E)$		90.5
Rate constant	$k_\mathrm{r}(T)=\int_0^\infty \bar{P}(E)\mathrm{e}^{-E/kT}\mathrm{d}E/hQ_\mathrm{R}(T)$	$Q_\mathrm{R}(T)$ is the partition function density of the reactants	90.6

Focus 18 on Reaction dynamics

Topic 87 Collision theory

Discussion questions

87.1 Discuss how the collision theory of gases builds on the kinetic-molecular theory.

87.2 Describe the essential features of the harpoon mechanism.

Exercises

87.1(a) Calculate the collision frequency, z, and the collision density, Z, in ammonia, $R = 190\,\text{pm}$, at 30 °C and 120 kPa. What is the percentage increase when the temperature is raised by 10 K at constant volume?
87.1(b) Calculate the collision frequency, z, and the collision density, Z, in carbon monoxide, $R = 180\,\text{pm}$, at 30 °C and 120 kPa. What is the percentage increase when the temperature is raised by 10 K at constant volume?

87.2(a) Collision theory depends on knowing the fraction of molecular collisions having at least the kinetic energy E_a along the line of flight. What is this fraction when (i) $E_a = 20\,\text{kJ mol}^{-1}$, (ii) $E_a = 100\,\text{kJ mol}^{-1}$ at (1) 350 K and (2) 900 K?
87.2(b) Collision theory depends on knowing the fraction of molecular collisions having at least the kinetic energy E_a along the line of flight. What is this fraction when (i) $E_a = 15\,\text{kJ mol}^{-1}$, (ii) $E_a = 150\,\text{kJ mol}^{-1}$ at (1) 300 K and (2) 800 K?

87.3(a) Calculate the percentage increase in the fractions in Exercise 87.2(a) when the temperature is raised by 10 K.
87.3(b) Calculate the percentage increase in the fractions in Exercise 87.2(b) when the temperature is raised by 10 K.

87.4(a) Use the collision theory of gas-phase reactions to calculate the theoretical value of the second-order rate constant for the reaction $H_2(g) + I_2(g) \rightarrow 2\,HI(g)$ at 650 K, assuming that it is elementary and bimolecular. The collision cross-section is $0.36\,\text{nm}^2$, the reduced mass is 3.32×10^{-27} kg, and the activation energy is $171\,\text{kJ mol}^{-1}$. (Assume a steric factor of 1.)
87.4(b) Use the collision theory of gas-phase reactions to calculate the theoretical value of the second-order rate constant for the reaction $D_2(g) + Br_2(g) \rightarrow 2\,DBr(g)$ at 450 K, assuming that it is elementary and bimolecular. Take the collision cross-section as $0.30\,\text{nm}^2$, the reduced mass as $3.930m_u$, and the activation energy as $200\,\text{kJ mol}^{-1}$. (Assume a steric factor of 1.)

87.5(a) For the gaseous reaction $A + B \rightarrow P$, the reactive cross-section obtained from the experimental value of the pre-exponential factor is $9.2 \times 10^{-22}\,\text{m}^2$. The collision cross-sections of A and B estimated from the transport properties are 0.95 and $0.65\,\text{nm}^2$ respectively. Calculate the P-factor for the reaction.
87.5(b) For the gaseous reaction $A + B \rightarrow P$, the reactive cross-section obtained from the experimental value of the pre-exponential factor is $8.7 \times 10^{-22}\,\text{m}^2$. The collision cross-sections of A and B estimated from the transport properties are 0.88 and $0.40\,\text{nm}^2$, respectively. Calculate the P-factor for the reaction.

Problems

87.1 In the dimerization of methyl radicals at 25 °C, the experimental pre-exponential factor is $2.4 \times 10^{10}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$. What are (a) the reactive cross-section, (b) the P-factor for the reaction if the C–H bond length is 154 pm?

87.2 Nitrogen dioxide reacts bimolecularly in the gas phase: $NO_2 + NO_2 \rightarrow NO + NO + O_2$. The temperature dependence of the second-order rate constant for the rate law $d[P]/dt = k_r[NO_2]^2$ is given below. What are the P-factor and the reactive cross-section for the reaction?

T/K	600	700	800	1000
$k_r/(\text{cm}^3\,\text{mol}^{-1}\,\text{s}^{-1})$	4.6×10^2	9.7×10^3	1.3×10^5	3.1×10^6

Take $\sigma = 0.60\,\text{nm}^2$.

87.3 The diameter of the methyl radical is about 308 pm. What is the maximum rate constant in the expression $d[C_2H_6]/dt = k_r[CH_3]^2$ for second-order recombination of radicals at room temperature? 10 per cent of a sample of ethane of volume $1.0\,\text{dm}^3$ at 298 K and 100 kPa is dissociated into methyl radicals. What is the minimum time for 90 per cent recombination?

87.4 Total cross-sections for reactions between alkali metal atoms and halogen molecules are given in the table below (R.D. Levine and R.B. Bernstein, *Molecular reaction dynamics,* Clarendon Press (1974), page 72). Assess the data in terms of the harpoon mechanism.

σ^*/nm^2	Cl_2	Br_2	I_2
Na	1.24	1.16	0.97
K	1.54	1.51	1.27
Rb	1.90	1.97	1.67
Cs	1.96	2.04	1.95

Electron affinities are approximately 1.3 eV (Cl_2), 1.2 eV (Br_2), and 1.7 eV (I_2), and ionization energies are 5.1 eV (Na), 4.3 eV (K), 4.2 eV (Rb), and 3.9 eV (Cs).

87.5[‡] One of the most historically significant studies of chemical reaction rates was that by M. Bodenstein (*Z. phys. Chem.* **29**, 295 (1899)) of the gas-phase reaction $2\,HI(g) \rightarrow H_2(g) + I_2(g)$ and its reverse, with rate constants k_r and k_r', respectively. The measured rate constants as a function of temperature are

T/K	647	666	683	700	716	781
$k_r/(22.4\,\text{dm}^3\,\text{mol}^{-1}\,\text{min}^{-1})$	0.230	0.588	1.37	3.10	6.70	105.9
$k_r'/(22.4\,\text{dm}^3\,\text{mol}^{-1}\,\text{min}^{-1})$	0.0140	0.0379	0.0659	0.172	0.375	3.58

[‡] These problems were supplied by Charles Trapp and Carmen Giunta.

Demonstrate that these data are consistent with the collision theory of bimolecular gas-phase reactions.

87.6‡ R. Atkinson (*J. Phys. Chem. Ref. Data* **26**, 215 (1997)) has reviewed a large set of rate constants relevant to the atmospheric chemistry of volatile organic compounds. The recommended rate constant for the bimolecular association of O_2 with an alkyl radical R at 298 K is $4.7\times10^9\,dm^3\,mol^{-1}\,s^{-1}$ for $R = C_2H_5$ and $8.4\times10^9\,dm^3\,mol^{-1}\,s^{-1}$ for R = cyclohexyl. Assuming no energy barrier, compute the steric factor, P, for each reaction. *Hint*: Obtain collision diameters from collision cross-sections of similar molecules in the *Resource section*.

Topic 88 Diffusion-controlled reactions

Discussion questions

88.1 Distinguish between a diffusion-controlled reaction and an activation-controlled reaction. Do both have activation energies?

88.2 Describe the role of the encounter pair in the cage effect.

Exercises

88.1(a) A typical diffusion coefficient for small molecules in aqueous solution at 25 °C is $6\times10^{-9}\,m^2\,s^{-1}$. If the critical reaction distance is 0.5 nm, what value is expected for the second-order rate constant for a diffusion-controlled reaction?

88.1(b) Suppose that the typical diffusion coefficient for a reactant in aqueous solution at 25 °C is $5.2\times10^{-9}\,m^2\,s^{-1}$. If the critical reaction distance is 0.4 nm, what value is expected for the second-order rate constant for the diffusion-controlled reaction?

88.2(a) Calculate the magnitude of the diffusion-controlled rate constant at 298 K for a species in (i) water, (ii) pentane. The viscosities are $1.00\times10^{-3}\,kg\,m^{-1}\,s^{-1}$ and $2.2\times10^{-4}\,kg\,m^{-1}\,s^{-1}$, respectively.

88.2(b) Calculate the magnitude of the diffusion-controlled rate constant at 298 K for a species in (i) decylbenzene, (ii) concentrated sulfuric acid. The viscosities are 3.36 cP and 27 cP, respectively.

88.3(a) Calculate the magnitude of the diffusion-controlled rate constant at 320 K for the recombination of two atoms in water, for which $\eta = 0.89$ cP. Assuming the concentration of the reacting species is $1.5\,mmol\,dm^{-3}$ initially, how long does it take for the concentration of the atoms to fall to half that value? Assume the reaction is elementary.

88.3(b) Calculate the magnitude of the diffusion-controlled rate constant at 320 K for the recombination of two atoms in benzene, for which $\eta = 0.601$ cP. Assuming the concentration of the reacting species is $2.0\,mmol\,dm^{-3}$ initially, how long does it take for the concentration of the atoms to fall to half that value? Assume the reaction is elementary.

88.4(a) Two neutral species, A and B, with diameters 655 pm and 1820 pm, respectively, undergo the diffusion-controlled reaction $A + B \rightarrow P$ in a solvent of viscosity $2.93\times10^{-3}\,kg\,m^{-1}\,s^{-1}$ at 40 °C. Calculate the initial rate $d[P]/dt$ if the initial concentrations of A and B are $0.170\,mol\,dm^{-3}$ and $0.350\,mol\,dm^{-3}$, respectively.

88.4(b) Two neutral species, A and B, with diameters 421 pm and 945 pm, respectively, undergo the diffusion-controlled reaction $A + B \rightarrow P$ in a solvent of viscosity 1.35 cP at 20 °C. Calculate the initial rate $d[P]/dt$ if the initial concentrations of A and B are $0.155\,mol\,dm^{-3}$ and $0.195\,mol\,dm^{-3}$, respectively.

Problems

88.1 Confirm that eqn 88.9 is a solution of eqn 88.8, where [J] is a solution of the same equation but with $k_r = 0$ and for the same initial conditions.

88.2^{LG} Use mathematical software, a spreadsheet, or the *Living graphs* (labelled ^{LG}) on the website of this book to explore the effect of varying the value of the rate constant k_r on the spatial variation of $[J]^*$ (see eqn 88.9 with [J] given in eqn 88.10) for a constant value of the diffusion constant D.

88.3‡ The compound α-tocopherol, a form of vitamin E, is a powerful antioxidant that may help to maintain the integrity of biological membranes. R.H. Bisby and A.W. Parker (*J. Amer. Chem. Soc.* **117**, 5664 (1995)) studied the reaction of photochemically excited duroquinone with the antioxidant in ethanol. Once the duroquinone was photochemically excited, a bimolecular reaction took place at a rate described as diffusion-limited. (a) Estimate the rate constant for a diffusion-limited reaction in ethanol. (b) The reported rate constant was $2.77\times10^9\,dm^3\,mol^{-1}\,s^{-1}$; estimate the critical reaction distance if the sum of diffusion constants is $1\times10^{-9}\,m^2\,s^{-1}$.

Topic 89 Transition-state theory

Discussion questions

89.1 Describe in outline the formulation of the Eyring equation.

89.2 Explain the physical origin of the kinetic salt effect. What might be the effect of the relative permittivity of the medium?

Exercises

89.1(a) The reaction of propylxanthate ion in acetic acid buffer solution has the mechanism $A^- + H^+ \rightarrow P$. Near 30 °C the rate constant is given by the empirical expression $k_r = (2.05\times10^{13})\,e^{-(8681\,K)/T}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. Evaluate the energy and entropy of activation at 30 °C.

89.1(b) The reaction $A^- + H^+ \rightarrow P$ has a rate constant given by the empirical expression $k_r = (6.92\times10^{12})e^{-(5925\,K)/T}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. Evaluate the energy and entropy of activation at 25 °C.

89.2(a) When the reaction in Exercise 89.1(a) occurs in a dioxane/water mixture which is 30 per cent dioxane by mass, the rate constant fits $k_r = (7.78\times10^{14})e^{-(9134\,K)/T}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ near 30 °C. Calculate $\Delta^{\ddagger}G$ for the reaction at 30 °C.

89.2(b) A rate constant is found to fit the expression $k_r = (4.98\times10^{13})\,e^{-(4972\,K)/T}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ near 25 °C. Calculate $\Delta^{\ddagger}G$ for the reaction at 25 °C.

89.3(a) The gas phase association reaction between F_2 and IF_5 is first-order in each of the reactants. The energy of activation for the reaction is 58.6 kJ mol^{-1}. At 65 °C the rate constant is $7.84\times10^{-3}\,\mathrm{kPa^{-1}\,s^{-1}}$. Calculate the entropy of activation at 65 °C.

89.3(b) A gas-phase recombination reaction is first-order in each of the reactants. The energy of activation for the reaction is 39.7 kJ mol^{-1}. At 65 °C the rate constant is $0.35\,\mathrm{m^3\,s^{-1}}$. Calculate the entropy of activation at 65 °C.

89.4(a) Calculate the entropy of activation for a collision between two structureless particles at 300 K, taking $M = 65\,\mathrm{g\,mol^{-1}}$ and $\sigma = 0.35\,\mathrm{nm^2}$.

89.4(b) Calculate the entropy of activation for a collision between two structureless particles at 450 K, taking $M = 92\,\mathrm{g\,mol^{-1}}$ and $\sigma = 0.45\,\mathrm{nm^2}$.

89.5(a) The pre-exponential factor for the gas-phase decomposition of ozone at low pressures is $4.6\times10^{12}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ and its activation energy is 10.0 kJ mol^{-1}. What are (a) the entropy of activation, (b) the enthalpy of activation, (c) the Gibbs energy of activation at 298 K?

89.5(b) The pre-exponential factor for a gas-phase decomposition of a gas at low pressures is $2.3\times10^{13}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ and its activation energy is 30.0 kJ mol^{-1}. What are (a) the entropy of activation, (b) the enthalpy of activation, (c) the Gibbs energy of activation at 298 K?

89.6(a) The rate constant of the reaction $H_2O_2(aq) + I^-(aq) + H^+(aq) \rightarrow H_2O(l) + HIO(aq)$ is sensitive to the ionic strength of the aqueous solution in which the reaction occurs. At 25 °C, $k_r = 12.2\,\mathrm{dm^6\,mol^{-2}\,min^{-1}}$ at an ionic strength of 0.0525. Use the Debye–Hückel limiting law to estimate the rate constant at zero ionic strength.

89.6(b) At 25 °C, $k_r = 1.55\,\mathrm{dm^6\,mol^{-2}\,min^{-1}}$ at an ionic strength of 0.0241 for a reaction in which the rate-determining step involves the encounter of two singly charged cations. Use the Debye–Hückel limiting law to estimate the rate constant at zero ionic strength.

Problems

89.1 The rates of thermolysis of a variety of *cis*- and *trans*-azoalkanes have been measured over a range of temperatures in order to settle a controversy concerning the mechanism of the reaction. In ethanol an unstable *cis*-azoalkane decomposed at a rate that was followed by observing the N_2 evolution, and this led to the rate constants listed below (P.S. Engel and D.J. Bishop, *J. Amer. Chem. Soc.* **97**, 6754 (1975)). Calculate the enthalpy, entropy, energy, and Gibbs energy of activation at −20 °C.

θ/°C	−24.82	−20.73	−17.02	−13.00	−8.95
$10^4\times k_r/\mathrm{s^{-1}}$	1.22	2.31	4.39	8.50	14.3

89.2 In an experimental study of a bimolecular reaction in aqueous solution, the second-order rate constant was measured at 25 °C and at a variety of ionic strengths and the results are tabulated below. It is known that a singly charged ion is involved in the rate-determining step. What is the charge on the other ion involved?

$I/(\mathrm{mol\,kg^{-1}})$	0.0025	0.0037	0.0045	0.0065	0.0085
$k_r/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})$	1.05	1.12	1.16	1.18	1.26

89.3 Derive the expression for k_r given in Example 89.1 by introducing the equations for the thermal wavelengths.

89.4 The rate constant of the reaction $I^-(aq) + H_2O_2(aq) \rightarrow H_2O(l) + IO^-(aq)$ varies slowly with ionic strength, even though the Debye–Hückel limiting law predicts no effect. Use the following data from 25 °C to find the dependence of $\log k_r$ on the ionic strength:

$I/(\mathrm{mol\,kg^{-1}})$	0.0207	0.0525	0.0925	0.1575
$k_r/(\mathrm{dm^3\,mol^{-1}\,min^{-1}})$	0.663	0.670	0.679	0.694

Evaluate the limiting value of k_r at zero ionic strength. What does the result suggest for the dependence of $\log\gamma$ on ionic strength for a neutral molecule in an electrolyte solution?

89.5‡ M. Cyfert, et al. (*Int. J. Chem. Kinet.* **28**, 103 (1996)) examined the oxidation of tris(1,10-phenanthroline)iron(II) by periodate in aqueous solution, a reaction which shows autocatalytic behaviour. To assess the kinetic salt effect, they measured rate constants at a variety of concentrations of Na_2SO_4 far in excess of reactant concentrations and reported the following data:

$[Na_2SO_4]/(\mathrm{mol\,kg^{-1}})$	0.2	0.15	0.1	0.05	0.025	0.0125	0.005
$k_r/(\mathrm{dm^{3/2}\,mol^{-1/2}\,s^{-1}})$	0.462	0.430	0.390	0.321	0.283	0.252	0.224

What can be inferred about the charge of the activated complex of the rate-determining step?

89.6‡ For the gas-phase reaction $A + A \rightarrow A_2$, the experimental rate constant, k_r, has been fitted to the Arrhenius equation with the pre-exponential factor $A = 4.07\times10^5\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ at 300 K and an activation energy of 65.43 kJ mol^{-1}. Calculate $\Delta^{\ddagger}S$, $\Delta^{\ddagger}H$, $\Delta^{\ddagger}U$, and $\Delta^{\ddagger}G$ for the reaction.

89.7 Use the Debye–Hückel limiting law to show that changes in ionic strength can affect the rate of reaction catalysed by H^+ from the deprotonation of a weak acid. Consider the mechanism $H^+ + B \rightarrow P$, where H^+ comes from the deprotonation of the weak acid, HA. The weak acid has a fixed concentration. First show that $\log[H^+]$, derived from the ionization of HA, depends on the activity coefficients of ions and thus depends on the ionic strength. Then find the relationship between log(rate) and $\log[H^+]$ to show that the rate also depends on the ionic strength.

89.8‡ Show that bimolecular reactions between nonlinear molecules are much slower than between atoms even when the activation energies of both reactions are equal. Use transition-state theory and make the following assumptions: (1) all vibrational partition functions are close to unity; (2) all rotational partition functions are approximately $1\times10^{1.5}$, which is a reasonable order-of-magnitude number; (3) the translational partition function for each species is 1×10^{26}.

89.9 This problem gives some familiarity with the difficulties involved in predicting the structure of activated complexes. It also demonstrates the importance of femtosecond spectroscopy to our understanding of chemical dynamics because direct experimental observation of the activated complex removes much of the ambiguity of theoretical predictions. Consider the attack of H on D_2, which is one step in the $H_2 + D_2$ reaction. (a) Suppose that the H approaches D_2 from the side and forms a complex in the form of an isosceles triangle. Take the H–D distance as 30 per cent greater than in H_2 (74 pm) and the D–D distance as 20 per cent greater than in H_2. Let the critical coordinate be the antisymmetric stretching vibration in which one H–D bond stretches as the other shortens. Let all the vibrations be at about 1000 cm^{-1}. Estimate k_r for this reaction at 400 K using the experimental activation energy of about 35 kJ mol^{-1}. (b) Now change the model of the activated complex in part (a) and make it linear. Use the same estimated molecular bond lengths and vibrational frequencies to calculate k_r for this choice of model. (c) Clearly, there is much scope for modifying the parameters of the models of the activated complex. Use mathematical software or write and run a program that allows you to vary the structure of the complex and the parameters in a plausible way, and look for a model (or more than one model) that gives a value of k_r close to the experimental value, 4×10^5 $dm^3\,mol^{-1}\,s^{-1}$.

89.10 The study of conditions that optimize the association of proteins in solution guides the design of protocols for formation of large crystals that are amenable to analysis by X-ray diffraction techniques. It is important to characterize protein dimerization because the process is considered to be the rate-determining step in the growth of crystals of many proteins. Consider the variation with ionic strength of the rate constant of dimerization in aqueous solution of a cationic protein P:

$I/(\text{mol kg}^{-1})$	0.0100	0.0150	0.0200	0.0250	0.0300	0.0350
k_r/k_r'	8.10	13.30	20.50	27.80	38.10	52.00

What can be deduced about the charge of P?

89.11 The Eyring equation can also be applied to physical processes. As an example, consider the rate of diffusion of an atom stuck to the surface of a solid. Suppose that in order to move from one site to another it has to reach the top of the barrier, where it can vibrate classically in the vertical direction and in one horizontal direction, but vibration along the other horizontal direction takes it into the neighbouring site. Find an expression for the rate of diffusion, and evaluate it for W atoms on a tungsten surface ($E_a = 60$ kJ mol^{-1}). Suppose that the vibration frequencies at the transition state are (a) the same as, (b) one-half the value for the adsorbed atom. What is the value of the diffusion coefficient D at 500 K? (Take the site separation as 316 pm and $\nu^{\ddagger} = 0.1$ THz.)

89.12 Suppose now that the adsorbed, migrating species treated in Problem 89.11 is a spherical molecule, and that it can rotate classically as well as vibrate at the top of the barrier, but that at the adsorption site itself it can only vibrate. What effect does this have on the diffusion constant? Take the molecule to be methane, for which $\tilde{B} = 5.24$ cm^{-1}.

Topic 90 The dynamics of molecular collisions

Discussion questions

90.1 Describe how the following techniques are used in the study of chemical dynamics: infrared chemiluminescence, laser-induced fluorescence, multiphoton ionization, resonant multiphoton ionization, and reaction product imaging.

90.2 Discuss the relationship between the saddle-point energy and the activation energy of a reaction.

90.3 A method for directing the outcome of a chemical reaction consists of using molecular beams to control the relative orientations of reactants during a collision. Consider the reaction $Rb + CH_3I \rightarrow RbI + CH_3$. How should CH_3I molecules and Rb atoms be oriented to maximize the production of RbI?

90.4 Consider a reaction with an attractive potential energy surface. Discuss how the initial distribution of reactant energy affects how efficiently the reaction proceeds. Repeat for a repulsive potential energy surface.

90.5 Describe how molecular beams are used to investigate intermolecular potentials.

Exercises

90.1(a) The interaction between two diatomic molecules is described by an attractive potential energy surface. What distribution of vibrational and translational energies among reactants and products is most likely to lead to a successful reaction?

90.1(b) The interaction between two diatomic molecules has a repulsive potential energy surface. What distribution of vibrational and translational energies among reactants and products is most likely to lead to a successful reaction?

90.2(a) If the cumulative reaction probability were independent of energy, what would be the temperature dependence of the rate constant predicted by the numerator of eqn 90.6?

90.2(b) If the cumulative reaction probability equalled 1 for energies less than a barrier height V and vanished for higher energies, what would be the temperature dependence of the rate constant predicted by the numerator of eqn 90.6?

Problems

90.1 Show that the intensities of a molecular beam before and after passing through a chamber of length L containing inert scattering atoms are related by $I = I_0 e^{-\mathcal{N}\sigma L}$, where σ is the collision cross-section and $\mathcal{N}$ is the number density of scattering atoms.

90.2 In a molecular beam experiment to measure collision cross-sections it was found that the intensity of a CsCl beam was reduced to 60 per cent of its intensity on passage through CH_2F_2 at 10 μTorr, but that when the target was Ar at the same pressure the intensity was reduced only by 10 per cent. What are the relative cross-sections of the two types of collision? Why is one much larger than the other?

90.3 Consider the collision between a hard-sphere molecule of radius R_1 and mass m, and an infinitely massive impenetrable sphere of radius R_2. Plot the scattering angle θ as a function of the impact parameter b. Carry out the calculation using simple geometrical considerations.

90.4 The dependence of the scattering characteristics of atoms on the energy of the collision can be modelled as follows. We suppose that the two colliding atoms behave as impenetrable spheres, as in Problem 90.3, but that the effective radius of the heavy atoms depends on the speed v of the light atom. Suppose its effective radius depends on v as R_2e^{-v/v^*} where v^* is a constant. Take $R_1 = \frac{1}{2}R_2$ for simplicity and an impact parameter $b = \frac{1}{2}R_2$, and plot the scattering angle as a function of (a) speed, (b) kinetic energy of approach.

Integrated activity

F18.1 Estimate the orders of magnitude of the partition functions involved in a rate expression. State the order of magnitude of q_m^T/N_A, q^R, q^V, q^E for typical molecules. Check that in the collision of two structureless molecules the order of magnitude of the pre-exponential factor is of the same order as that predicted by collision theory. Go on to estimate the P-factor for a reaction in which $A + B \rightarrow P$, and A and B are nonlinear triatomic molecules.

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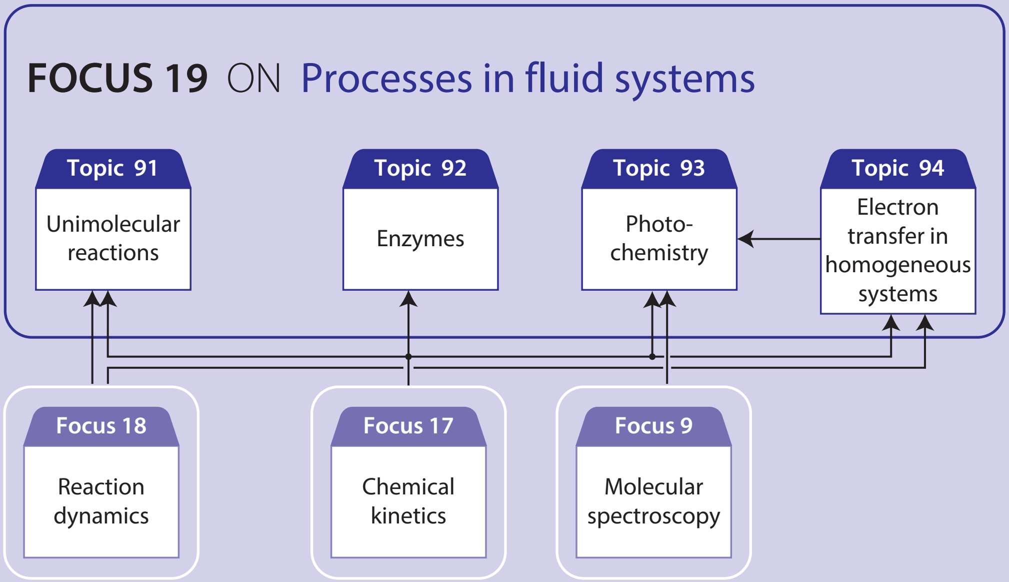
FOCUS 19 ON Processes in fluid systems



In this group of Topics we develop four examples of important reaction mechanisms in fluid systems: the gas-phase and liquid solutions. We describe a special class of 'unimolecular reactions' in the gas phase that depend on the collisions (of the types described in *Reaction dynamics*) between reactants. These processes can be explained by the 'Lindemann–Hinshelwood mechanism' and the 'RRK model' (**Topic 91**).

The rates of reactions (as explored in *Chemical kinetics*) increase upon the addition of a catalyst to the reaction mixture. In **Topic 92** we discuss the general mechanism of action of 'enzymes', which are biological catalysts. We show how to assemble expressions for their influence on the rate of reactions and the effect of substances that inhibit their function.

'Photochemistry' is the study of reactions that are initiated by light by using techniques of *Molecular spectroscopy*. In **Topic 93** we explore mechanisms of photochemical reactions, with special emphasis on electron and energy transfer processes.

Electron transfer between molecules in homogeneous systems is described in more detail in **Topic 94**. We provide a theoretical approach for the calculation of electron transfer rates, and then compare the results with experimental data.

What is the impact of this material?

Plants, algae, and some species of bacteria evolved apparatus that perform 'photosynthesis', the capture of visible and near-infrared radiation for the purpose of synthesizing high-energy molecules in the cell. In *Impact* 19.1 we explore plant photosynthesis in some detail.

To read more about the impact of this material, scan the QR code or go to http://bcs.whfreeman.com/webpub/chemistry/qmc2e/impact/qchem_impact19.html.

TOPIC 91

Unimolecular reactions

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➤ Why do you need to know this material?

The analysis of first-order gas-phase reactions illustrates how kinetic data are used to build insight into the detailed mechanism of chemical reactions.

➤ What is the key idea?

The Lindemann–Hinshelwood mechanism and the RRK model of 'unimolecular' reactions account for the first-order kinetics of gas-phase reactions.

➤ What do you need to know already?

You need to be familiar with rate laws (Topic 82), the steady-state approximation (Topic 86), and collision theory (Topic 87).

Many reactions take place by mechanisms that involve several elementary steps. We focus here on the kinetic analysis of a special class of reactions in the gas phase.

91.1 The Lindemann–Hinshelwood mechanism

A number of gas-phase reactions follow first-order kinetics, as in the isomerization of cyclopropane, *cyclo*-$C_3H_6 \rightarrow CH_3CH{=}CH_2$, for which $v = k_r[\textit{cyclo}\text{-}C_3H_6]$. The problem with the interpretation of first-order rate laws is that presumably a molecule acquires enough energy to react as a result of its collisions with other molecules. However, collisions are simple bimolecular events, so how can they result in a first-order rate law? First-order gas-phase reactions are widely called 'unimolecular reactions' because they also involve an elementary unimolecular step in which the reactant molecule changes into the product. This term must be used with caution, however, because the overall mechanism has bimolecular as well as unimolecular steps.

The first successful explanation of unimolecular reactions was provided by Frederick Lindemann in 1921 and then elaborated by Cyril Hinshelwood. In the **Lindemann–Hinshelwood mechanism** it is supposed that a reactant molecule A becomes energetically excited by collision with another A molecule in a bimolecular step (Fig. 91.1):

$$A + A \rightarrow A^* + A \qquad \frac{d[A^*]}{dt} = k_a[A]^2 \tag{91.1a}$$

The energized molecule (A*) might lose its excess energy by collision with another molecule:

$$A + A^* \rightarrow A + A \qquad \frac{d[A^*]}{dt} = -k_a'[A][A^*] \tag{91.1b}$$

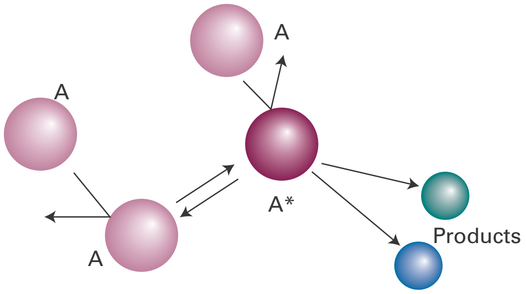

Figure 91.1 A representation of the Lindemann–Hinshelwood mechanism of unimolecular reactions. The species A is excited by collision with A, and the excited A molecule (A*) may either be deactivated by a collision with A or go on to decay by a unimolecular process to form products.

Alternatively, the excited molecule might shake itself apart and form products P. That is, it might undergo the unimolecular decay

$$\mathrm{A^* \rightarrow P} \qquad \frac{\mathrm{d[A^*]}}{\mathrm{d}t}=-k_{\mathrm{b}}[\mathrm{A^*}] \tag{91.1c}$$

If the unimolecular step is slow enough to be the rate-determining step, the overall reaction will have first-order kinetics, as observed. This conclusion can be demonstrated explicitly by applying the steady-state approximation to the net rate of formation of A*:

$$\frac{\mathrm{d[A^*]}}{\mathrm{d}t}=k_{\mathrm{a}}[\mathrm{A}]^2-k_{\mathrm{a}}'[\mathrm{A}][\mathrm{A^*}]-k_{\mathrm{b}}[\mathrm{A^*}]\approx 0 \tag{91.2}$$

This equation solves to

$$[\mathrm{A^*}]=\frac{k_{\mathrm{a}}[\mathrm{A}]^2}{k_{\mathrm{b}}+k_{\mathrm{a}}'[\mathrm{A}]} \tag{91.3}$$

so the rate law for the formation of P is

$$\frac{\mathrm{d[P]}}{\mathrm{d}t}=k_{\mathrm{b}}[\mathrm{A^*}]=\frac{k_{\mathrm{a}}k_{\mathrm{b}}[\mathrm{A}]^2}{k_{\mathrm{b}}+k_{\mathrm{a}}'[\mathrm{A}]} \tag{91.4}$$

At this stage the rate law is not first-order. However, if the rate of deactivation by (A*,A) collisions is much greater than the rate of unimolecular decay, in the sense that $k_{\mathrm{a}}'[\mathrm{A}][\mathrm{A^*}]>>k_{\mathrm{b}}[\mathrm{A^*}]$, or (after cancelling the [A*]), $k_{\mathrm{a}}'[\mathrm{A}]>>k_{\mathrm{b}}$, then we can neglect k_{b} in the denominator and obtain

$$\frac{\mathrm{d[P]}}{\mathrm{d}t}=k_{\mathrm{r}}[\mathrm{A}] \quad \text{with } k_{\mathrm{r}}=\frac{k_{\mathrm{a}}k_{\mathrm{b}}}{k_{\mathrm{a}}'} \tag{91.5}$$

Equation 91.5 is a first-order rate law, as we set out to show.

The Lindemann–Hinshelwood mechanism can be tested because it predicts that, as the concentration (and therefore the partial pressure) of A is reduced, the reaction should switch to overall second-order kinetics. Thus, when $k_{\mathrm{a}}'[\mathrm{A}]\ll k_{\mathrm{b}}$, the rate law in eqn 91.4 becomes

$$\frac{\mathrm{d[P]}}{\mathrm{d}t}=k_{\mathrm{a}}[\mathrm{A}]^2 \tag{91.6}$$

The physical reason for the change of order is that at low pressures the rate-determining step is the bimolecular formation of A*. If we write the full rate law in eqn 91.4 as

$$\frac{\mathrm{d[P]}}{\mathrm{d}t}=k_{\mathrm{r}}[\mathrm{A}] \quad \text{with } k_{\mathrm{r}}=\frac{k_{\mathrm{a}}k_{\mathrm{b}}[\mathrm{A}]}{k_{\mathrm{b}}+k_{\mathrm{a}}'[\mathrm{A}]} \tag{91.7}$$

Lindemann–Hinshelwood mechanism Rate law

then the expression for the effective rate constant, k_{r}, can be rearranged to

$$\frac{1}{k_{\mathrm{r}}}=\frac{k_{\mathrm{a}}'}{k_{\mathrm{a}}k_{\mathrm{b}}}+\frac{1}{k_{\mathrm{a}}[\mathrm{A}]} \tag{91.8}$$

Lindemann–Hinshelwood mechanism Effective rate constant

Hence, a test of the theory is to plot $1/k_{\mathrm{r}}$ against 1/[A], and to expect a straight line. This behaviour is observed often at low concentrations, but deviations are common at high concentrations. In the following section we develop the description of the mechanism to take into account experimental results over a range of concentrations and pressures.

Example 91.1 Analysing the Lindemann–Hinshelwood mechanism

At 300 K the effective rate constant for a gaseous reaction A → P which has a Lindemann–Hinshelwood mechanism is $k_{\mathrm{r},1}=2.50\times10^{-4}\ \mathrm{s^{-1}}$ at $[\mathrm{A}]_1=5.21\times10^{-4}\ \mathrm{mol\ dm^{-3}}$ and $k_{\mathrm{r},2}=2.10\times10^{-5}\ \mathrm{s^{-1}}$ at $[\mathrm{A}]_2=4.81\times10^{-6}\ \mathrm{mol\ dm^{-3}}$. Calculate the rate constant for the activation step in the mechanism.

Method Use eqn 91.8 to write an expression for the difference $1/k_{\mathrm{r},2}-1/k_{\mathrm{r},1}$ and then use the data to solve for k_{a}, the rate constant for the activation step.

Answer It follows from eqn 91.8 that

$$\frac{1}{k_{\mathrm{r},2}}-\frac{1}{k_{\mathrm{r},1}}=\frac{1}{k_{\mathrm{a}}}\left(\frac{1}{[\mathrm{A}]_2}-\frac{1}{[\mathrm{A}]_1}\right)$$

and

$$\begin{aligned}k_{\mathrm{a}}&=\frac{1/[\mathrm{A}]_2-1/[\mathrm{A}]_1}{1/k_{\mathrm{r},2}-1/k_{\mathrm{r},1}}\\&=\frac{1/(4.81\times10^{-6}\ \mathrm{mol\ dm^{-3}})-1/(5.21\times10^{-4}\ \mathrm{mol\ dm^{-3}})}{1/(2.10\times10^{-5}\ \mathrm{s^{-1}})-1/(2.50\times10^{-4}\ \mathrm{s^{-1}})}\\&=4.72\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}\end{aligned}$$

Self-test 91.1 The effective rate constants for a gaseous reaction A → P which has a Lindemann–Hinshelwood mechanism are $1.70\times10^{-3}\ \mathrm{s^{-1}}$ and $2.20\times10^{-4}\ \mathrm{s^{-1}}$ at $[\mathrm{A}]=4.37\times10^{-4}\ \mathrm{mol\ dm^{-3}}$ and $1.00\times10^{-5}\ \mathrm{mol\ dm^{-3}}$, respectively. Calculate the rate constant for the activation step in the mechanism.

Answer: $24.6\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$

91.2 The RRK model

The steric factor *P* (Topic 87) can also be estimated for unimolecular gas-phase reactions, and its introduction brings the Lindemann–Hinshelwood mechanism into closer agreement with experimental results. For example, Fig. 91.2 shows

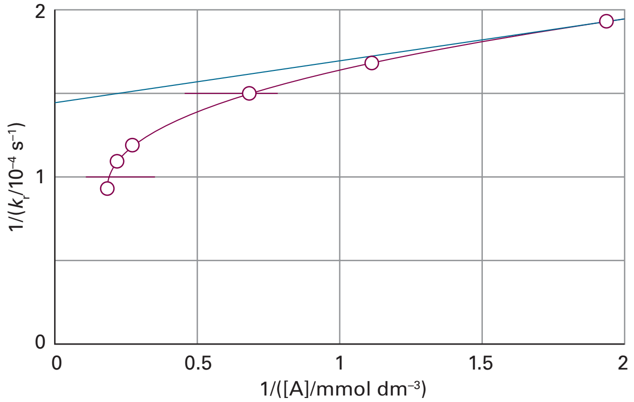

Figure 91.2 The pressure dependence of the unimolecular isomerization of *trans*-CHD=CHD, showing a pronounced departure from the straight line predicted by the Lindemann–Hinshelwood mechanism.

a typical plot of experimental values of $1/k_r$ against $1/[A]$. The plot has a pronounced curvature, corresponding to a larger value of k_r (a smaller value of $1/k_r$) at high pressures (low $1/[A]$) than would be expected by a Lindemann–Hinshelwood extrapolation of the reasonably linear low pressure (high $1/[A]$) data.

The improved model was proposed in 1926 by O.K. Rice and H.C. Ramsperger and almost simultaneously by L.S. Kassel, and is now known as the **Rice–Ramsperger–Kassel model** (RRK model). The model has been elaborated, largely by R.A. Marcus, into the 'RRKM model'. Here we outline Kassel's original approach to the RRK model; the details are set out in the following *Justification*. The essential feature of the model is that although a molecule might have enough energy to react, that energy is distributed over all the modes of motion of the molecule, and reaction will occur only when enough of that energy has migrated into a particular location (such as a bond) in the molecule. This distribution effect leads to a P factor of the form

$$P=\left(1-\frac{E^{*}}{E}\right)^{s-1} \qquad \text{RRK theory} \qquad (91.9a)$$

where s is the number of modes of motion over which the energy E may be dissipated and E^* is the energy required for the bond of interest to break. The resulting **Kassel form** of the unimolecular rate constant for the decay of A^* to products is

$$k_b(E)=\left(1-\frac{E^{*}}{E}\right)^{s-1} k_b \quad \text{for } E \geq E \qquad \text{Kassel form} \qquad (91.9b)$$

where k_b is the rate constant used in the original Lindemann theory for the decomposition of the activated intermediate (eqn 91.1c).

Justification 91.1 The RRK model of unimolecular reactions

To set up the RRK model, we suppose that a molecule consists of s identical harmonic oscillators, each of which has frequency ν. In practice, of course, the vibrational modes of a molecule have different frequencies, but assuming that they are all the same is a reasonable first approximation. Next, we suppose that the vibrations are excited to a total energy $E=nh\nu$ and then set out to calculate the number of ways N in which the energy can be distributed over the oscillators.

We can represent the n quanta as follows:

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These quanta must be put in s containers (the s oscillators), which can be represented by inserting $s-1$ walls, denoted by |. One such distribution is

□□|□□□□|□□||□□□|□□□□□□□□|(cont'd)
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The total number of arrangements of each quantum and wall (of which there are $n+s-1$ in all) is $(n+s-1)!$, where, as usual, $x!=x(x-1)\cdots1$. However the $n!$ arrangements of the n quanta are indistinguishable, as are the $(s-1)!$ arrangements of the $s-1$ walls. Therefore, to find N we must divide $(n+s-1)!$ by these two factorials. It follows that

$$N=\frac{(n+s-1)!}{n!(s-1)!}$$

The distribution of the energy throughout the molecule means that it is too sparsely spread over all the modes for any particular bond to be sufficiently highly excited to undergo dissociation. We suppose that a bond will break only if it is excited to at least an energy $E^*=n^*h\nu$. Therefore, we isolate one critical oscillator as the one that undergoes dissociation if it has *at least* n^* of the quanta, leaving up to $n-n^*$ quanta to be accommodated in the remaining $s-1$ oscillators (and therefore with $s-2$ walls in the partition in place of the $s-1$ walls we used above). For example, consider 28 quanta distributed over 6 oscillators, with excitation by at least 6 quanta in a critical oscillator required for dissociation of the associated bond. Then all the following partitions will result in dissociation:

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(The leftmost partition is the critical oscillator.) However, these partitions are equivalent to

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and we see that we have the problem of permuting 28 – 6 = 22 (in general, $n - n^*$) quanta and 5 (in general, $s - 1$) walls, and therefore a total of 27 (in general, $n - n^* + s - 1$) objects. Therefore, the calculation is exactly like the one above for N, except that we have to find the number of distinguishable permutations of $n - n^*$ quanta in s containers (and therefore $s - 1$ walls). The number N^* is therefore obtained from the expression for N by replacing n by $n - n^*$ and is

$$N^* = \frac{(n-n^*+s-1)!}{(n-n^*)!(s-1)!}$$

From the preceding discussion we conclude that the probability that one specific oscillator will have undergone sufficient excitation to dissociate is the ratio N^*/N, which is

$$P = \frac{N^*}{N} = \frac{n!(n-n^*+s-1)!}{(n-n^*)!(n+s-1)!}$$

This equation is still awkward to use, even when written out in terms of its factors:

$$\begin{aligned} P &= \frac{n(n-1)(n-2)\ldots 1}{(n-n^*)(n-n^*-1)\ldots 1} \times \frac{(n-n^*+s-1)(n-n^*+s-2)\ldots 1}{(n+s-1)(n+s-2)\ldots 1} \\ &= \frac{(n-n^*+s-1)(n-n^*+s-2)\ldots(n-n^*+1)}{(n+s-1)(n+s-2)\ldots(n+2)(n+1)} \end{aligned}$$

However, because $s - 1$ is small (in the sense $s - 1 \ll n - n^*$), we can approximate this expression by

$$P = \frac{\overbrace{(n-n^*)(n-n^*)\ldots(n-n^*)}^{s-1\,\text{factors}}}{\underbrace{(n)(n)\ldots(n)}_{s-1\,\text{factors}}} = \left(\frac{n-n^*}{n}\right)^{s-1}$$

An alternative derivation for this expression for P is developed in Problem 91.2. Because the energy of the excited molecule is $E = nh\nu$ and the critical energy is $E^* = n^*h\nu$, this expression may be written

$$P = \left(1 - \frac{E^*}{E}\right)^{s-1}$$

as in eqn 91.9a.

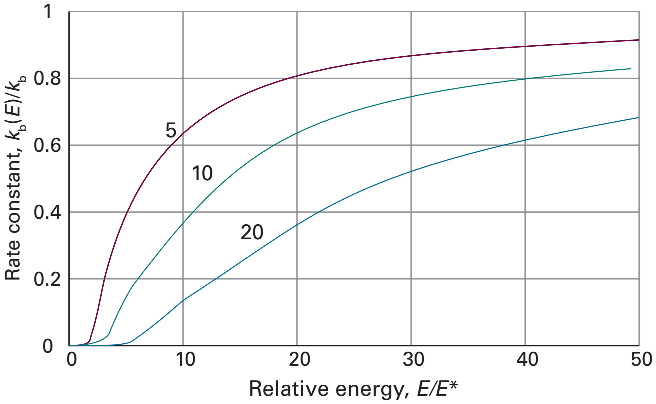

Figure 91.3 The energy dependence of the rate constant given by eqn 91.9b for three values of s.

The energy dependence of the rate constant given by eqn 91.9b is shown in Fig. 91.3 for various values of s. We see that the rate constant is smaller at a given excitation energy if s is large, as it takes longer for the excitation energy to migrate through all the oscillators of a large molecule and accumulate in the critical mode. As E becomes very large, however, the term in parentheses approaches 1, and $k_b(E)$ becomes independent of the energy and the number of oscillators in the molecule, as there is now enough energy to accumulate immediately in the critical mode regardless of the size of the molecule.

Brief illustration 91.1 The RRK model

In *Brief illustration* 87.3 we calculated a value of $P = 1.8 \times 10^{-6}$ for the reaction $H_2 + C_2H_4 \rightarrow C_2H_6$. Although this is not a unimolecular process, it is interesting to analyse it on the basis of the RRK theory because in some sense the collision energy must accumulate in a region where bonds are broken and formed. Thus, C_2H_4 has six atoms and therefore $s = 12$ vibrational modes. We can estimate the ratio E^*/E by solving

$$\left(1 - \frac{E^*}{E}\right)^{11} = 1.8 \times 10^{-6} \quad \text{or} \quad \frac{E^*}{E} = 1 - (1.8 \times 10^{-6})^{1/11} = 0.70$$

This result suggests in one interpretation that the energy needed to proceed in the reaction (identified here with the energy to break the carbon–carbon bond in C_2H_4) is typically 70 per cent of the energy of a typical collision. If all eight atoms are taken to be involved in sharing the energy of the collision, the ratio works out as 0.54.

Self-test 91.2 Apply the same analysis to the reaction in Self-test 87.3, where it is found that $P = 0.019$ for $NO + Cl_2 \rightarrow NOCl + Cl$. Take the number of atoms in the complex to be 4, so $s = 6$.

Answer: 0.55

Checklist of concepts

☐ 1. In the **Lindemann–Hinshelwood mechanism** of 'unimolecular' gas-phase reactions, it is supposed that a bimolecular activation step is followed by a rate-determining unimolecular decay step.

☐ 2. In the **RRK model**, the energy distributed over the modes of motion of the activated molecule is supposed to accumulate in a single bond.

Checklist of equations

Property	Equation	Comment	Equation number
Lindemann–Hinshelwood rate law	$\mathrm{d}[\mathrm{P}]/\mathrm{d}t = k_\mathrm{r}[\mathrm{A}]$, with $k_\mathrm{r} = k_\mathrm{a}k_\mathrm{b}[\mathrm{A}]/(k_\mathrm{b} + k_\mathrm{a}'[\mathrm{A}])$	$k_\mathrm{r} = k_\mathrm{a}k_\mathrm{b}/k_\mathrm{a}'$ if $k_\mathrm{a}'[\mathrm{A}] \gg k_\mathrm{b}$	91.7
Effective rate constant	$1/k_\mathrm{r} = k_\mathrm{a}'/k_\mathrm{a}k_\mathrm{b} + 1/k_\mathrm{a}[\mathrm{A}]$	Lindemann–Hinshelwood mechanism	91.8
Steric factor	$P = (1 - E^*/E)^{s-1}$	RRK theory	91.9a

TOPIC 92

Enzymes

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➤ Why do you need to know this material?

The role of enzymes in controlling chemical reactions is central to biology and the maintenance of life.

➤ What is the key idea?

Enzymes are homogeneous catalysts, which are in the same phase as the reaction mixture they catalyse and can have a dramatic effect on the rates of the reactions they control.

➤ What do you need to know already?

You need to be familiar with the analysis of reaction mechanisms in terms of the steady-state approximation (Topic 86) and the effect of a catalyst on the activation energy of a reaction (Topic 85).

Figure 92.1 (which is identical to Fig. 85.5) shows that a catalyst lowers the activation energy of the reaction by providing an alternative path that avoids the slow, rate-determining step of the uncatalysed reaction. A **homogeneous catalyst** is a catalyst in the same phase as the reaction mixture. For example, the decomposition of hydrogen peroxide in aqueous solution is catalysed by iodide ions. **Enzymes**, which are homogeneous biological catalysts, are very specific and can have a dramatic effect on the reactions they control. Topic 97 deals with **heterogeneous catalysts**, which are in a different phase from the reaction mixture.

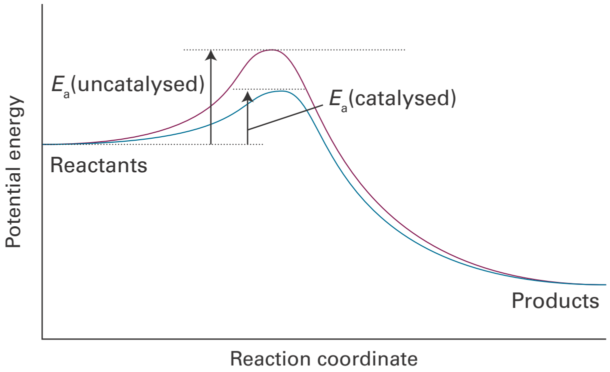

Figure 92.1 A catalyst provides a different path with a lower activation energy. The result is an increase in the rate of formation of product.

Homogeneous catalysts can be very effective. For instance, the activation energy for the decomposition of hydrogen peroxide in solution is 76 kJ mol^{-1}, and the reaction is slow at room temperature. When a small amount of iodide ion is added, the activation energy falls to 57 kJ mol^{-1} and the rate constant increases by a factor of 2000. The enzyme catalase reduces the activation energy even further, to 8 kJ mol^{-1}, corresponding to an acceleration of the reaction by a factor of 10^{15} at 298 K.

92.1 Features of enzymes

Enzymes are homogeneous biological catalysts acting in the aqueous environment of cells. These ubiquitous compounds are special proteins or nucleic acids that contain an **active site**, which is responsible for binding the **substrates**, the reactants, and processing them into products. As is true of any catalyst, the active site returns to its original state after the products are released. Many enzymes consist primarily of proteins, some featuring organic or inorganic cofactors in their active sites. However, certain RNA molecules can also be biological catalysts, forming *ribozymes*. A very important example of a ribozyme is the *ribosome*, a large assembly of proteins and catalytically active RNA molecules responsible for the synthesis of proteins in the cell.

The structure of the active site is specific to the reaction that it catalyses, with groups in the substrate interacting with groups in the active site by intermolecular interactions, such as hydrogen bonding, electrostatic forces, and van der Waals interactions. Figure 92.2 shows two models that explain the binding of a substrate to the active site of an enzyme. In the **lock-and-key model**, the active site and substrate have complementary three-dimensional structures and dock without the need for major atomic rearrangements. Experimental evidence favours the **induced fit model**, in which binding of the substrate induces a conformational change in the active site. Only after the change does the substrate fit snugly in the active site.

Enzyme-catalysed reactions are prone to inhibition by molecules that interfere with the formation of product. Many drugs for the treatment of disease function by inhibiting enzymes. For example, an important strategy in the treatment of acquired immune deficiency syndrome (AIDS) involves the steady administration of a specially designed protease inhibitor. The drug inhibits an enzyme that is key to the formation of the protein envelope surrounding the genetic material of the human immunodeficiency virus (HIV). Without a properly formed envelope, HIV cannot replicate in the host organism.

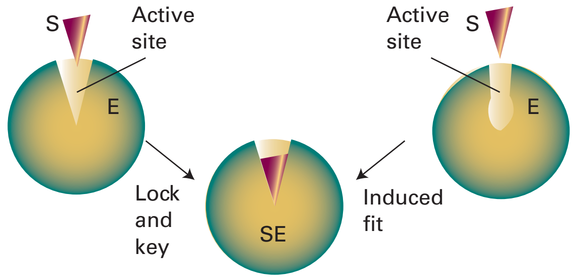

Figure 92.2 Two models that explain the binding of a substrate to the active site of an enzyme. In the lock-and-key model, the active site and substrate have complementary three-dimensional structures and dock without the need for major atomic rearrangements. In the induced fit model, binding of the substrate induces a conformational change in the active site. The substrate fits well in the active site after the conformational change has taken place.

92.2 The Michaelis–Menten mechanism

Experimental studies of enzyme kinetics are typically conducted by monitoring the initial rate of product formation in a solution in which the enzyme is present at very low concentration. Indeed, enzymes are such efficient catalysts that significant accelerations may be observed even when their concentration is more than three orders of magnitude smaller than that of the substrate.

The principal features of many enzyme-catalysed reactions are as follows:

- For a given initial concentration of substrate, $[\mathrm{S}]_0$, the initial rate of product formation is proportional to the total concentration of enzyme, $[\mathrm{E}]_0$.
- For a given $[\mathrm{E}]_0$ and low values of $[\mathrm{S}]_0$, the rate of product formation is proportional to $[\mathrm{S}]_0$.
- For a given $[\mathrm{E}]_0$ and high values of $[\mathrm{S}]_0$, the rate of product formation becomes independent of $[\mathrm{S}]_0$, reaching a maximum value known as the **maximum velocity**, $v_{\max}$.

The **Michaelis–Menten mechanism** accounts for these features. According to this mechanism, an enzyme–substrate complex (ES) is formed in the first step and the substrate is either released unchanged or after modification to form products:

$$\mathrm{E}+\mathrm{S} \underset{k_a'}{\overset{k_a}{\rightleftarrows}} \mathrm{ES}$$

$$\mathrm{ES} \xrightarrow{k_b} \mathrm{P}+\mathrm{E}$$

Michaelis–Menten mechanism

We show in the following *Justification* that this mechanism leads to the **Michaelis–Menten equation** for the rate of product formation,

$$v=\frac{k_b[\mathrm{E}]_0}{1+K_\mathrm{M}/[\mathrm{S}]_0} \qquad (92.1)$$

Michaelis–Menten equation

where $K_\mathrm{M}=(k_a'+k_b)/k_a$ is the **Michaelis constant**, characteristic of a given enzyme acting on a given substrate and having the dimensions of a molar concentration.

Justification 92.1 The Michaelis–Menten equation

The rate of product formation according to the Michaelis–Menten mechanism is

$$v=k_b[\mathrm{ES}]$$

We can obtain the concentration of the enzyme–substrate complex by invoking the steady-state approximation and writing

$$\frac{\mathrm{d}[\mathrm{ES}]}{\mathrm{d}t}=k_a[\mathrm{E}][\mathrm{S}]-k_a'[\mathrm{ES}]-k_b[\mathrm{ES}]\cong 0$$

It follows that

$$[\mathrm{ES}]=\left(\frac{k_\mathrm{a}}{k_\mathrm{a}'+k_\mathrm{b}}\right)[\mathrm{E}][\mathrm{S}]$$

where [E] and [S] are the concentrations of *free* enzyme and substrate, respectively. Now we define the Michaelis constant as

$$K_\mathrm{M}=\frac{k_\mathrm{a}'+k_\mathrm{b}}{k_\mathrm{a}}=\frac{[\mathrm{E}][\mathrm{S}]}{[\mathrm{ES}]}$$

To express the rate law in terms of the concentrations of enzyme and substrate added, we note that $[\mathrm{E}]_0=[\mathrm{E}]+[\mathrm{ES}]$ and

$$[\mathrm{E}]_0=\frac{K_\mathrm{M}[\mathrm{ES}]}{[\mathrm{S}]}+[\mathrm{ES}]=[\mathrm{ES}]\left\{1+\frac{K_\mathrm{M}}{[\mathrm{S}]}\right\}$$

Moreover, because the substrate is typically in large excess relative to the enzyme, the free substrate concentration is approximately equal to the initial substrate concentration and we can write $[\mathrm{S}]\approx[\mathrm{S}]_0$. It then follows that

$$[\mathrm{ES}]=\frac{[\mathrm{E}]_0}{1+K_\mathrm{M}/[\mathrm{S}]_0}$$

Equation 92.1 is obtained when this expression for [ES] is substituted into that for the rate of product formation ($v=k_\mathrm{b}[\mathrm{ES}]$).

Equation 92.1 shows that, in accord with experimental observations (Fig. 92.3),

- When $[\mathrm{S}]_0 \ll K_\mathrm{M}$, the rate is proportional to $[\mathrm{S}]_0$:

$$v=\frac{k_\mathrm{b}}{K_\mathrm{M}}[\mathrm{S}]_0[\mathrm{E}]_0 \tag{92.2a}$$

- When, $[\mathrm{S}]_0 \gg K_\mathrm{M}$, the rate reaches its maximum value and is independent of $[\mathrm{S}]_0$:

$$v=v_\mathrm{max}=k_\mathrm{b}[\mathrm{E}]_0 \tag{92.2b}$$

Substitution of the definition of v_max into eqn 92.1 gives

$$v=\frac{v_\mathrm{max}}{1+K_\mathrm{M}/[\mathrm{S}]_0} \tag{92.3a}$$

which can be rearranged into a form amenable to data analysis by linear regression by taking reciprocals of both sides:

$$\frac{1}{v}=\frac{1}{v_\mathrm{max}}+\left(\frac{K_\mathrm{M}}{v_\mathrm{max}}\right)\frac{1}{[\mathrm{S}]_0} \tag{92.3b}$$

Lineweaver–Burk plot

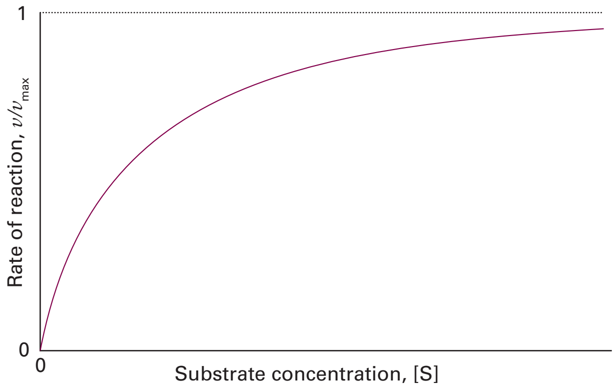

Figure 92.3 The variation of the rate of an enzyme-catalysed reaction with substrate concentration. The approach to a maximum rate, v_max, for large [S] is explained by the Michaelis–Menten mechanism.

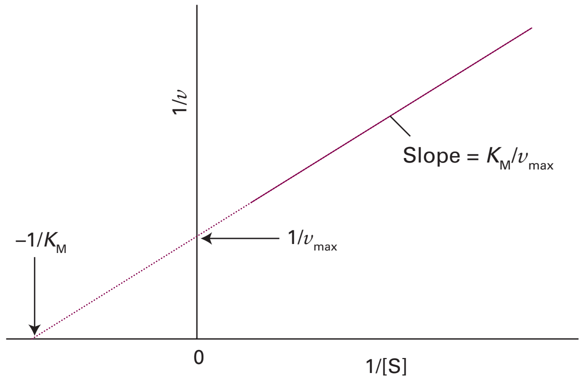

Figure 92.4 A Lineweaver–Burk plot for the analysis of an enzyme-catalysed reaction that proceeds by a Michaelis–Menten mechanism, and the significance of the intercepts and the slope.

A **Lineweaver–Burk plot** is a plot of $1/v$ against $1/[\mathrm{S}]_0$, and according to eqn 92.3b it should yield a straight line with slope of $K_\mathrm{M}/v_\mathrm{max}$, a *y*-intercept at $1/v_\mathrm{max}$, and an *x*-intercept at $-1/K_\mathrm{M}$ (Fig. 92.4). The value of k_b is then calculated from the *y*-intercept and eqn 92.2b. However, the plot cannot give the individual rate constants k_a and k_a' that appear in the expression for K_M. The stopped-flow technique described in Topic 82 can give the additional data needed, because we can find the rate of formation of the enzyme–substrate complex by monitoring the concentration after mixing the enzyme and substrate. This procedure gives a value for k_a, and k_a' is then found by combining this result with the values of k_b and K_M.

Example 92.1 Analysing a Lineweaver–Burk plot

The enzyme carbonic anhydrase catalyses the hydration of CO_2 in red blood cells to give bicarbonate (hydrogencarbonate) ion:

$$\mathrm{CO_2(g)+H_2O(l)\rightarrow HCO_3^-(aq)+H^+(aq)}$$

The following data were obtained for the reaction at pH = 7.1, 273.5 K, and an enzyme concentration of 2.3 nmol dm^{-3}:

$[\mathrm{CO_2}]$/(mmol dm^{-3})	1.25	2.5	5	20
v/(mmol dm^{-3} s^{-1})	2.78×10^{-2}	5.00×10^{-2}	8.33×10^{-2}	1.67×10^{-1}

Determine the maximum velocity and the Michaelis constant for the reaction at 273.5 K.

Method Prepare a Lineweaver–Burk plot and determine the values of K_M and v_{max} by linear regression analysis.

Answer We draw up the following table:

$1/([\mathrm{CO_2}]$/(mmol dm^{-3}))	0.800	0.400	0.200	0.0500
$1/(v$/(mmol dm^{-3} s^{-1}))	36.0	20.0	12.0	6.0

Figure 92.5 shows the Lineweaver–Burk plot for the data. The slope is 40.0 and the y-intercept is 4.00. Hence,

$$v_{\mathrm{max}}/(\mathrm{mmol\,dm^{-3}\,s^{-1}})=\frac{1}{\mathrm{intercept}}=\frac{1}{4.00}=0.250$$

and

$$K_{\mathrm{M}}/(\mathrm{mmol\,dm^{-3}})=\frac{\mathrm{slope}}{\mathrm{intercept}}=\frac{40.00}{4.00}=10.0$$

A note on good practice The slope and the intercept are unitless: we have remarked previously that all graphs should be plotted as pure numbers.

Self-test 92.1 The enzyme α-chymotrypsin is secreted in the pancreas of mammals and cleaves peptide bonds made between certain amino acids. Several solutions containing the small peptide N-glutaryl-l-phenylalanine-p-nitroanilide at different concentrations were prepared and the same small amount of α-chymotrypsin was added to each one. The following data were obtained on the initial rates of the formation of product:

[S]/(mmol dm^{-3})	0.334	0.450	0.667	1.00	1.33	1.67
v/(mmol dm^{-3} s^{-1})	0.152	0.201	0.269	0.417	0.505	0.667

Determine the maximum velocity and the Michaelis constant for the reaction.

Answer: v_{max} = 2.80 mmol dm^{-3} s^{-1}, K_M = 5.89 mmol dm^{-3}

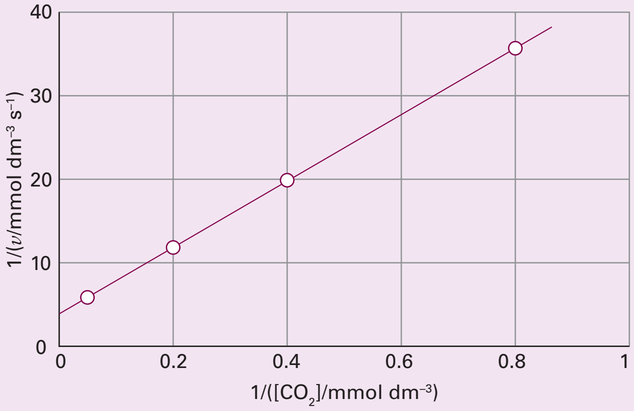

Figure 92.5 The Lineweaver–Burk plot of the data for Example 92.1.

92.3 The catalytic efficiency of enzymes

The **turnover frequency**, or **catalytic constant**, of an enzyme, k_{cat}, is the number of catalytic cycles (turnovers) performed by the active site in a given interval divided by the duration of the interval. This quantity has units of a first-order rate constant and, in terms of the Michaelis–Menten mechanism, is numerically equivalent to k_b, the rate constant for release of product from the enzyme–substrate complex. It follows from the identification of k_{cat} with k_b and from eqn 92.2b that

$$k_{\mathrm{cat}}=k_{\mathrm{b}}=\frac{v_{\mathrm{max}}}{[\mathrm{E}]_0} \qquad \text{Turnover frequency} \qquad (92.4)$$

The **catalytic efficiency**, η (eta), of an enzyme is the ratio k_{cat}/K_M. The higher the value of η, the more efficient is the enzyme. We can think of the catalytic efficiency as the effective rate constant of the enzymatic reaction. From $K_M=(k_a'+k_b)/k_a$ and eqn 92.4, it follows that

$$\eta=\frac{k_{\mathrm{cat}}}{K_{\mathrm{M}}}=\frac{k_{\mathrm{a}}k_{\mathrm{b}}}{k_{\mathrm{a}}'+k_{\mathrm{b}}} \qquad \text{Catalytic efficiency} \qquad (92.5)$$

The efficiency reaches its maximum value of k_a when $k_b \gg k_a'$. Because k_a is the rate constant for the formation of a complex from two species that are diffusing freely in solution, the maximum efficiency is related to the maximum rate of diffusion of E and S in solution. This limit (which is discussed further in Topic 88) leads to rate constants of about 10^8–10^9 dm^3 mol^{-1} s^{-1} for molecules as large as enzymes at room temperature. The enzyme catalase has $\eta = 4.0\times10^8$ dm^3 mol^{-1} s^{-1} and is said to have attained 'catalytic perfection', in the sense that the rate of the reaction it catalyses is controlled only by diffusion: it acts as soon as a substrate makes contact.

Brief illustration 92.1 The catalytic efficiency of an enzyme

To determine the catalytic efficiency of carbonic anhydrase at 273.5 K from the results from Example 92.1, we begin by using eqn 92.4 to calculate k_{cat}:

$$k_{\text{cat}}=\frac{v_{\max}}{[\text{E}]_0}=\frac{2.5\times10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{2.3\times10^{-9}\ \text{mol dm}^{-3}}=1.1\times10^{5}\ \text{s}^{-1}$$

The catalytic efficiency follows from eqn 92.5:

$$\eta=\frac{k_{\text{cat}}}{K_{\text{M}}}=\frac{1.1\times10^{5}\ \text{s}^{-1}}{10.0\times10^{-3}\ \text{mol dm}^{-3}}=1.1\times10^{7}\ \text{dm}^{3}\ \text{mol}^{-1}\ \text{s}^{-1}$$

Self-test 92.2 The enzyme-catalysed conversion of a substrate at 298 K has $K_{\text{M}}=0.015\ \text{mol dm}^{-3}$ and $v_{\max}=4.25\times10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$ when the enzyme concentration is $3.60\times10^{-9}\ \text{mol dm}^{-3}$. Calculate k_{cat} and η. Is the enzyme 'catalytically perfect'?

Answer: $k_{\text{cat}}=1.18\times10^{5}\ \text{s}^{-1}$, $\eta=7.9\times10^{6}\ \text{dm}^{3}\ \text{mol}^{-1}\ \text{s}^{-1}$; the enzyme is not 'catalytically perfect'

92.4 Mechanisms of enzyme inhibition

An inhibitor, I, decreases the rate of product formation from the substrate by binding to the enzyme, to the ES complex, or to the enzyme and ES complex simultaneously. The most general kinetic scheme for enzyme inhibition is then

$$\text{E}+\text{S}\underset{k_a'}{\overset{k_a}{\rightleftarrows}}\text{ES}$$

$$\text{ES}\xrightarrow{k_b}\text{P}+\text{E}$$

$$\text{EI}\rightleftharpoons\text{E}+\text{I}\qquad K_{\text{I}}=\frac{[\text{E}][\text{I}]}{[\text{EI}]}\tag{92.6a}$$

$$\text{ESI}\rightleftharpoons\text{ES}+\text{I}\qquad K_{\text{I}}'=\frac{[\text{ES}][\text{I}]}{[\text{ESI}]}\tag{92.6b}$$

The lower the values of K_{I} and K_{I}', the more efficient are the inhibitors. The rate of product formation is always given by $v=k_b[\text{ES}]$, because only ES leads to product. As shown in the following *Justification*, the rate of reaction in the presence of an inhibitor is

$$v=\frac{v_{\max}}{\alpha'+\alpha K_{\text{M}}/[\text{S}]_0}\tag{92.7}$$

Effect of inhibition on the rate

where $\alpha=1+[\text{I}]/K_{\text{I}}$ and $\alpha'=1+[\text{I}]/K_{\text{I}}'$. This equation is very similar to the Michaelis–Menten equation for the uninhibited enzyme (eqn 92.1) and is also amenable to analysis by a Lineweaver–Burk plot:

$$\frac{1}{v}=\frac{\alpha'}{v_{\max}}+\left(\frac{\alpha K_{\text{M}}}{v_{\max}}\right)\frac{1}{[\text{S}]_0}\tag{92.8}$$

Justification 92.2 Enzyme inhibition

By mass balance, the total concentration of enzyme is

$$[\text{E}]_0=[\text{E}]+[\text{EI}]+[\text{ES}]+[\text{ESI}]$$

By using eqns 92.6a and 92.6b and the definitions

$$\alpha=1+\frac{[\text{I}]}{K_{\text{I}}}\quad\text{and}\quad\alpha'=1+\frac{[\text{I}]}{K_{\text{I}}'}$$

it follows that

$$[\text{E}]_0=[\text{E}]\alpha+[\text{ES}]\alpha'$$

By using $K_{\text{M}}=[\text{E}][\text{S}]/[\text{ES}]$ and replacing [S] with $[\text{S}]_0$ we can write

$$[\text{E}]_0=\frac{K_{\text{M}}[\text{ES}]}{[\text{S}]_0}\alpha+[\text{ES}]\alpha'=[\text{ES}]\left(\frac{\alpha K_{\text{M}}}{[\text{S}]_0}+\alpha'\right)$$

The expression for the rate of product formation is then

$$v=k_b[\text{ES}]=\frac{k_b[\text{E}]_0}{\alpha K_{\text{M}}/[\text{S}]_0+\alpha'}$$

which, upon replacement of $k_b[\text{E}]_0$ with $v_{\max}$, gives eqn 92.7.

There are three major modes of inhibition that give rise to distinctly different kinetic behaviour (Fig. 92.6). In **competitive inhibition** the inhibitor binds only to the active site of the enzyme and thereby inhibits the attachment of the substrate. This condition corresponds to $\alpha>1$ and $\alpha'=1$ (because ESI does not form). In this limit, eqn 92.8 becomes

$$\frac{1}{v}=\frac{1}{v_{\max}}+\left(\frac{\alpha K_{\text{M}}}{v_{\max}}\right)\frac{1}{[\text{S}]_0}$$

Competitive inhibition

The y-intercept is unchanged but the slope of the Lineweaver–Burk plot increases by a factor of α relative to the slope for data on the uninhibited enzyme (Fig. 92.6a). In **uncompetitive inhibition** the inhibitor binds to a site of the enzyme that is removed from the active site, but only if the substrate is already present. The inhibition occurs because ESI reduces the concentration of ES, the active type of complex. In this case $\alpha=1$ (because EI does not form) and $\alpha'>1$ and eqn 92.8 becomes

$$\frac{1}{v}=\frac{\alpha'}{v_{\max}}+\left(\frac{K_{\text{M}}}{v_{\max}}\right)\frac{1}{[\text{S}]_0}$$

Uncompetitive inhibition

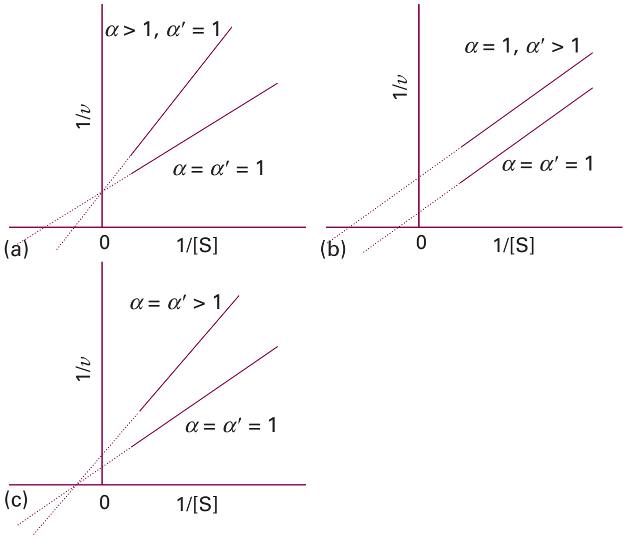

Figure 92.6 Lineweaver–Burk plots characteristic of the three major modes of enzyme inhibition: (a) competitive inhibition, (b) uncompetitive inhibition, and (c) non-competitive inhibition, showing the special case $\alpha = \alpha' > 1$.

The y-intercept of the Lineweaver–Burk plot increases by a factor of α' relative to the y-intercept for data on the uninhibited enzyme but the slope does not change (Fig. 92.6b). In **non-competitive inhibition** (also called **mixed inhibition**) the inhibitor binds to a site other than the active site, and its presence reduces the ability of the substrate to bind to the active site. Inhibition occurs at both the E and ES sites. This condition corresponds to $\alpha > 1$ and $\alpha' > 1$. Both the slope and the y-intercept of the Lineweaver–Burk plot increase upon addition of the inhibitor. Figure 92.6c shows the special case of $K_I = K_I'$ and $\alpha = \alpha'$, which results in intersection of the lines at the x-axis.

In all cases, the efficiency of the inhibitor may be obtained by determining K_M and $v_{\max}$ from a control experiment with uninhibited enzyme and then repeating the experiment with a known concentration of inhibitor. From the slope and y-intercept of the Lineweaver–Burk plot for the inhibited enzyme, the mode of inhibition, the values of α or α', and the values of K_I and K_I' may be obtained.

Example 92.2 Distinguishing between types of inhibition

Five solutions of a substrate, S, were prepared with the concentrations given in the first column below and each one was divided into four equal volumes. The same concentration of enzyme was present in each one. An inhibitor, I, was then added in four different concentrations to the samples, and the initial rate of formation of product was determined with the results given below. Does the inhibitor act competitively or non-competitively? Determine K_I and K_M.

	[I]/(mmol dm^{-3})					
[S]$_0$/(mmol dm^{-3})	**0**	**0.20**	**0.40**	**0.60**	**0.80**	
0.050	0.033	0.026	0.021	0.018	0.016	v/(μmol dm^{-3} s^{-1})
0.10	0.055	0.045	0.038	0.033	0.029	
0.20	0.083	0.071	0.062	0.055	0.050	
0.40	0.111	0.100	0.091	0.084	0.077	
0.60	0.116	0.116	0.108	0.101	0.094	

Method Draw a series of Lineweaver–Burk plots for different inhibitor concentrations. If the plots resemble those in Fig. 92.6a, then the inhibition is competitive. On the other hand, if the plots resemble those in Fig. 92.6c, then the inhibition is non-competitive. To find K_I, we need to determine the slope at each value of [I], which is equal to $\alpha K_M/v_{\max}$, or $K_M/v_{\max} + K_M[\mathrm{I}]/K_I v_{\max}$, then plot this slope against [I]: the intercept at $[\mathrm{I}] = 0$ is the value of $K_M/v_{\max}$ and the slope is $K_M/K_I v_{\max}$.

Answer First we draw up a table of $1/[\mathrm{S}]_0$ and $1/v$ for each value of [I]:

	[I]/(mmol dm^{-3})					
1/([S]$_0$/(mmol dm^{-3}))	**0**	**0.20**	**0.40**	**0.60**	**0.80**	
20	30	38	48	56	62	1/(v/(μmol dm^{-3} s^{-1}))
10	18	22	26	30	34	
5.0	12	14	16	18	20	
2.5	9.01	10.0	11.0	11.9	13.0	
1.7	7.94	8.62	9.26	9.90	10.6	

The five plots (one for each [I]) are given in Fig. 92.7. We see that they pass through the same intercept on the vertical axis, so the inhibition is competitive. The mean of the (least-squares) intercepts is 5.83, so $v_{\max} = 0.172\,\mu\mathrm{mol\,dm^{-3}\,s^{-1}}$ (note how it picks up the units for v in the data). The (least-squares) slopes of the lines are as follows:

[I]/(mmol dm^{-3})	0	0.20	0.40	0.60	0.80
Slope	1.219	1.627	2.090	2.489	2.832

These values are plotted in Fig. 92.8. The intercept at $[\mathrm{I}] = 0$ is 1.234, so $K_M = 0.212\,\mathrm{mmol\,dm^{-3}}$. The (least-squares) slope of the line is 2.045, so

$$K_I/(\mathrm{mmol\,dm^{-3}}) = \frac{K_M}{\mathrm{slope}\times v_{\max}} = \frac{0.212}{2.045\times 0.172} = 0.603$$

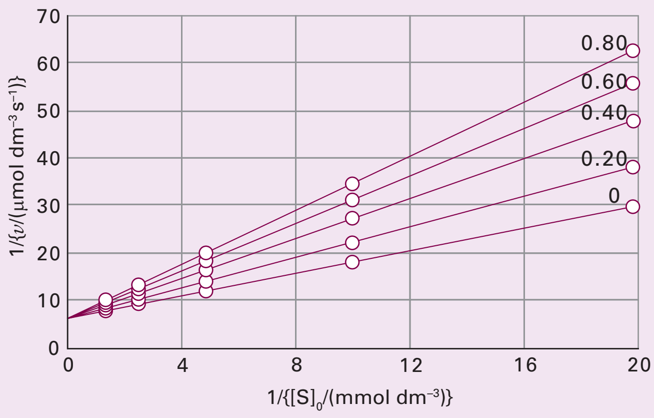

Figure 92.7 Lineweaver–Burk plots for the data in Example 92.2. Each line corresponds to a different concentration of inhibitor.

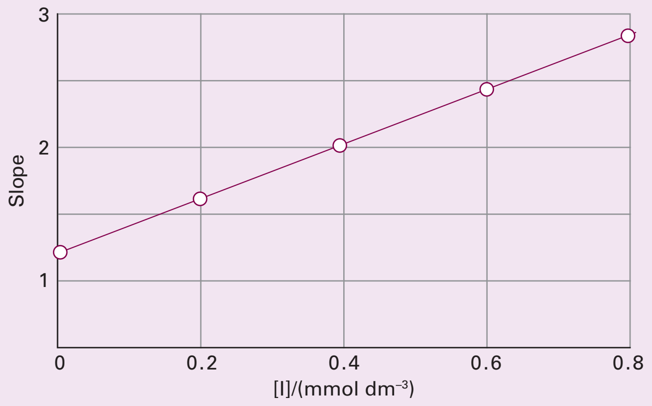

Figure 92.8 Plot of the slopes of the plots in Fig. 92.7 against [I] based on the data in Example 92.2.

Self-test 92.3 Repeat the question using the following data:

$[\text{S}]_0/$ (mmol dm^{-3})	$[\text{I}]/(\text{mmol dm}^{-3})$					
	0	**0.20**	**0.40**	**0.60**	**0.80**	
0.050	0.020	0.015	0.012	0.0098	0.0084	$v/(\mu\text{mol dm}^{-3}\,\text{s}^{-1})$
0.10	0.035	0.026	0.021	0.017	0.015	
0.20	0.056	0.042	0.033	0.028	0.024	
0.40	0.080	0.059	0.047	0.039	0.034	
0.60	0.093	0.069	0.055	0.046	0.039	

Answer: Non-competitive, $K_M = 0.30\,\text{mmol dm}^{-3}$, $K_I = 0.57\,\text{mmol dm}^{-3}$

Checklist of concepts

☐ 1. A **homogeneous catalyst** is a catalyst in the same phase as the reaction mixture.

☐ 2. **Enzymes** are homogeneous biological catalysts.

☐ 3. The **Michaelis–Menten mechanism** of enzyme kinetics accounts for the dependence of rate on the concentration of the substrate and the enzyme.

☐ 4. A **Lineweaver–Burk plot** is used to determine the parameters that occur in the Michaelis–Menten mechanism.

☐ 5. In **competitive inhibition** of an enzyme, the inhibitor binds only to the active site of the enzyme.

☐ 6. In **uncompetitive inhibition** the inhibitor binds to a site of the enzyme that is removed from the active site, but only if the substrate is already present.

☐ 7. In **non-competitive inhibition**, the inhibitor binds to a site other than the active site.

Checklist of equations

Property	Equation	Comment	Equation number
Michaelis–Menten equation	$v=v_{\mathrm{max}}/(1+K_{\mathrm{M}}/[\mathrm{S}]_0)$		92.3a
Lineweaver–Burk plot	$1/v=1/v_{\mathrm{max}}+(K_{\mathrm{M}}/v_{\mathrm{max}})(1/[\mathrm{S}]_0)$		92.3b
Turnover frequency	$k_{\mathrm{cat}}=v_{\mathrm{max}}/[\mathrm{E}]_0$	Definition	92.4
Catalytic efficiency	$\eta=k_{\mathrm{cat}}/K_{\mathrm{M}}$	Definition	92.5
Effect of inhibition	$v=v_{\mathrm{max}}/(\alpha'+\alpha K_{\mathrm{M}}/[\mathrm{S}]_0)$	Assumes Michaelis–Menten mechanism	92.7

TOPIC 93

Photochemistry

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➤ Why do you need to know this material?

Many chemical and biological processes, including photosynthesis and vision, can be initiated by the absorption of electromagnetic radiation, so you need to know how to include the effect of light in rate laws. You also need to see how to obtain insight into these processes by the quantitative analysis of their mechanisms.

➤ What is the key idea?

The mechanisms of many photochemical reactions lead to relatively simple rate laws that yield rate constants and quantitative measures of the efficiency with which radiant energy induces reactions.

➤ What do you need to know already?

You need to be familiar with the concepts of singlet and triplet states (Topic 21), modes of radiative decay (fluorescence and phosphorescence, Topic 46), concepts of electronic spectroscopy (Topic 45), and the formulation of a rate law from a proposed mechanism (Topic 86).

Photochemical processes are initiated by the absorption of electromagnetic radiation. Among the most important of these processes are those that capture the radiant energy of the Sun. Some of these reactions lead to the heating of the atmosphere during the daytime by absorption of ultraviolet radiation. Others include the absorption of visible radiation during photosynthesis. Without photochemical processes, the Earth would be simply a warm, sterile rock.

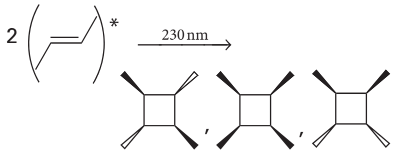
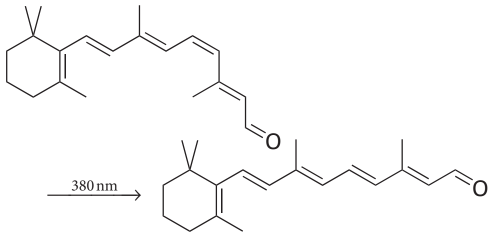
93.1 Photochemical processes

Table 93.1 summarizes common photochemical reactions. Photochemical processes are initiated by the absorption of radiation by at least one component of a reaction mixture. In a **primary process**, products are formed directly from the excited state of a reactant. Examples include fluorescence (Topic 46) and the *cis*–*trans* photoisomerization of retinal. Products of a **secondary process** originate from intermediates that are formed directly from the excited state of a reactant, such as oxidative processes initiated by the oxygen atoms formed by ozone photodissociation.

Competing with the formation of photochemical products are numerous primary photophysical processes that can deactivate the excited state (Table 93.2). Therefore, it is important to consider the timescales of the formation and decay of excited states before describing the mechanisms of photochemical reactions.

Electronic transitions caused by absorption of ultraviolet and visible radiation occur within 10^{-16}–10^{-15} s. We expect, then, the upper limit for the rate constant of a first-order photochemical reaction to be about $10^{16}\,\mathrm{s}^{-1}$. Fluorescence is slower than absorption, with typical lifetimes of 10^{-12}–10^{-6} s. Therefore, the excited singlet state can initiate very fast photochemical reactions in the femtosecond (10^{-15} s) to picosecond (10^{-12} s) range. Examples of such ultrafast reactions are the initial events of vision and of photosynthesis. Typical intersystem crossing (ISC, Topic 46) and phosphorescence times for large organic molecules are 10^{-12}–10^{-4} s and 10^{-6}–10^{-1} s, respectively. As a consequence of their long lifetimes, excited triplet states are photochemically important. Indeed, because phosphorescence decay is several

Table 93.1 Examples of photochemical processes

Process	General form	Example
Ionization	$A^* \rightarrow A^+ + e^-$	$NO^* \xrightarrow{134\,\text{nm}} NO^+ + e^-$
Electron transfer	$A^* + B \rightarrow A^+ + B^-$ or $A^- + B^+$	$[Ru(bpy)_3]^{2+*} + Fe^{3+} \xrightarrow{452\,\text{nm}} [Ru(bpy)_3]^{3+} + Fe^{2+}$
Dissociation	$A^* \rightarrow B + C$	$O_3^* \xrightarrow{1180\,\text{nm}} O_2 + O$
	$A^* + B{-}C \rightarrow A + B + C$	$Hg^* + CH_4 \xrightarrow{254\,\text{nm}} Hg + CH_3 + H$
Addition	$2\,A^* \rightarrow B$	
	$A^* + B \rightarrow AB$	
Abstraction	$A^* + B{-}C \rightarrow A{-}B + C$	$Hg^* + H_2 \xrightarrow{254\,\text{nm}} HgH + H$
Isomerization or rearrangement	$A^* \rightarrow A'$	

* Excited state.

Table 93.2 Common photophysical processes†

Primary absorption	$S + h\nu \rightarrow S^*$
Excited-state absorption	$S^* + h\nu \rightarrow S^{**}$
	$T^* + h\nu \rightarrow T^{**}$
Fluorescence	$S^* \rightarrow S + h\nu$
Stimulated emission	$S^* + h\nu \rightarrow S + 2h\nu$
Intersystem crossing (ISC)	$S^* \rightarrow T^*$
Phosphorescence	$T^* \rightarrow S + h\nu$
Internal conversion (IC)	$S^* \rightarrow S$
Collision-induced emission	$S^* + M \rightarrow S + M + h\nu$
Collisional deactivation	$S^* + M \rightarrow S + M$
	$T^* + M \rightarrow S + M$
Electronic energy transfer:	
Singlet–singlet	$S^* + S \rightarrow S + S^*$
Triplet–triplet	$T^* + T \rightarrow T + T^*$
Excimer formation	$S^* + S \rightarrow (SS)^*$
Energy pooling	
Singlet–singlet	$S^* + S^* \rightarrow S^{**} + S$
Triplet–triplet	$T^* + T^* \rightarrow S^* + S$

† An asterisk (*) denotes an excited state, ** a more excited state, S a singlet state, T a triplet state, and M a third body.

orders of magnitude slower than most typical reactions, species in excited triplet states can undergo a very large number of collisions with other reactants before they are deactivated.

Brief illustration 93.1 The nature of the excited state

To judge whether the excited singlet or triplet state of the reactant is a suitable product precursor, we compare the emission lifetimes with the time constant for chemical reaction of the reactant, τ (Topic 83). Consider a unimolecular photochemical reaction with rate constant $k_r = 1.7 \times 10^4\,\text{s}^{-1}$ and therefore time constant $\tau = 1/(1.7 \times 10^4\,\text{s}^{-1}) = 59\,\mu\text{s}$ that involves a reactant with an observed fluorescence lifetime of 1.0 ns and an observed phosphorescence lifetime of 1.0 ms. The excited singlet state is too short-lived to be a major source of product in this reaction. On the other hand, the relatively long-lived excited triplet state is a good candidate for a precursor.

Self-test 93.1 Consider a molecule with a fluorescence lifetime of 10.0 ns that undergoes unimolecular photoisomerization. What approximate value of the half-life would be consistent with the excited singlet state being the product precursor?

Answer: The value of $t_{1/2}$ should be less than about 7 ns

93.2 The primary quantum yield

The rates of deactivation of the excited state by radiative, non-radiative, and chemical processes determine the yield of product in a photochemical reaction. The **primary quantum yield**, ϕ, is defined as the number of photophysical or photochemical events that lead to primary products, divided by the number of photons absorbed by the molecule in the same interval:

$$\phi = \frac{\text{number of events}}{\text{number of photons absorbed}} \quad \textit{Definition} \quad \text{Primary quantum yield} \qquad (93.1a)$$

When both the numerator and the denominator of this expression are divided by the time interval over which the events occur, we see that the primary quantum yield is also the rate of radiation-induced primary events divided by the rate of photon absorption, I_{abs}:

$$\phi = \frac{\text{rate of process}}{\text{rate of photon absorption}} = \frac{v}{I_{\text{abs}}} \quad \text{Primary quantum yield in terms of rates of processes} \qquad (93.1b)$$

Example 93.1 Calculating a primary quantum yield

In an experiment to determine the quantum yield of a photochemical reaction, the absorbing substance was exposed to 490 nm light from a 100 W source for 2700 s, with 60 per cent of the incident light being absorbed. As a result of irradiation, 0.344 mol of the absorbing substance decomposed. Determine the primary quantum yield.

Method We need to calculate the terms used in eqn 93.1a. To calculate the number of absorbed photons, N_{abs}, which is the denominator of the expression on the right-hand side of eqn 93.1a, we note that:

- The energy absorbed by the substance is $E_{\text{abs}} = fPt$, where P is the incident power, t is the time of exposure, and the factor f (in this case $f = 0.60$) is the proportion of incident light that is absorbed.
- E_{abs} is also related to the number, N_{abs}, of absorbed photons through $E_{\text{abs}} = N_{\text{abs}}hc/\lambda$, where hc/λ is the energy of a single photon of wavelength λ (eqn 3.3 of *Foundations*, Topic 3).
- By combining both expressions for the absorbed energy, the value of N_{abs} follows readily.

The number of photochemical events, and hence the numerator of the expression on the right-hand side of eqn 93.1a, is simply the number of decomposed molecules $N_{\text{decomposed}}$. The primary quantum yield follows from $\phi = N_{\text{decomposed}}/N_{\text{abs}}$.

Answer From the expressions for the absorbed energy, it follows that

$$E_{\text{abs}} = 0.60\,Pt = N_{\text{abs}}\left(\frac{hc}{\lambda}\right)$$

and that

$$N_{\text{abs}} = \frac{0.60\,Pt\lambda}{hc}$$

Now we use eqn 93.1a to write

$$\phi = \frac{N_{\text{decomposed}}}{N_{\text{abs}}} = \frac{N_{\text{decomposed}}hc}{0.60\,Pt\lambda}$$

With $N_{\text{decomposed}} = (0.344\text{ mol}) \times (6.022 \times 10^{23}\text{ mol}^{-1})$, $P = 100\text{ W} = 100\text{ J s}^{-1}$, $t = 2700$ s, and $\lambda = 490\text{ nm} = 4.90 \times 10^{-7}$ m, it follows that

$$\phi = \frac{(0.344\,\text{mol}) \times (6.022 \times 10^{23}\,\text{mol}^{-1}) \times (6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{8}\,\text{m s}^{-1})}{0.60 \times (100\,\text{J s}^{-1}) \times (2700\,\text{s}) \times (4.90 \times 10^{-7}\,\text{m})}$$
$$= 0.52$$

Self-test 93.2 In an experiment to measure the quantum yield of a photochemical reaction, the absorbing substance was exposed to 320 nm radiation from an 87.5 W source for 38 min. The intensity of the transmitted light was 0.35 that of the incident light. As a result of irradiation, 0.324 mol of the absorbing substance decomposed. Determine the primary quantum yield.

Answer: $\phi = 0.93$

A molecule in an excited state must either decay to the ground state or form a photochemical product. Therefore, the total number of molecules deactivated by radiative processes, non-radiative processes, and photochemical reactions must be equal to the number of excited species produced by absorption of light. We conclude that the sum of primary quantum yields ϕ_i for *all* photophysical and photochemical events i must be equal to 1, regardless of the number of reactions involving the excited state:

$$\sum_i \phi_i = \sum_i \frac{v_i}{I_{\text{abs}}} = 1 \qquad (93.2)$$

It follows that, for an excited singlet state that decays to the ground state only via the photophysical processes described in Section 93.1 (and without reacting), we write

$$\phi_{\text{F}} + \phi_{\text{IC}} + \phi_{\text{ISC}} = 1$$

where ϕ_{F}, ϕ_{IC}, and ϕ_{ISC} are the quantum yields of fluorescence, internal conversion, and intersystem crossing, respectively. If intersystem crossing leads to formation of a triplet state, then the quantum yield of photon emission by fluorescence and phosphorescence is $\phi_{\text{emission}}=\phi_{\text{F}}+\phi_{\text{P}}$, which is less than 1. If the excited singlet state also participates in a primary photochemical reaction with quantum yield ϕ_{r}, we write

$$\phi_{\text{F}}+\phi_{\text{IC}}+\phi_{\text{ISC}}+\phi_{\text{r}}=1$$

We can now strengthen the link between reaction rates and primary quantum yield already established by eqns 93.1 and 93.2. By taking the constant I_{abs} out of the summation in eqn 93.2 and rearranging, we obtain $I_{\text{abs}}=\Sigma_i v_i$. Substituting this result into eqn 93.2 gives the general result

$$\phi_i=\frac{v_i}{\sum_i v_i} \qquad (93.3)$$

Therefore, the primary quantum yield may be determined directly from the experimental rates of *all* photophysical and photochemical processes that deactivate the excited state.

93.3 Mechanism of decay of excited singlet states

Consider the formation and decay of an excited singlet state in the absence of a chemical reaction:

Absorption:	$S+h\nu_{\text{i}}\rightarrow S^*$	$v_{\text{abs}}=I_{\text{abs}}$
Fluorescence:	$S^*\rightarrow S+h\nu_{\text{f}}$	$v_{\text{F}}=k_{\text{F}}[S^*]$
Internal conversion:	$S^*\rightarrow S$	$v_{\text{IC}}=k_{\text{IC}}[S^*]$
Intersystem crossing:	$S^*\rightarrow T^*$	$v_{\text{ISC}}=k_{\text{ISC}}[S^*]$

in which S is an absorbing singlet-state species, S* an excited singlet state, T* an excited triplet state, and $h\nu_{\text{i}}$ and $h\nu_{\text{f}}$ the energies of the incident and fluorescent photons, respectively. From the methods presented in Topic 86 and the rates of the steps that form and destroy the excited singlet state S*, we write the rate of formation and decay of S* as

$$\text{Rate of formation of } S^*=I_{\text{abs}}$$

$$\begin{aligned}\text{Rate of disappearance of } S^*&=k_{\text{F}}[S^*]+k_{\text{ISC}}[S^*]+k_{\text{IC}}[S^*]\\&=(k_{\text{F}}+k_{\text{ISC}}+k_{\text{IC}})[S^*]\end{aligned}$$

It follows that the excited state decays by a first-order process, so, when the light is turned off, the concentration of S* varies with time t as

$$[S^*](t)=[S^*]_0\,\mathrm{e}^{-t/\tau_0} \qquad (93.4)$$

where the **observed lifetime**, τ_0, of the first excited singlet state is defined as

$$\tau_0=\frac{1}{k_{\text{F}}+k_{\text{ISC}}+k_{\text{IC}}} \qquad \textit{Definition} \qquad (93.5)$$

Observed lifetime of the excited singlet state

We show in the following *Justification* that the quantum yield of fluorescence is

$$\phi_{\text{F},0}=\frac{k_{\text{F}}}{k_{\text{F}}+k_{\text{ISC}}+k_{\text{IC}}} \qquad (93.6)$$

Quantum yield of fluorescence

Justification 93.1 The quantum yield of fluorescence

Most fluorescence measurements are conducted by illuminating a relatively dilute sample with a continuous and intense beam of light. It follows that [S*] is small and constant, so we may invoke the steady-state approximation (Topic 86) and write

$$\begin{aligned}\frac{\mathrm{d}[S^*]}{\mathrm{d}t}&=I_{\text{abs}}-k_{\text{F}}[S^*]-k_{\text{ISC}}[S^*]-k_{\text{IC}}[S^*]\\&=I_{\text{abs}}-(k_{\text{F}}+k_{\text{ISC}}+k_{\text{IC}})[S^*]\approx 0\end{aligned}$$

Consequently,

$$I_{\text{abs}}=(k_{\text{F}}+k_{\text{ISC}}+k_{\text{IC}})[S^*]$$

By using this expression and eqn 93.1b, we write the quantum yield of fluorescence as

$$\phi_{\text{F},0}=\frac{v_{\text{F}}}{I_{\text{abs}}}=\frac{k_{\text{F}}[S^*]}{(k_{\text{F}}+k_{\text{ISC}}+k_{\text{IC}})[S^*]}$$

which, by cancelling the [S*], simplifies to eqn 93.6.

The observed fluorescence lifetime can be measured by using a pulsed-laser technique (Topic 40). First, the sample is excited with a short light pulse from a laser using a wavelength at which S absorbs strongly. Then, the exponential decay of the fluorescence intensity after the pulse is monitored. From eqns 93.5 and 93.6, it follows that

$$\begin{aligned}\tau_0&=\frac{1}{k_{\text{F}}+k_{\text{ISC}}+k_{\text{IC}}}=\frac{k_{\text{F}}}{k_{\text{F}}+k_{\text{ISC}}+k_{\text{IC}}}\times\frac{1}{k_{\text{F}}}\\&=\frac{\phi_{\text{F},0}}{k_{\text{F}}}\end{aligned} \qquad (93.7)$$

Brief illustration 93.2 The fluorescence rate constant

The fluorescence quantum yield and observed fluorescence lifetime of tryptophan in water are $\phi_{F,0}=0.20$ and $\tau_0=2.6\,\text{ns}$, respectively. It follows from eqn 93.7 that the fluorescence rate constant k_F is

$$k_F=\frac{\phi_{F,0}}{\tau_0}=\frac{0.20}{2.6\times10^{-9}\,\text{s}}=7.7\times10^7\,\text{s}^{-1}$$

Self-test 93.3 A substance has a fluorescence quantum yield of $\phi_{F,0}=0.35$. In an experiment to measure the fluorescence lifetime of this substance, it was observed that the fluorescence emission decayed with a half-life of 5.6 ns. Determine the fluorescence rate constant of this substance.

Answer: $k_F=4.3\times10^7\,\text{s}^{-1}$

93.4 Quenching

The shortening of the lifetime of the excited state by the presence of another species is called **quenching**. Quenching may be either a desired process, such as in energy or electron transfer, or an undesired side reaction that can decrease the quantum yield of a desired photochemical process. Quenching effects may be studied by monitoring the emission from the excited state that is involved in the photochemical reaction.

The addition of a quencher, Q, opens an additional channel for deactivation of S*:

$$\text{Quenching: } S^*+Q\rightarrow S+Q \qquad v_Q=k_Q[Q][S^*]$$

The **Stern–Volmer equation**, which is derived in the following *Justification*, relates the fluorescence quantum yields, $\phi_{F,0}$ and ϕ_F, measured in the absence and presence, respectively, of a quencher Q at a molar concentration [Q]:

$$\frac{\phi_{F,0}}{\phi_F}=1+\tau_0 k_Q[Q] \qquad \text{Stern–Volmer equation} \qquad (93.8)$$

This equation tells us that a plot of $\phi_{F,0}/\phi_F$ against [Q] should be a straight line with slope $\tau_0 k_Q$. Such a plot is called a **Stern–Volmer plot** (Fig. 93.1). The method may also be applied to the quenching of phosphorescence.

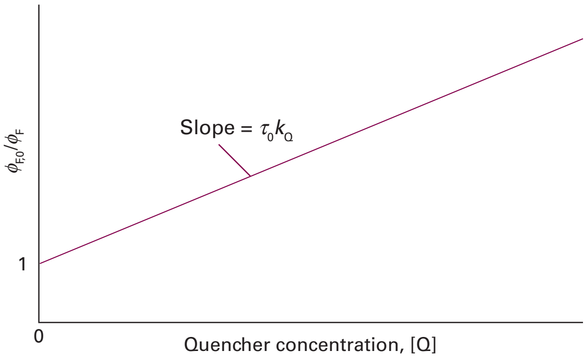


Figure 93.1 The format of a Stern–Volmer plot and the interpretation of the slope in terms of the rate constant for quenching and the observed fluorescence lifetime in the absence of quenching.

Justification 93.2 The Stern–Volmer equation

With the addition of quenching, the steady-state approximation for [S*] now gives

$$\frac{d[S^*]}{dt}=I_{abs}-(k_F+k_{ISC}+k_{IC}+k_Q[Q])[S^*]\approx0$$

and the fluorescence quantum yield in the presence of the quencher is

$$\phi_F=\frac{k_F}{k_F+k_{ISC}+k_{IC}+k_Q[Q]}$$

It follows that

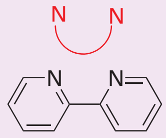
$$\begin{aligned}\frac{\phi_{F,0}}{\phi_F}&=\frac{k_F}{k_F+k_{ISC}+k_{IC}}\times\frac{k_F+k_{ISC}+k_{IC}+k_Q[Q]}{k_F}\\&=\frac{k_F+k_{ISC}+k_{IC}+k_Q[Q]}{k_F+k_{ISC}+k_{IC}}\\&=1+\frac{k_Q}{k_F+k_{ISC}+k_{IC}}[Q]\end{aligned}$$

By using eqn 93.7, this expression simplifies to eqn 93.8.

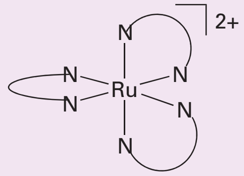
Because the fluorescence intensity and lifetime are both proportional to the fluorescence quantum yield (specifically, from eqn 93.7, $\tau=\phi_F/k_F$), plots of $I_{F,0}/I_F$ and τ_0/τ (where the subscript 0 indicates a measurement in the absence of quencher) against [Q] should also be linear with the same slope and intercept as those shown for eqn 93.8.

Example 93.2 Determining the quenching rate constant

The molecule 2,2′-bipyridine (**1**, bpy) forms a complex with the Ru^{2+} ion. Ruthenium(II) tris-(2,2′-bipyridyl), $Ru(bpy)_3^{2+}$ (**2**), has a strong metal-to-ligand charge transfer (MLCT) transition (Topic 45) at 450 nm.



1 2,2′-Bipyridine (bpy)



2 $[Ru(bpy)_3]^{2+}$

The quenching of the $^*\mathrm{Ru(bpy)}_3^{2+}$ excited state by $\mathrm{Fe(OH_2)}_6^{3+}$ in acidic solution was monitored by measuring emission lifetimes at 600 nm. Determine the quenching rate constant for this reaction from the following data:

$[\mathrm{Fe(OH_2)}_6^{3+}]/(10^{-4}\,\mathrm{mol\,dm^{-3}})$	0	1.6	4.7	7	9.4
$\tau/(10^{-7}\,\mathrm{s})$	6	4.05	3.37	2.96	2.17

Method Rewrite the Stern–Volmer equation (eqn 93.8) for use with lifetime data; then fit the data to a straight line.

Answer Upon substitution of τ_0/τ for $\phi_{\mathrm{F},0}/\phi_\mathrm{F}$ in eqn 93.8 and after rearrangement, we obtain

$$\frac{1}{\tau}=\frac{1}{\tau_0}+k_\mathrm{Q}[\mathrm{Q}]$$

Figure 93.2 shows a plot of $1/\tau$ against $[\mathrm{Fe}^{3+}]$ and the results of a fit to this equation. The slope of the line is 2.8×10^9, so $k_\mathrm{Q}=2.8\times10^9\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. This example shows that measurements of emission lifetimes are preferred because they yield the value of k_Q directly. To determine the value of k_Q from intensity or quantum yield measurements, we need to make an independent measurement of τ_0.

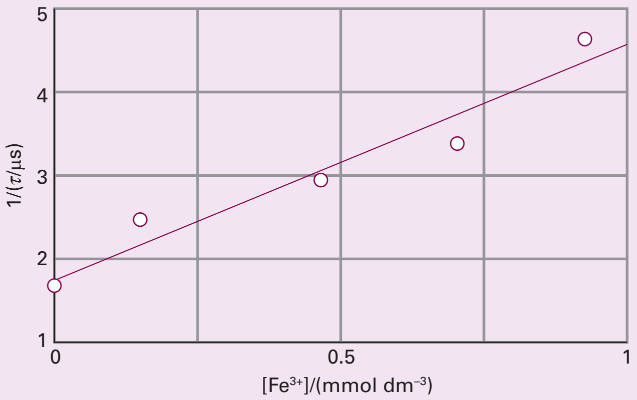


Figure 93.2 The Stern–Volmer plot of the data for Example 93.2.

Self-test 93.4 The quenching of tryptophan fluorescence by dissolved $\mathrm{O_2}$ gas was monitored by measuring emission lifetimes at 348 nm in aqueous solutions. Determine the quenching rate constant for this process from the following data:

$[\mathrm{O_2}]/(10^{-2}\,\mathrm{mol\,dm^{-3}})$	0	2.3	5.5	8	10.8
$\tau/(10^{-9}\,\mathrm{s})$	2.6	1.5	0.92	0.71	0.57

Answer: $1.3\times10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$

Three common mechanisms for bimolecular quenching of an excited singlet (or triplet) state are:

Collisional deactivation:	$\mathrm{S^*+Q\rightarrow S+Q}$
Resonance energy transfer:	$\mathrm{S^*+Q\rightarrow S+Q^*}$
Electron transfer:	$\mathrm{S^*+Q\rightarrow S^{+/-}+Q^{-/+}}$

The quenching rate constant itself does not give much insight into the mechanism of quenching. For the system of Example 93.2, it is known that the quenching of the excited state of $\mathrm{Ru(bpy)}_3^{2+}$ is a result of electron transfer to Fe^{3+}, but the quenching data do not allow us to prove the mechanism.

There are, however, some criteria that govern the relative efficiencies of collisional quenching, resonance energy transfer, and electron transfer. Collisional quenching is particularly efficient when Q is a species, such as iodide ion, which receives energy from S* and then decays to the ground state primarily by releasing energy as heat. As we show in detail in Topic 94, according to the **Marcus theory** of electron transfer, which was proposed by R.A. Marcus in 1965, the rates of electron transfer (from ground or excited states) depend on:

- The distance between the donor and acceptor, with electron transfer becoming more efficient as the distance between donor and acceptor decreases.
- The reaction Gibbs energy, $\Delta_\mathrm{r}G$, with electron transfer becoming more efficient as the reaction becomes more exergonic (up to a point, as we see in Topic 94). For example, it follows from the thermodynamic principles that lead to the electrochemical series (Topic 77) that efficient photo-oxidation of S requires that the reduction potential of S* be lower than the reduction potential of Q.
- The reorganization energy, the energy cost incurred by molecular rearrangements of donor, acceptor, and solvent medium during electron transfer. The electron transfer rate is predicted to increase as this reorganization energy is matched closely by the reaction Gibbs energy.

Electron transfer can also be studied by time-resolved spectroscopy (Topic 40). The oxidized and reduced products often have electronic absorption spectra distinct from those of their neutral parent compounds. Therefore, the rapid appearance of such known features in the absorption spectrum after excitation by a laser pulse may be taken as indication of quenching by electron transfer. In the following section we explore resonance energy transfer in detail.

93.5 Resonance energy transfer

We visualize the process $\mathrm{S^*+Q\rightarrow S+Q^*}$ as follows. The oscillating electric field of the incoming electromagnetic radiation induces an oscillating electric dipole moment in S. Energy is absorbed by S if the frequency of the incident radiation, ν, is such that $\nu = \Delta E_S/h$, where ΔE_S is the energy separation between the ground and excited electronic states of S and h is Planck's constant. This is the 'resonance condition' for absorption of radiation (essentially the Bohr frequency condition, eqn 4.4 of Topic 4). The oscillating dipole on S now can affect electrons bound to a nearby Q molecule by inducing an oscillating dipole moment in them. If the frequency of oscillation of the electric dipole moment in S is such that $\nu = \Delta E_Q/h$, then Q will absorb energy from S.

The efficiency, η_T, of resonance energy transfer is defined as

$$\eta_T = 1 - \frac{\phi_F}{\phi_{F,0}} \qquad \textit{Definition} \qquad \text{Efficiency of resonance energy transfer} \tag{93.9}$$

According to the **Förster theory** of resonance energy transfer, energy transfer is efficient when:

- The energy donor and acceptor are separated by a short distance (of the order of nanometres).
- Photons emitted by the excited state of the donor can be absorbed directly by the acceptor.

In the following *Justification* we see that, for donor–acceptor systems held rigidly either by covalent bonds or by a protein 'scaffold', η_T increases with decreasing distance, R, according to

$$\eta_T = \frac{R_0^6}{R_0^6 + R^6} \qquad \text{Efficiency of energy transfer in terms of the donor–acceptor distance} \tag{93.10}$$

where R_0 is a parameter (with dimensions of distance) that is characteristic of each donor–acceptor pair. It can be regarded as the distance at which energy transfer is 50 per cent efficient for a given donor–acceptor pair. (You can verify this assertion by using $R = R_0$ in eqn 93.10.) Equation 93.10 has been verified experimentally and values of R_0 are available for a number of donor–acceptor pairs (Table 93.3).

Table 93.3 Values of R_0 for some donor–acceptor pairs*

Donor‡	Acceptor	R_0/nm
Naphthalene	Dansyl	2.2
Dansyl	ODR	4.3
Pyrene	Coumarin	3.9
1.5-I IEDANS	FITC	4.9
Tryptophan	1.5-I IEDANS	2.2
Tryptophan	Haem (heme)	2.9

*Additional values may be found in J.R. Lacowicz, *Principles of fluorescence spectroscopy*, Kluwer Academic/Plenum (1999).
‡Abbreviations:
Dansyl: 5-dimethylamino-1-naphthalenesulfonic acid
FITC: fluorescein 5-isothiocyanate
1.5-I IEDANS: 5-((((2-iodoacetyl)amino)ethyl)amino)naphthalene-1-sulfonic acid
ODR: octadecyl-rhodamine

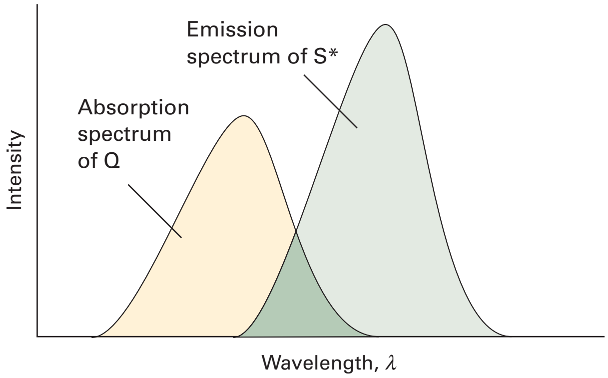


Figure 93.3 According to the Förster theory, the rate of energy transfer from a molecule S* in an excited state to a quencher molecule Q is optimized at radiation frequencies in which the emission spectrum of S* overlaps with the absorption spectrum of Q, as shown in the (green) shaded region.

The emission and absorption spectra of molecules span a range of wavelengths, so the second requirement of the Förster theory is met when the emission spectrum of the donor molecule overlaps significantly with the absorption spectrum of the acceptor. In the overlap region, photons emitted by the donor have the appropriate energy to be absorbed by the acceptor (Fig. 93.3).

Justification 93.3 The Förster theory of resonance energy transfer

Resonance energy transfer arises from the interaction between two oscillating dipoles with moments μ_S and μ_Q. From Topic 35, the energy of the dipole–dipole interaction, $V_{\text{dipole–dipole}}$, is

$$V_{\text{dipole–dipole}} \propto \frac{\mu_S \mu_Q}{R^3}$$

where R is the distance between the dipoles. As explained in Topic 16, the rate of a transition from a state i to a state f at a radiation frequency ν is proportional to the square modulus of the matrix element of the perturbation between the two states:

$$w_{f \leftarrow i} \propto \left| H_{fi}^{(1)} \right|^2$$

For energy transfer, the wavefunctions of the initial and final states may be denoted as $\psi_{S^*}\psi_Q$ and $\psi_S\psi_{Q^*}$, respectively, and $H^{(1)}$ may be written from $V_{\text{dipole–dipole}}$. It follows that the rate of energy transfer, w_T, at a fixed distance R is given by

$$\begin{aligned} w_T &\propto \frac{1}{R^6}\left(\int \psi_S \psi_{Q^*} \mu_S \mu_Q \psi_{S^*} \psi_Q \, d\tau\right)^2 \\ &= \frac{1}{R^6}\left(\int \psi_S \mu_S \psi_{S^*} \, d\tau\right)^2 \left(\int \psi_{Q^*} \mu_Q \psi_Q \, d\tau\right)^2 \end{aligned}$$

We have used the fact that the terms related to S are functions of coordinates that are independent of those for the functions related to Q. As usual, we need to interpret theoretical expressions. In this case, we see that:

- The theory predicts correctly that the rate of energy transfer is proportional to R^{-6}.
- The integrals in the last expression are squares of transition dipole moments at the radiation frequency ν, the first corresponding to emission of S* to S and the second to absorption of Q to Q*. Therefore, the theory predicts that the energy transfer rate is optimized when both emission of radiation by S* and absorption of radiation by Q are efficient at the frequency ν.

In practice, it is more convenient to measure the efficiency of energy transfer and not the rate itself. In much the same way that we defined the quantum yield as a ratio of rates, we can also define the efficiency of energy transfer, η_T, as the ratio

$$\eta_T = \frac{w_T}{w_T + w_0} \qquad w_0 = (k_F + k_{IC} + k_{ISC})[S^*] \tag{93.11}$$

where w_0 is the rate of deactivation of S* in the absence of the quencher. The efficiency may be expressed in terms of the experimental fluorescence quantum yields $\phi_{F,0}$ and ϕ_F of the donor in the absence and presence of the acceptor, respectively. To proceed, we use eqn 93.3 to write

$$\phi_{F,0} = \frac{\nu_F}{w_0} \qquad \phi_F = \frac{\nu_F}{w_0 + w_T}$$

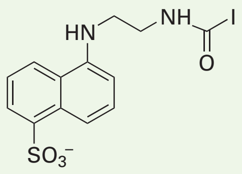
where ν_F is the rate of fluorescence. Substituting these results into eqn 93.11 gives, after a little algebra, eqn 93.9.

Alternatively, w_0 can be expressed in terms of the parameter R_0, the characteristic distance at which $w_T = w_0$ for a specified pair of S and Q (Table 93.3). By using $w_T \propto R^{-6}$ and $w_0 \propto R_0^{-6}$, the expression for η_T can be rearranged into eqn 93.10.

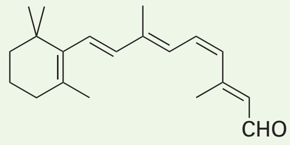
Equation 93.10 forms the basis of **fluorescence resonance energy transfer** (FRET), in which the dependence of the energy transfer efficiency, η_T, on the distance, R, between energy donor and acceptor is used to measure distances in biological systems. In a typical FRET experiment, a site on a biopolymer or membrane is labelled covalently with an energy donor and another site is labelled covalently with an energy acceptor. In certain cases, the donor or acceptor may be natural constituents of the system, such as amino acid groups, cofactors, or enzyme substrates. The distance between the labels is then calculated from the known value of R_0 and eqn 93.10. Several tests have shown that the FRET technique is useful for measuring distances ranging from 1 to 9 nm.

Brief illustration 93.3 The FRET technique

As an illustration of the FRET technique, consider a study of the protein rhodopsin. When an amino acid on the surface of rhodopsin was labelled covalently with the energy donor 1.5-I AEDANS (**3**), the fluorescence quantum yield of the label decreased from 0.75 to 0.68 due to quenching by the visual pigment 11-*cis*-retinal (**4**). From eqn 93.9, we calculate $\eta_T = 1 - (0.68/0.75) = 0.093$ and from eqn 93.10 and the known value of $R_0 = 5.4$ nm for the 1.5-I AEDANS/11-*cis*-retinal pair we calculate $R = 7.9$ nm. Therefore, we take 7.9 nm to be the distance between the surface of the protein and 11-*cis*-retinal.



3 1.5-I AEDANS



4 11-*cis*-Retinal

Self-test 93.5 An amino acid on the surface of a protein was labelled covalently with 1.5-I AEDANS and another was labelled covalently with FITC (fluorescein 5-isothiocyanate). The fluorescence quantum yield of 1.5-I AEDANS decreased by 10 per cent due to quenching by FITC. What is the distance between the amino acids?

Answer: 7.1 nm

If donor and acceptor molecules diffuse in solution or in the gas phase, Förster theory predicts that the efficiency of quenching by energy transfer increases as the average distance travelled between collisions of donor and acceptor decreases. That is, the quenching efficiency increases with concentration of quencher, as predicted by the Stern–Volmer equation.

Checklist of concepts

☐ 1. The **primary quantum yield** of a photochemical reaction is the number of reactant molecules producing specified primary products for each photon absorbed.

☐ 2. The **observed lifetime** of an excited state is related to the quantum yield and rate constant of emission.

☐ 3. A **Stern–Volmer plot** is used to analyse the kinetics of fluorescence quenching in solution.

☐ 4. Collisional deactivation, electron transfer, and resonance energy transfer are common fluorescence quenching processes.

☐ 5. The efficiency of resonance energy transfer decreases with increasing separation between donor and acceptor molecules.

Checklist of equations

Property	Equation	Comment	Equation number
Primary quantum yield	$\phi = v/I_{\text{abs}}$		93.1b
Excited-state lifetime	$\tau_0 = 1/(k_{\text{F}} + k_{\text{ISC}} + k_{\text{IC}})$	No quencher present	93.5
Quantum yield of fluorescence	$\phi_{\text{F},0} = k_{\text{F}}/(k_{\text{F}} + k_{\text{ISC}} + k_{\text{IC}})$	Without quencher present	93.6
Observed excited-state lifetime	$\tau_0 = \phi_{\text{F},0}/k_{\text{F}}$		93.7
Stern–Volmer equation	$\phi_{\text{F},0}/\phi_{\text{F}} = 1 + \tau_0 k_{\text{Q}}[\text{Q}]$		93.8
Efficiency of resonance energy transfer	$\eta_{\text{T}} = 1 - \phi_{\text{F}}/\phi_{\text{F},0}$	Definition	93.9
	$\eta_{\text{T}} = R_0^6/(R_0^6 + R^6)$	Förster theory	93.10

TOPIC 94

Electron transfer in homogeneous systems

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➤ Why do you need to know this material?

Electron transfer reactions between protein-bound cofactors or between proteins play an important role in a variety of biological processes, including photosynthesis. Electron transfer is also important in homogeneous, non-biological catalysis.

➤ What is the key idea?

The rate constant of electron transfer in a donor–acceptor complex depends on the distance between electron donor and acceptor, the standard reaction Gibbs energy, and the energy needed to reach a particular arrangement of atoms.

➤ What do you need to know already?

This Topic makes use of transition-state theory (Topic 89). It also uses the concept of tunnelling (Topic 10), the steady-state approximation (Topic 86), the Franck–Condon principle (Topic 45), and the discussion of the rate of change of a system affected by a perturbation (Topic 16).

Here we apply the concepts of transition-state theory and quantum theory to the study of a deceptively simple process, electron transfer between molecules in homogeneous systems. We describe a theoretical approach to the calculation of rate constants and discuss the theory in the light of experimental results on a variety of systems, including protein complexes. We shall see that relatively simple expressions may be used to predict the rates of electron transfer with reasonable accuracy.

94.1 The rate law

Consider electron transfer from a donor species D to an acceptor species A in solution. The overall reaction is

$$\mathrm{D}+\mathrm{A}\rightarrow\mathrm{D}^{+}+\mathrm{A}^{-}\qquad v=k_{\mathrm{r}}[\mathrm{D}][\mathrm{A}]\tag{94.1}$$

In the first step of the mechanism, D and A must diffuse through the solution and collide to form a complex, DA, in which the donor and acceptor are separated by d, the distance between the outer surface of each species.

$$\mathrm{D}+\mathrm{A}\underset{k_{\mathrm{a}}'}{\overset{k_{\mathrm{a}}}{\rightleftharpoons}}\mathrm{DA}\tag{94.2a}$$

Next, electron transfer occurs within the DA complex to yield $\mathrm{D}^{+}\mathrm{A}^{-}$:

$$\mathrm{DA}\underset{k_{\mathrm{et}}'}{\overset{k_{\mathrm{et}}}{\rightleftharpoons}}\mathrm{D}^{+}\mathrm{A}^{-}\tag{94.2b}$$

The complex $\mathrm{D}^{+}\mathrm{A}^{-}$ can also break apart and the ions diffuse through the solution:

$$\mathrm{D}^{+}\mathrm{A}^{-}\xrightarrow{k_{\mathrm{d}}}\mathrm{D}^{+}+\mathrm{A}^{-}\tag{94.2c}$$

We show in the following *Justification* that on the basis of this model

$$\frac{1}{k_{\mathrm{r}}}=\frac{1}{k_{\mathrm{a}}}+\frac{k_{\mathrm{a}}'}{k_{\mathrm{a}}k_{\mathrm{et}}}\left(1+\frac{k_{\mathrm{et}}'}{k_{\mathrm{d}}}\right)\qquad\text{Electron transfer rate constant}\tag{94.3}$$

Justification 94.1 The rate constant for electron transfer in solution

We begin by identifying the rate of the overall reaction (eqn 94.1) with the rate of formation of separated ions:

$$v = k_r[\mathrm{D}][\mathrm{A}] = k_d[\mathrm{D^+A^-}]$$

There are two reaction intermediates, DA and $\mathrm{D^+A^-}$, and we apply the steady-state approximation (Topic 86) to both. From

$$\frac{\mathrm{d}[\mathrm{D^+A^-}]}{\mathrm{d}t} = k_{et}[\mathrm{DA}] - k'_{et}[\mathrm{D^+A^-}] - k_d[\mathrm{D^+A^-}] = 0$$

it follows that

$$[\mathrm{DA}] = \frac{k'_{et} + k_d}{k_{et}}[\mathrm{D^+A^-}]$$

and from

$$\begin{aligned}\frac{\mathrm{d}[\mathrm{DA}]}{\mathrm{d}t} &= k_a[\mathrm{D}][\mathrm{A}] - k'_a[\mathrm{DA}] - k_{et}[\mathrm{DA}] + k'_{et}[\mathrm{D^+A^-}]\\ &= k_a[\mathrm{D}][\mathrm{A}] - \left\{\frac{(k'_a + k_{et})(k'_{et} + k_d)}{k_{et}} - k'_{et}\right\}[\mathrm{D^+A^-}] = 0\end{aligned}$$

it follows that

$$[\mathrm{D^+A^-}] = \frac{k_a k_{et}}{k'_a k'_{et} + k'_a k_d + k_d k_{et}}[\mathrm{D}][\mathrm{A}]$$

When this expression is multiplied by k_d, the resulting equation has the form of the rate of electron transfer, $v = k_r[\mathrm{D}][\mathrm{A}]$, with k_r given by

$$k_r = \frac{k_a k_{et} k_d}{k'_a k'_{et} + k'_a k_d + k_d k_{et}}$$

To obtain eqn 94.3, divide the numerator and denominator on the right-hand side of this expression by $k_d k_{et}$ and solve for the reciprocal of k_r.

To gain insight into eqn 94.3 and the factors that determine the rate of electron transfer reactions in solution, we assume that the main decay route for $\mathrm{D^+A^-}$ is dissociation of the complex into separated ions, or $k_d \gg k'_{et}$ and $1 + k'_{et}/k_d \approx 1$. It follows that

$$\frac{1}{k_r} \approx \frac{1}{k_a} + \frac{k'_a}{k_a k_{et}} = \frac{1}{k_a}\left(1 + \frac{k'_a}{k_{et}}\right)$$

- When $k_{et} \gg k'_a$, $k_r \approx k_a$ and the rate of product formation is controlled by diffusion of D and A in solution, which fosters formation of the DA complex.
- When $k_{et} \ll k'_a$, $k_r \approx (k_a/k'_a)k_{et} = Kk_{et}$, where K is the equilibrium constant for the diffusive encounter. The process is controlled by k_{et} and therefore by the activation energy of electron transfer in the DA complex.

Physical interpretation

94.2 The rate constant

This analysis can be taken further by introducing the implication from transition-state theory (Topic 89) that

$$k_{et} \propto \mathrm{e}^{-\Delta G/RT} \qquad (94.4)$$

where $\Delta^{\ddagger}G$ is the Gibbs energy of activation. Our remaining task, therefore, is to find expressions for the proportionality constant and $\Delta^{\ddagger}G$.

Our discussion concentrates on the following two key aspects of the theory of electron transfer processes, which was developed independently by R.A. Marcus, N.S. Hush, V.G. Levich, and R.R. Dogonadze:

- Electrons are transferred by tunnelling through a potential energy barrier, the height of which is partly determined by the ionization energies of the DA and $\mathrm{D^+A^-}$ complexes. Electron tunnelling influences the magnitude of the proportionality constant.
- The complex DA and the solvent molecules surrounding it undergo structural rearrangements prior to electron transfer. The energy associated with these rearrangements and the standard reaction Gibbs energy determine $\Delta^{\ddagger}G$.

According to the Franck–Condon principle (Topic 45), electronic transitions are so fast that they can be regarded as taking place in a stationary nuclear framework. This principle also applies to an electron transfer process in which an electron migrates from one energy surface, representing the dependence of the energy of DA on its geometry, to another representing the energy of $\mathrm{D^+A^-}$. We can represent the potential energy (and the Gibbs energy) surfaces of the two complexes (the reactant complex, DA, and the product complex, $\mathrm{D^+A^-}$) by the parabolas characteristic of harmonic oscillators, with the displacement coordinate corresponding to the changing geometries (Fig. 94.1). This coordinate represents a collective mode of the donor, acceptor, and solvent. The Franck–Condon principle then implies that electron transfer can occur only after thermal fluctuations bring the geometry of DA to $q^{\ddagger}$ in Fig 94.1, the value of the nuclear coordinate at which the two parabolas intersect and the reactant and product have the same geometrical configuration.

(a) The role of electron tunnelling

The proportionality constant in eqn 94.4 is a measure of the probability that the system will convert from reactants (DA) to products ($\mathrm{D^+A^-}$) at $q^{\ddagger}$ by electron transfer within the thermally excited DA complex. To understand the process, we must turn our attention to the effect that the rearrangement of nuclear

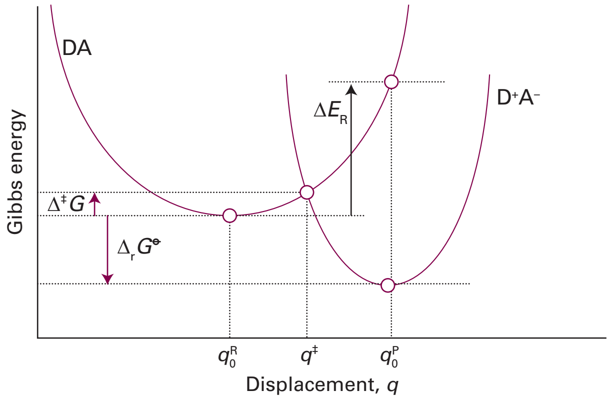


Figure 94.1 The Gibbs energy surfaces of the complexes DA and D^+A^- involved in an electron transfer process are represented by parabolas characteristic of harmonic oscillators, with the displacement coordinate q corresponding to the changing geometries of the system.

coordinates has on electronic energy levels of DA and D^+A^- for a given distance d between D and A (Fig. 94.2). Initially, the electron to be transferred occupies the HOMO of DA, and the overall energy of DA is lower than that of D^+A^- (Fig 94.2a). As the nuclei rearrange to a configuration represented by $q^{\ddagger}$ in Fig. 94.2b, the highest occupied electronic level of DA and the lowest unoccupied electronic level of D^+A^- become degenerate and electron transfer becomes energetically feasible. Over reasonably short distances d, the main mechanism of electron transfer is tunnelling through the potential energy barrier depicted in Fig 94.2b. After an electron moves from the HOMO of DA to the LUMO of D^+A^-, the system relaxes to the configuration represented by q_0^P in Fig 94.2c. As shown in the illustration, now the energy of D^+A^- is lower than that of DA, reflecting the thermodynamic tendency for A to remain reduced and for D to remain oxidized.

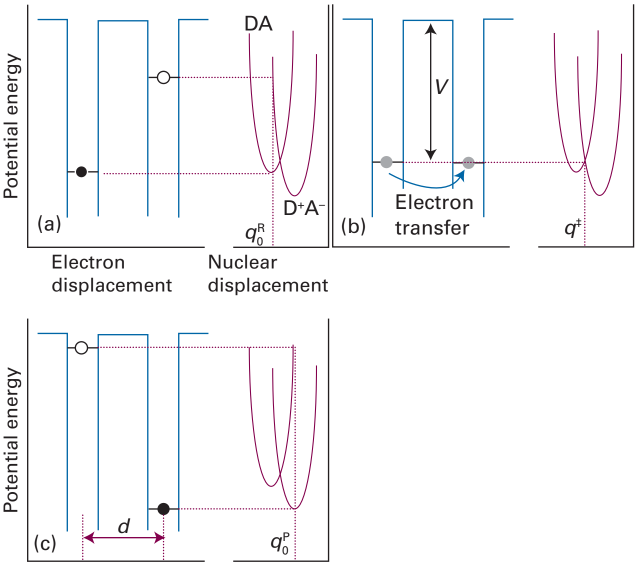


Figure 94.2 (a) At the nuclear configuration denoted by q_0^R, the electron to be transferred in DA is in an occupied electronic energy level and the lowest unoccupied energy level of D^+A^- is of too high an energy to be a good electron acceptor. (b) As the nuclei rearrange to a configuration represented by $q^{\ddagger}$, DA and D^+A^- become degenerate and electron transfer occurs by tunnelling through the barrier. (c) The system relaxes to the equilibrium nuclear configuration of D^+A^- denoted by q_0^P, in which the lowest unoccupied electronic level of DA is higher in energy than the highest occupied electronic level of D^+A^-. Adapted from R.A. Marcus and N. Sutin (*Biochim. Biophys. Acta* **811**, 265 (1985)).

The tunnelling event responsible for electron transfer is similar to that described in Topic 10, except that in this case the electron tunnels from an electronic level of DA, with wavefunction ψ_{DA}, to an electronic level of D^+A^-, with wavefunction $\psi_{D^+A^-}$. The rate of an electronic transition from a level described by the wavefunction ψ_{DA} to a level described by $\psi_{D^+A^-}$ is, from time-dependent perturbation theory (Topic 16), proportional to the square of the integral

$$H_{et}=\int \psi_{DA}\hat{h}\psi_{D^+A^-}\,d\tau$$

where $\hat{h}$ is a hamiltonian that describes the coupling of the electronic wavefunctions. The probability of tunnelling through a potential barrier typically has an exponential dependence on distance, so we suspect that the distance dependence of H_{et}^2 is

$$H_{et}(d)^2=H_{et}^{\circ 2}e^{-\beta d} \qquad (94.5)$$

where d is the edge-to-edge distance between D and A, β is a parameter that measures the sensitivity of the electronic coupling matrix element to distance, and H_{et}° is the value of the electronic coupling matrix element when D and A are in contact ($d=0$).

Brief illustration 94.1 The distance dependence of the coupling

The value of β depends on the medium through which the electron must travel from donor to acceptor. In a vacuum, $28\,\text{nm}^{-1}<\beta<35\,\text{nm}^{-1}$, whereas $\beta\approx 9\,\text{nm}^{-1}$ when the intervening medium is a molecular link between donor and acceptor. Electron transfer between protein-bound cofactors can occur at distances of up to about 2.0 nm, a long distance on a molecular scale, corresponding to about 20 carbon atoms, with the protein providing an intervening medium between donor and acceptor.

Self-test 94.1 By how much does H_{DA} change when d is increased from 1.0 nm to 2.0 nm, with $\beta\approx 9\,\text{nm}^{-1}$?

Answer: Decrease by a factor of 8100

(b) The reorganization energy

The pre-exponential factor in k_{et} is proportional to the tunnelling probability, which in turn is proportional to $H_{\mathrm{et}}(d)^2$, as expressed by eqn 94.5. Therefore, we can expect the full expression for k_{et} to have the form

$$k_{\mathrm{et}}=CH_{\mathrm{et}}(d)^2\,\mathrm{e}^{-\Delta^{\ddagger}G/RT} \qquad (94.6)$$

with C a constant of proportionality and $H_{\mathrm{et}}(d)^2$ given by eqn 94.5. We show in the following *Justification* that the Gibbs energy of activation $\Delta^{\ddagger}G$ is

$$\Delta^{\ddagger}G=\frac{(\Delta_{\mathrm{r}}G^{\ominus}+\Delta E_{\mathrm{R}})^2}{4\Delta E_{\mathrm{R}}} \qquad \text{Gibbs energy of activation} \qquad (94.7)$$

where $\Delta_{\mathrm{r}}G^{\ominus}$ is the standard reaction Gibbs energy for the electron transfer process $\mathrm{DA}\rightarrow\mathrm{D^+A^-}$, and ΔE_{R} is the **reorganization energy**, the energy change associated with molecular rearrangements that must take place so that DA can take on the equilibrium geometry of $\mathrm{D^+A^-}$. These molecular rearrangements include the relative reorientation of the D and A molecules in DA and the relative reorientation of the solvent molecules surrounding DA. Equation 94.7 shows that $\Delta^{\ddagger}G=0$, with the implication that the reaction is not slowed down by an activation barrier when $\Delta_{\mathrm{r}}G^{\ominus}=-\Delta E_{\mathrm{R}}$, corresponding to the cancellation of the reorganization energy term by the standard reaction Gibbs energy.

Justification 94.2 The Gibbs energy of activation of electron transfer

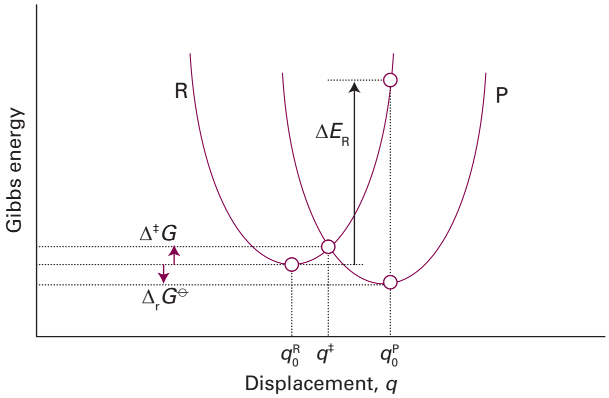


Figure 94.3 The model system used in *Justification* 94.2.

The simplest way to derive an expression for the Gibbs energy of activation of electron transfer processes is to construct a model in which the surfaces for DA (the 'reactant complex', denoted R) and for $\mathrm{D^+A^-}$ (the 'product complex', denoted P) are described by classical harmonic oscillators (and therefore parabolic potential energies, $\frac{1}{2}k_{\mathrm{f}}x^2$, Topic 12) with identical reduced masses μ and angular frequencies $\omega=(k_{\mathrm{f}}/\mu)^{1/2}$, but displaced minima, as shown in Fig. 94.3. Because each parabola has the form $\frac{1}{2}k_{\mathrm{f}}x^2=\frac{1}{2}\mu\omega^2x^2$, with $x=q-q_0^{\mathrm{R}}$ for R and $x=q-q_0^{\mathrm{P}}$ for P, the molar Gibbs energies $G_{\mathrm{m,R}}(q)$ and $G_{\mathrm{m,P}}(q)$ of the reactant and product complexes, respectively, may be written as

$$\begin{aligned}G_{\mathrm{m,R}}(q)&=G_{\mathrm{m,R}}(q_0^{\mathrm{R}})+\tfrac{1}{2}N_{\mathrm{A}}\mu\omega^2(q-q_0^{\mathrm{R}})^2\\ G_{\mathrm{m,P}}(q)&=G_{\mathrm{m,P}}(q_0^{\mathrm{P}})+\tfrac{1}{2}N_{\mathrm{A}}\mu\omega^2(q-q_0^{\mathrm{P}})^2\end{aligned}$$

where q_0^{R} and q_0^{P} are the values of q at which the minima of the reactant and product parabolas occur, respectively. The standard reaction Gibbs energy for the electron transfer process $\mathrm{R}\rightarrow\mathrm{P}$ is $\Delta_{\mathrm{r}}G^{\ominus}=G_{\mathrm{m,P}}(q_0^{\mathrm{P}})-G_{\mathrm{m,R}}(q_0^{\mathrm{R}})$, the difference in standard molar Gibbs energy between the minima of the parabolas. In Fig. 94.3, $\Delta_{\mathrm{r}}G^{\ominus}<0$. Note that

$$\begin{aligned}G_{\mathrm{m,R}}(q^{\ddagger})&=G_{\mathrm{m,R}}(q_0^{\mathrm{R}})+\tfrac{1}{2}N_{\mathrm{A}}\mu\omega^2(q^{\ddagger}-q_0^{\mathrm{R}})^2\\ G_{\mathrm{m,P}}(q^{\ddagger})&=G_{\mathrm{m,P}}(q_0^{\mathrm{P}})+\tfrac{1}{2}N_{\mathrm{A}}\mu\omega^2(q^{\ddagger}-q_0^{\mathrm{P}})^2\end{aligned}$$

and, as $G_{\mathrm{m,R}}(q^{\ddagger})=G_{\mathrm{m,P}}(q^{\ddagger})$, it follows that

$$\Delta_{\mathrm{r}}G^{\ominus}=G_{\mathrm{m,P}}(q_0^{\mathrm{P}})-G_{\mathrm{m,R}}(q_0^{\mathrm{R}})=\tfrac{1}{2}N_{\mathrm{A}}\mu\omega^2\{(q^{\ddagger}-q_0^{\mathrm{R}})^2-(q^{\ddagger}-q_0^{\mathrm{P}})^2\}$$

The value of q corresponding to the transition state of the complex, $q^{\ddagger}$, may be written in terms of the parameter α, the fractional change in q:

$$q^{\ddagger}=q_0^{\mathrm{R}}+\alpha(q_0^{\mathrm{P}}-q_0^{\mathrm{R}})$$

If $\alpha=0$, $q^{\ddagger}=q_0^{\mathrm{R}}$ and, if $\alpha=1$, then $q^{\ddagger}=q_0^{\mathrm{P}}$. It then follows that

$$\begin{aligned}\Delta_{\mathrm{r}}G^{\ominus}&=\tfrac{1}{2}N_{\mathrm{A}}\mu\omega^2\{[q_0^{\mathrm{R}}+\alpha(q_0^{\mathrm{P}}-q_0^{\mathrm{R}})-q_0^{\mathrm{R}}]^2-[q_0^{\mathrm{R}}+\alpha(q_0^{\mathrm{P}}-q_0^{\mathrm{R}})-q_0^{\mathrm{P}}]^2\}\\ &=\tfrac{1}{2}N_{\mathrm{A}}\mu\omega^2\{[\alpha(q_0^{\mathrm{P}}-q_0^{\mathrm{R}})]^2-[(\alpha-1)(q_0^{\mathrm{P}}-q_0^{\mathrm{R}})]^2\}\\ &=\tfrac{1}{2}N_{\mathrm{A}}\mu\omega^2(2\alpha-1)(q_0^{\mathrm{P}}-q_0^{\mathrm{R}})^2\end{aligned}$$

Next, we see from Fig. 94.3 that $\Delta^{\ddagger}G=G_{\mathrm{m,R}}(q^{\ddagger})-G_{\mathrm{m,R}}(q_0^{\mathrm{R}})$. It then follows that

$$\begin{aligned}\Delta^{\ddagger}G&=\tfrac{1}{2}N_{\mathrm{A}}\mu\omega^2(q^{\ddagger}-q_0^{\mathrm{R}})^2=\tfrac{1}{2}N_{\mathrm{A}}\mu\omega^2\{\alpha(q_0^{\mathrm{P}}-q_0^{\mathrm{R}})\}^2\\ &=\tfrac{1}{2}N_{\mathrm{A}}\mu\omega^2\alpha^2(q_0^{\mathrm{P}}-q_0^{\mathrm{R}})^2\end{aligned}$$

We now define the reorganization energy, ΔE_{R}, as

$$\Delta E_{\mathrm{R}}=\tfrac{1}{2}N_{\mathrm{A}}\mu\omega^2(q_0^{\mathrm{P}}-q_0^{\mathrm{R}})^2$$

which can be interpreted as $G_{\mathrm{m,R}}(q_0^{\mathrm{P}})-G_{\mathrm{m,R}}(q_0^{\mathrm{R}})$ and, consequently, as the (Gibbs) energy required to deform the equilibrium configuration of R to the equilibrium configuration of P (as shown in Fig. 94.3). Then

$$\Delta^{\ddagger}G=\alpha^2\Delta E_{\mathrm{R}} \quad \text{and} \quad \Delta_{\mathrm{r}}G^{\ominus}=(2\alpha-1)\Delta E_{\mathrm{R}}$$

From the second of these two relations it follows that

$$\alpha = \frac{1}{2}\left(\frac{\Delta_r G^{\ominus}}{\Delta E_R} + 1\right)$$

By inserting this equation into $\Delta^{\ddagger}G = \alpha^2 \Delta E_R$, we obtain eqn 94.7. We can obtain an identical relation if we allow the harmonic oscillators to have different angular frequencies and hence different curvatures.

The only missing piece of the expression for k_{et} is the value of the constant of proportionality C in eqn 94.6. Detailed calculation, which we do not repeat here, gives

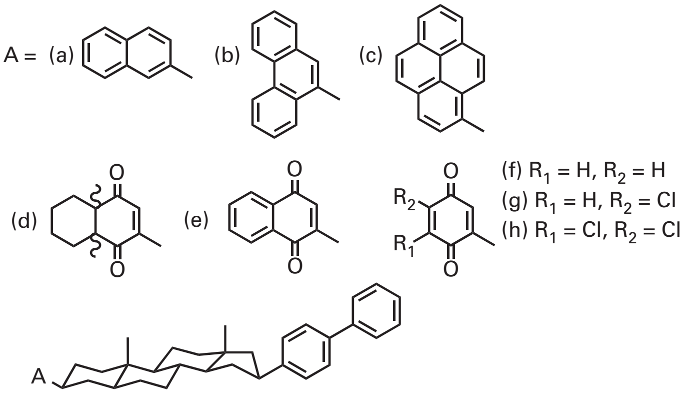
$$C = \frac{1}{h}\left(\frac{\pi^3}{RT\Delta E_R}\right)^{1/2} \qquad (94.8)$$

Equation 94.6 has some limitations, as might be expected because perturbation-theory arguments have been used. For instance, it describes processes with weak electronic coupling between donor and acceptor. Weak coupling is observed when the electroactive species are sufficiently far apart that the wavefunctions $\psi_{D^+A^-}$ and ψ_{DA} do not overlap extensively and the tunnelling is an exponential function of distance. An example of a weakly coupled system is the cytochrome *c*/cytochrome b_5 complex, in which the electroactive haem-bound iron ions shuttle between oxidation states Fe(II) and Fe(III) during electron transfer and are about 1.7 nm apart. Strong coupling is observed when the wavefunctions $\psi_{D^+A^-}$ and ψ_{DA} overlap very extensively and, as well as other complications, the tunnelling probability is no longer a simple exponential function of distance. Examples of strongly coupled systems are mixed-valence, binuclear d-metal complexes with the general structure $L_mM^{n+}{-}B{-}M^{p+}L_m$, in which the electroactive metal ions are separated by a bridging ligand B. In these systems, $d < 1.0$ nm. The weak-coupling limit applies to a large number of electron transfer reactions, including those between proteins during metabolism.

The most meaningful experimental tests of the dependence of k_{et} on d are those in which the same donor and acceptor are positioned at a variety of distances, perhaps by covalent attachment to molecular linkers (see **1** for an example). Under these conditions, the term $e^{-\Delta^{\ddagger}G/RT}$ becomes a constant and, after taking the natural logarithm of eqn 94.6 and using eqn 94.5, we obtain

$$\ln k_{et} = -\beta d + \text{constant} \qquad (94.9)$$

which implies that a plot of ln k_{et} against d should be a straight line of slope $-\beta$.



1 An electron donor–acceptor system

The dependence of k_{et} on the standard reaction Gibbs energy has been investigated in systems where the edge-to-edge distance and the reorganization energy are constant for a series of reactions. Then, by using eqn 94.7 for $\Delta^{\ddagger}G$, eqn 94.6 becomes

$$\ln k_{et} = -\frac{RT}{4\Delta E_R}\left(\frac{\Delta_r G^{\ominus}}{RT}\right)^2 - \tfrac{1}{2}\left(\frac{\Delta_r G^{\ominus}}{RT}\right) + \text{constant} \qquad (94.10)$$

and a plot of ln k_{et} (or log k_{et} = ln k_{et}/ln 10) against $\Delta_r G^{\ominus}$ (or $-\Delta_r G^{\ominus}$) is predicted to be shaped like a downward parabola (Fig. 94.4). Equation 94.10 implies that the rate constant increases as $\Delta_r G^{\ominus}$ decreases but only up to $-\Delta_r G^{\ominus} = \Delta E_R$. Beyond that, the reaction enters the **inverted region**, in which the rate constant decreases as the reaction becomes more exergonic ($\Delta_r G^{\ominus}$ becomes more negative). The inverted region has been observed in a series of special compounds in which the electron donor and acceptor are linked covalently to a molecular spacer of known and fixed size (Fig. 94.5).

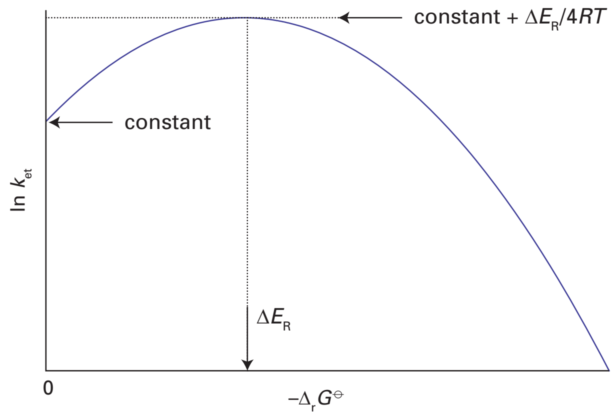


Figure 94.4 The parabolic dependence of ln k_{et} on $-\Delta_r G^{\ominus}$ predicted by eqn 94.10.

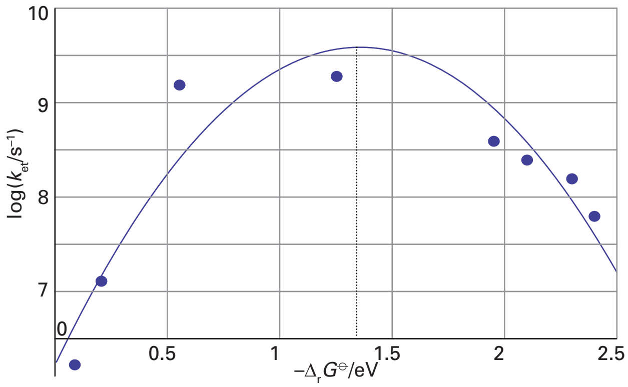


Figure 94.5 Variation of log k_{et} with $-\Delta_r G^{\ominus}$ for a series of compounds with the structures given in **1** and as described in *Brief illustration* 94.2. Based on J.R. Miller, et al. (*J. Am. Chem. Soc.* **106**, 3047 (1984)).

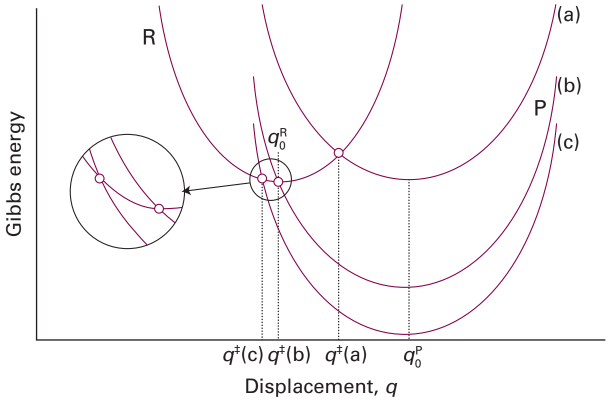


Figure 94.6 (a) $\Delta^{\ddagger}G>0$ and the transition state is at $q^{\ddagger}(\text{a})>q_R^0$. As the process becomes more exergonic, the activation Gibbs energy decreases and the rate constant increases. (b) When $\Delta^{\ddagger}G=0$ and $q^{\ddagger}(\text{b})=q_R^0$, the rate constant for the process reaches a maximum as there is no activation barrier to overcome. (c) As the process becomes even more exergonic, $\Delta^{\ddagger}G$ becomes positive again but now the transition state is at $q^{\ddagger}(\text{c})<q_R^0$. The rate constant for the process decreases steadily as the activation barrier for the process increases with decreasing $\Delta_r G^{\ominus}$.

The behaviour predicted by eqn 94.10 and observed experimentally can be explained by considering the dependence of $\Delta^{\ddagger}G$ on $\Delta_r G^{\ominus}$. We let the minimum energy of P vary while keeping q_0^P constant, which corresponds to changing the magnitude of $\Delta_r G^{\ominus}$. Figure 94.6 shows the effect of increasing the exergonicity of the process. At (a), $\Delta^{\ddagger}G>0$. As the process becomes more exergonic, represented by the parabolas moving towards (b), the activation Gibbs energy decreases and the rate constant increases. At (b), $\Delta^{\ddagger}G=0$, there is no activation barrier to overcome, and the rate constant reaches a maximum. According to eqn 94.10, this condition occurs when $-\Delta_r G^{\ominus}=\Delta E_R$. Finally, as the parabola continues to track towards (c), $\Delta^{\ddagger}G$ becomes positive again and the rate constant decreases.

Brief illustration 94.2 The determination of the reorganization energy

Kinetic measurements were conducted in 2-methyltetrahydrofuran at 296 K for a series of compounds with the structures given in **1**. The distance between the donor (the reduced biphenyl group) and the acceptor is constant for all compounds in the series because the molecular linker remains the same. Each acceptor has a characteristic standard reduction potential, so it follows that the standard Gibbs energy for the electron transfer process is different for each compound in the series. The line in Fig. 94.5 is a fit to a version of eqn 94.10 and the maximum of the parabola occurs at $-\Delta_r G^{\ominus}=\Delta E_R=1.4\,\text{eV}=1.4\times10^2\,\text{kJ mol}^{-1}$.

Self-test 94.2 Some (invented) data on a series of complexes are as follows:

$-\Delta_r G^{\ominus}/\text{eV}$	0.20	0.60	1.0	1.3	1.6	2.0	2.4
log k_{et}	8.2	9.7	10.2	10.1	9.4	7.7	5.1

Determine the reorganization energy.

Answer: 1.05 eV

Checklist of concepts

☐ 1. Electron transfer can occur only after thermal fluctuations bring the nuclear coordinate to the point at which the donor and acceptor have the same configuration.

☐ 2. The tunneling probability is supposed to depend exponentially on the separation of the donor and acceptor.

☐ 3. The **reorganization energy** is the energy change associated with molecular rearrangements that must take place so that DA can acquire the equilibrium geometry of D^+A^-.

☐ 4. In the **inverted region**, the rate constant k_{et} decreases as the reaction becomes more exergonic ($\Delta_r G^{\ominus}$ becomes more negative).

Checklist of equations

Property	Equation	Comment	Equation number
Electron transfer rate constant	$1/k_r = 1/k_a + (k'_a/k_a k_{et})(1+k'_{et}/k_d)$	Steady-state approximation	94.3
Tunnelling probability	$H_{et}(d)^2 = H_{et}^{\circ 2}e^{-\beta d}$	Assumed	94.5
Rate constant	$k_{et} = CH_{et}(d)^2 e^{-\Delta^{\ddagger}G/RT}$	Transition-state theory	94.6
Gibbs energy of activation	$\Delta^{\ddagger}G = (\Delta_r G^{\ominus} + \Delta E_R)^2/4\Delta E_R$	Assumes parabolic potential energy	94.7
Dependence on separation	$\ln k_{et} = -\beta d + \text{constant}$		94.9
Dependence on $\Delta_r G^{\ominus}$	$\ln k_{et} = a\Delta_r G^{\ominus 2} + b\Delta_r G^{\ominus} + c$	$a = -1/4\Delta E_R RT$, $b = -1/2RT$, $c = \text{constant}$	94.10

Focus 19 on Processes in fluid systems

Topic 91 Unimolecular reactions

Discussion questions

91.1 Discuss the limitations of the generality of the expression $k_r = k_a k_b[\mathrm{A}]/(k_b + k_a'[\mathrm{A}])$ for the effective rate constant of a unimolecular reaction according to the Lindemann–Hinshelwood mechanism.

91.2 Discuss the significance of the steric *P*-factor in the RRK model.

Exercises

91.1(a) The effective rate constant for a gaseous reaction which has a Lindemann–Hinshelwood mechanism is $2.50 \times 10^{-4}\ \mathrm{s^{-1}}$ at 1.30 kPa and $2.10 \times 10^{-5}\ \mathrm{s^{-1}}$ at 12 Pa. Calculate the rate constant for the activation step in the mechanism.

91.1(b) The effective rate constant for a gaseous reaction which has a Lindemann–Hinshelwood mechanism is $1.7 \times 10^{-3}\ \mathrm{s^{-1}}$ at 1.09 kPa and $2.2 \times 10^{-4}\ \mathrm{s^{-1}}$ at 25 Pa. Calculate the rate constant for the activation step in the mechanism.

91.2(a) Consider the unimolecular decomposition of a nonlinear molecule containing five atoms. If $P = 3.0 \times 10^{-5}$, what is the value of E^*/E?

91.2(b) Consider the unimolecular decomposition of a linear molecule containing four atoms. If $P = 0.025$, what is the value of E^*/E?

91.3(a) Suppose that an energy of 250 kJ mol^{-1} is available in a collision but 200 kJ mol^{-1} is needed to break a particular bond in a molecule with $s = 10$. Use the RRK model to calculate the steric *P*-factor.

91.3(b) Suppose that an energy of 500 kJ mol^{-1} is available in a collision but 300 kJ mol^{-1} is needed to break a particular bond in a molecule with $s = 12$. Use the RRK model to calculate the steric *P*-factor.

Problems

91.1 In Problem 83.14 the isomerization of cyclopropane over a limited pressure range was examined. If the Lindemann–Hinshelwood mechanism of first-order reactions is to be tested we also need data at low pressures. These have been obtained (H.O. Pritchard, et al. *Proc. R. Soc.* **A217**, 563 (1953)):

p/Torr	84.1	11.0	2.89	0.569	0.120	0.067
$10^4\ k_r/\mathrm{s^{-1}}$	2.98	2.23	1.54	0.857	0.392	0.303

Test the Lindemann–Hinshelwood theory with these data.

91.2 According to the RRK model (see *Justification* 91.1),

$$P = \frac{n!(n-n^*+s-1)!}{(n-n^*)!(n+s-1)!}$$

Use Stirling's approximation in the form $\ln x! \approx x \ln x - x$ (eqn 51.2b of Topic 51) to deduce that $P \approx ((n-n^*)/n)^{s-1}$ when $s - 1 \ll n - n^*$. *Hint*: Replace terms of the form $n - n^* + s - 1$ by $n - n^*$ inside logarithms but retain $n - n^* + s - 1$ when it is a factor of a logarithm.

Topic 92 Enzymes

Discussion questions

92.1 Discuss the features, advantages, and limitations of the Michaelis–Menten mechanism of enzyme action.

92.2 A plot of the rate of an enzyme-catalysed reaction against temperature has a maximum, in an apparent deviation from the behaviour predicted by the Arrhenius equation (Topic 85). Suggest a molecular interpretation for this effect.

92.3 Distinguish between competitive, non-competitive, and uncompetitive inhibition of enzymes. Discuss how these modes of inhibition may be detected experimentally.

92.4 Some enzymes are inhibited by high concentrations of their own products. Sketch a plot of reaction rate against concentration of substrate for an enzyme that is prone to product inhibition.

Exercises

92.1(a) Consider the base-catalysed reaction

$$(1)\ \mathrm{AH}+\mathrm{B} \underset{k_a'}{\overset{k_a}{\rightleftarrows}} \mathrm{BH}^+ + \mathrm{A}^- \qquad \text{(both fast)}$$

$$(2)\ \mathrm{A}^- + \mathrm{AH} \xrightarrow{k_b} \text{product} \qquad \text{(slow)}$$

Deduce the rate law.

92.1(b) Consider the acid-catalysed reaction

$$(1)\ \mathrm{HA}+\mathrm{H}^+ \underset{k_a'}{\overset{k_a}{\rightleftarrows}} \mathrm{HAH}^+ \qquad \text{(both fast)}$$

$$(2)\ \mathrm{HAH}^+ + \mathrm{B} \xrightarrow{k_b} \mathrm{BH}^+ + \mathrm{AH} \qquad \text{(slow)}$$

Deduce the rate law.

92.2(a) The enzyme-catalysed conversion of a substrate at 25 °C has a Michaelis constant of 0.046 mol dm^{-3}. The rate of the reaction is 1.04×10^{-3} mol dm^{-3} s^{-1} when the substrate concentration is 0.105 mol dm^{-3}. What is the maximum velocity of this reaction?

92.2(b) The enzyme-catalysed conversion of a substrate at 25 °C has a Michaelis constant of 0.032 mol dm^{-3}. The rate of the reaction is 2.05×10^{-4} mol dm^{-3} s^{-1} when the substrate concentration is 0.875 mol dm^{-3}. What is the maximum velocity of this reaction?

92.3(a) Consider an enzyme-catalysed reaction that follows Michaelis–Menten kinetics with $K_M = 3.0\times10^{-3}$ mol dm^{-3}. What concentration of a competitive inhibitor characterized by $K_I = 2.0\times10^{-5}$ mol dm^{-3} will reduce the rate of formation of product by 50 per cent when the substrate concentration is held at 1.0×10^{-4} mol dm^{-3}?

92.3(b) Consider an enzyme-catalysed reaction that follows Michaelis–Menten kinetics with $K_M = 7.5\times10^{-4}$ mol dm^{-3}. What concentration of a competitive inhibitor characterized by $K_I = 5.6\times10^{-4}$ mol dm^{-3} will reduce the rate of formation of product by 75 per cent when the substrate concentration is held at 1.0×10^{-4} mol dm^{-3}?

Problems

92.1 Michaelis and Menten derived their rate law by assuming a rapid pre-equilibrium of E, S, and ES. Derive the rate law in this manner, and identify the conditions under which it becomes the same as that based on the steady-state approximation (eqn 92.1).

92.2 Use mathematical software, a spreadsheet, or the *Living graphs* (labelled $^{\mathrm{LG}}$) on the website of this book to solve the following problems:

(a)$^{\mathrm{LG}}$ Use the Michaelis–Menten equation (eqn 92.1) to generate two families of curves showing the dependence of v on [S]: one in which K_M varies but $v_{\max}$ is constant, and another in which $v_{\max}$ varies but K_M is constant.
(b)$^{\mathrm{LG}}$ Use eqn 92.7 to explore the effect of competitive, uncompetitive, and non-competitive inhibition on the shapes of the plots of v against [S] for constant K_M and $v_{\max}$.

92.3 For many enzymes, the mechanism of action involves the formation of two intermediates:

$$\begin{aligned}
&\mathrm{E}+\mathrm{S}\rightarrow\mathrm{ES} && v=k_a[\mathrm{E}][\mathrm{S}]\\
&\mathrm{ES}\rightarrow\mathrm{E}+\mathrm{S} && v=k_a'[\mathrm{ES}]\\
&\mathrm{ES}\rightarrow\mathrm{ES}' && v=k_b[\mathrm{ES}]\\
&\mathrm{ES}'\rightarrow\mathrm{E}+\mathrm{P} && v=k_c[\mathrm{ES}']
\end{aligned}$$

Show that the rate of formation of product has the same form as that shown in eqn 92.1, but with $v_{\max}$ and K_M given by

$$v_{\max}=\frac{k_b k_c[\mathrm{E}]_0}{k_b+k_c} \quad \text{and} \quad K_M=\frac{k_c(k_a'+k_b)}{k_a(k_b+k_c)}$$

92.4 The enzyme-catalysed conversion of a substrate at 25 °C has a Michaelis constant of 9.0×10^{5} mol dm^{-3} and a maximum velocity of 2.24×10^{-5} mol dm^{-3} s^{-1} when the enzyme concentration is 1.60×10^{-9} mol dm^{-3}. (a) Calculate k_{cat} and η. (b) Is the enzyme 'catalytically perfect'?

92.5 The following results were obtained for the action of an ATPase on ATP at 20 °C, when the concentration of the ATPase was 20 nmol dm^{-3}:

[ATP]/(μmol dm^{-3})	0.60	0.80	1.4	2.0	3.0
v/(μmol dm^{-3} s^{-1})	0.81	0.97	1.30	1.47	1.69

Determine the Michaelis constant, the maximum velocity of the reaction, the turnover frequency, and the catalytic efficiency of the enzyme.

92.6 There are different ways to represent and analyse data for enzyme catalysed reactions. For example, in the *Eadie–Hofstee plot*, $v/[\mathrm{S}]_0$ is plotted against v. Alternatively, in the *Hanes plot*, $v/[\mathrm{S}]_0$ is plotted against $[\mathrm{S}]_0$. (a) Using the simple Michaelis–Menten mechanism, derive relations between $v/[\mathrm{S}]_0$ and v and between $v/[\mathrm{S}]_0$ and $[\mathrm{S}]_0$. (b) Discuss how the values of K_M and $v_{\max}$ are obtained from analysis of the Eadie–Hofstee and Hanes plots. (c) Determine the Michaelis constant and the maximum velocity of the reaction from Problem 92.5 by using Eadie–Hofstee and Hanes plots to analyse the data.

92.7 In general, the catalytic efficiency of an enzyme depends on the pH of the medium in which it operates. One way to account for this behaviour is to propose that the enzyme and the enzyme–substrate complex are active only in specific protonation states. This proposition can be summarized by the following mechanism:

$$\mathrm{EH}+\mathrm{S} \underset{k_a'}{\overset{k_a}{\rightleftarrows}} \mathrm{ESH}$$

$$\mathrm{ESH} \xrightarrow{k_b} \mathrm{E}+\mathrm{P}$$

$$\mathrm{EH} \rightleftharpoons \mathrm{E}^- + \mathrm{H}^+ \qquad K_{\mathrm{E,a}}=\frac{[\mathrm{E}^-][\mathrm{H}^+]}{[\mathrm{EH}]}$$

$$\mathrm{EH}_2^+ \rightleftharpoons \mathrm{EH} + \mathrm{H}^+ \qquad K_{\mathrm{E,b}}=\frac{[\mathrm{EH}][\mathrm{H}^+]}{[\mathrm{EH}_2^+]}$$

$$\mathrm{ESH} \rightleftharpoons \mathrm{ES}^- + \mathrm{H}^+ \qquad K_{\mathrm{ES,a}}=\frac{[\mathrm{ES}^-][\mathrm{H}^+]}{[\mathrm{ESH}]}$$

$$\mathrm{ESH}_2 \rightleftharpoons \mathrm{ESH}^- + \mathrm{H}^+ \qquad K_{\mathrm{ES,b}}=\frac{[\mathrm{ESH}^-][\mathrm{H}^+]}{[\mathrm{ESH}_2]}$$

in which only the EH and ESH forms are active. (a) For the mechanism above, show that

$$v=\frac{v_{\max}'}{1+K_M'/[\mathrm{S}]_0}$$

with

$$v_{\max}'=\frac{v_{\max}}{1+\dfrac{[\mathrm{H}^+]}{K_{\mathrm{ES,b}}}+\dfrac{K_{\mathrm{ES,a}}}{[\mathrm{H}^+]}}$$

$$K_M'=K_M\,\frac{1+\dfrac{[\mathrm{H}^+]}{K_{\mathrm{E,b}}}+\dfrac{K_{\mathrm{E,a}}}{[\mathrm{H}^+]}}{1+\dfrac{[\mathrm{H}^+]}{K_{\mathrm{ES,b}}}+\dfrac{K_{\mathrm{ES,a}}}{[\mathrm{H}^+]}}$$

where $v_{\max}$ and K_M correspond to the form EH of the enzyme. (b) For pH values ranging from 0 to 14, plot $v'_{\max}$ against pH for a hypothetical reaction for which $v_{\max} = 1.0 \times 10^{-6}$ mol dm^{-3} s^{-1}, $K_{ES,b} = 1.0 \times 10^{-6}$ mol dm^{-3}, and $K_{ES,a} = 1.0 \times 10^{-8}$. Is there a pH at which $v_{\max}$ reaches a maximum value? If so, determine the pH. (c) Redraw the plot in part (b) by using the same value of $v_{\max}$, but $K_{ES,b} = 1.0 \times 10^{-4}$ mol dm^{-3} and $K_{ES,a} = 1.0 \times 10^{-10}$ mol dm^{-3}. Account for any differences between this plot and the plot from part (b).

92.8 The enzyme carboxypeptidase catalyses the hydrolysis of polypeptides and here we consider its inhibition. The following results were obtained when the rate of the enzymolysis of carbobenzoxy-glycyl-ᴅ-phenylalanine (CBGP) was monitored without inhibitor:

$[\text{CBGP}]_0/(10^{-2}$ mol dm$^{-3})$	1.25	3.84	5.81	7.13
Relative reaction rate	0.398	0.669	0.859	1.000

All rates in this problem were measured with the same concentration of enzyme and are relative to the rate measured when $[\text{CBGP}]_0 = 0.0713$ mol dm^{-3} in the absence of inhibitor. When 2.0×10^{-3} mol dm^{-3} phenylbutyrate ion was added to a solution containing the enzyme and substrate, the following results were obtained:

$[\text{CBGP}]_0/(10^{-2}$ mol dm$^{-3})$	1.25	2.50	4.00	5.50
Relative reaction rate	0.172	0.301	0.344	0.548

In a separate experiment, the effect of 5.0×10^{-2} mol dm^{-3} benzoate ion was monitored and the results were:

$[\text{CBGP}]_0/(10^{-2}$ mol dm$^{-3})$	1.75	2.50	5.00	10.00
Relative reaction rate	0.183	0.201	0.231	0.246

Determine the mode of inhibition of carboxypeptidase by the phenylbutyrate ion and benzoate ion.

92.9 Some enzymes are inhibited by high concentrations of their own substrates. (a) Show that when substrate inhibition is important the reaction rate v is given by

$$v = \frac{v_{\max}}{1 + K_M/[\text{S}]_0 + [\text{S}]_0/K_I}$$

where K_I is the equilibrium constant for dissociation of the inhibited enzyme–substrate complex. (b) What effect does substrate inhibition have on a plot of $1/v$ against $1/[\text{S}]_0$?

Topic 93 Photochemistry

Discussion questions

93.1 Describe an experimental procedure for the determination of the quantum yield.

93.2 Discuss experimental procedures that make it possible to differentiate between quenching by energy transfer, collisions, and electron transfer.

Exercises

93.1(a) In the photochemical reaction $\text{A} \rightarrow 2\,\text{B} + \text{C}$, the quantum yield with 500 nm light is 2.1×10^2 mol einstein^{-1} (1 einstein = 1 mol photons). After exposure of 300 mmol of A to the light, 2.28 mmol of B is formed. How many photons were absorbed by A?

93.1(b) In the photochemical reaction $\text{A} \rightarrow \text{B} + \text{C}$, the quantum yield with 500 nm light is 1.2×10^2 mol einstein^{-1} (1 einstein = 1 mol photons). After exposure of 200 mmol A to the light, 1.77 mmol B is formed. How many photons were absorbed by A?

93.2(a) Consider the quenching of an organic fluorescent species with $\tau_0 = 6.0$ ns by a d-metal ion with $k_Q = 3.0 \times 10^8$ dm^3 mol^{-1} s^{-1}. Predict the concentration of quencher required to decrease the fluorescence intensity of the organic species to 50 per cent of the unquenched value.

93.2(b) Consider the quenching of an organic fluorescent species with $\tau_0 = 3.5$ ns by a d-metal ion with $k_Q = 2.5 \times 10^9$ dm^3 mol^{-1} s^{-1}. Predict the concentration of quencher required to decrease the fluorescence intensity of the organic species to 75 per cent of the unquenched value.

Problems

93.1 In an experiment to measure the quantum yield of a photochemical reaction, the absorbing substance was exposed to 320 nm radiation from a 87.5 W source for 28.0 min. The intensity of the transmitted light was 0.257 that of the incident light. As a result of irradiation, 0.324 mol of the absorbing substance decomposed. Determine the quantum yield.

93.2‡ Ultraviolet radiation photolyses O_3 to O_2 and O. Determine the rate at which ozone is consumed by 305 nm radiation in a layer of the stratosphere of thickness 1 km. The quantum yield is 0.94 at 220 K, the concentration about 8×10^{-9} mol dm^{-3}, the molar absorption coefficient 260 dm^3 mol^{-1} cm^{-1}, and the flux of 305 nm radiation about 1×10^{14} photons cm^{-2} s^{-1}. (Data from W.B. DeMore, et al. *Chemical kinetics and photochemical data for use in stratospheric modeling: Evaluation Number 11,* JPL Publication 94–26 (1994).)

93.3 Dansyl chloride, which absorbs maximally at 330 nm and fluoresces maximally at 510 nm, can be used to label amino acids in fluorescence microscopy and FRET studies. Tabulated below is the variation of the fluorescence intensity of an aqueous solution of dansyl chloride with time after excitation by a short laser pulse (with I_0 the initial fluorescence intensity). The ratio of intensities is equal to the ratio of the rates of photon emission.

t/ns	5.0	10.0	15.0	20.0
I_F/I_0	0.45	0.21	0.11	0.05

(a) Calculate the observed fluorescence lifetime of dansyl chloride in water.
(b) The fluorescence quantum yield of dansyl chloride in water is 0.70. What is the fluorescence rate constant?

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‡ This problem was supplied by Charles Trapp and Carmen Giunta.

93.4 When benzophenone is illuminated with ultraviolet light it is excited into a singlet state. This singlet changes rapidly into a triplet, which phosphoresces. Triethylamine acts as a quencher for the triplet. In an experiment in methanol as solvent, the phosphorescence intensity varied with amine concentration as shown below. A time-resolved laser spectroscopy experiment had also shown that the half-life of the fluorescence in the absence of quencher is 29 µs. What is the value of k_Q?

$[Q]/(\text{mol dm}^{-3})$	0.0010	0.0050	0.0100
I_F/(arbitrary units)	0.41	0.25	0.16

93.5 An electronically excited state of Hg can be quenched by N_2 according to

$$\text{Hg}^*(\text{g}) + \text{N}_2(\text{g}, v=0) \rightarrow \text{Hg}(\text{g}) + \text{N}_2(\text{g}, v=1)$$

in which energy transfer from Hg* excites N_2 vibrationally. Fluorescence lifetime measurements of samples of Hg with and without N_2 present are summarized below ($T = 300$ K):

$p_{N_2} = 0.0\,\text{atm}$

Relative fluorescence intensity	1.000	0.606	0.360	0.22	0.135
t/µs	0.0	5.0	10.0	15.0	20.0

$p_{N_2} = 9.74 \times 10^{-4}\,\text{atm}$

Relative fluorescence intensity	1.000	0.585	0.342	0.200	0.117
t/µs	0.0	3.0	6.0	9.0	12.0

You may assume that all gases are perfect. Determine the rate constant for the energy transfer process.

93.6 An amino acid on the surface of an enzyme was labelled covalently with 1.5-I AEDANS and it is known that the active site contains a tryptophan residue. The fluorescence quantum yield of tryptophan decreased by 15 per cent due to quenching by 1.5-I AEDANS. What is the distance between the active site and the surface of the enzyme?

93.7 The Förster theory of resonance energy transfer and the basis for the FRET technique can be tested by performing fluorescence measurements on a series of compounds in which an energy donor and an energy acceptor are covalently linked by a rigid molecular linker of variable and known length. L. Stryer and R.P. Haugland (*Proc. Natl. Acad. Sci. USA* **58**, 719 (1967)) collected the following data on a family of compounds with the general composition dansyl-(L-prolyl)$_n$-naphthyl, in which the distance R between the naphthyl donor and the dansyl acceptor was varied from 1.2 nm to 4.6 nm by increasing the number of prolyl units in the linker:

R/nm	1.2	1.5	1.8	2.8	3.1	3.4	3.7	4.0	4.3	4.6
η_T	0.99	0.94	0.97	0.82	0.74	0.65	0.40	0.28	0.24	0.16

Are the data described adequately by eqn 93.10? If so, what is the value of R_0 for the naphthyl–dansyl pair?

93.8 The first step in plant photosynthesis is absorption of light by chlorophyll molecules bound to proteins knows as 'light-harvesting complexes', where the fluorescence of a chlorophyll molecule is quenched by nearby chlorophyll molecules. Given that for a pair of chlorophyll *a* molecules $R_0 = 5.6$ nm, by what distance should two chlorophyll *a* molecules be separated to shorten the fluorescence lifetime from 1 ns (a typical value for monomeric chlorophyll *a* in organic solvents) to 10 ps?

Topic 94 Electron transfer in homogeneous systems

Discussion questions

94.1 Discuss how the following factors determine the rate of electron transfer in homogeneous systems: the distance between electron donor and acceptor, the standard Gibbs energy of the process, and the reorganization energy of the redox active species and the surrounding medium.

94.2 What role does tunnelling play in electron transfer?

94.3 Explain why the rate constant decreases as the reaction becomes more exergonic in the inverted region.

Exercises

94.1(a) For a pair of electron donor and acceptor at 298 K, $H_{et}(d) = 0.04\,\text{cm}^{-1}$, $\Delta_r G^{\ominus} = -0.185$ eV, and $k_{et} = 37.5\,\text{s}^{-1}$. Estimate the value of the reorganization energy.

94.1(b) For a pair of electron donor and acceptor at 298 K, $k_{et} = 2.02 \times 10^5\,\text{s}^{-1}$ for $\Delta_r G^{\ominus} = -0.665$ eV. The standard reaction Gibbs energy changes to $\Delta_r G^{\ominus} = -0.975$ eV when a substituent is added to the electron acceptor and the rate constant for electron transfer changes to $k_{et} = 3.33 \times 10^6\,\text{s}^{-1}$. Assuming that the distance between donor and acceptor is the same in both experiments, estimate the values of $H_{et}(d)$ and ΔE_R.

94.2(a) For a pair of electron donor and acceptor, $k_{et} = 2.02 \times 10^5\,\text{s}^{-1}$ when $d = 1.11$ nm, and $k_{et} = 4.51 \times 10^4\,\text{s}^{-1}$ when $d = 1.23$ nm. Assuming that $\Delta_r G^{\ominus}$ and ΔE_R are the same in both experiments, estimate the value of β.

94.2(b) Refer to Exercise 94.2(a). Estimate the value of k_{et} when $d = 1.59$ nm.

Problems

94.1 Consider the reaction $D + A \rightarrow D^+ + A^-$. The rate constant k_r may be determined experimentally or may be predicted by the *Marcus cross-relation*, $k_r = (k_{DD}k_{AA}K)^{1/2} f$, where k_{DD} and k_{AA} are the experimental rate constants for the electron self-exchange processes $^*D + D^+ \rightarrow {}^*D^+ + D$ and $^*A + A^+ \rightarrow {}^*A^+ + A$, respectively, and f is a function of $K = [D^+][A^-]/[D]$ [A], k_{DD}, k_{AA}, and the collision frequencies. Derive the approximate form of the Marcus cross-relation, $f = 1$ $k_r = (k_{DD}k_{AA}K)^{1/2}$, by following these steps. (a) Use eqn 94.7 to write expressions for $\Delta^{\ddagger}G$, $\Delta^{\ddagger}G_{DD}$, and $\Delta^{\ddagger}G_{AA}$, keeping in mind that $\Delta_r G^{\ominus} = 0$ for the electron self-exchange reactions. (b) Assume that the reorganization energy $\Delta E_{R,DA}$ for the reaction $D + A \rightarrow D^+ + A^-$ is the average of the reorganization energies $\Delta E_{\mathrm{R,DD}}$ and $\Delta E_{\mathrm{R,AA}}$ of the electron self-exchange reactions. Then show that in the limit of small magnitude of $\Delta_r G^{\ominus}$, or $|\Delta_r G^{\ominus}| \ll \Delta E_{\mathrm{R,DA}}$, $\Delta^{\ddagger}G = \frac{1}{2}(\Delta^{\ddagger}G_{\mathrm{DD}} + \Delta^{\ddagger}G_{\mathrm{AA}} + \Delta_r G^{\ominus})$, where $\Delta_r G^{\ominus}$ is the standard Gibbs energy for the reaction $\mathrm{D} + \mathrm{A} \rightarrow \mathrm{D}^+ + \mathrm{A}^-$. (c) Use an equation of the form of eqn 94.4 to write expressions for k_{DD} and k_{AA}. (d) Use eqn 94.4 and the result above to write an expression for k_r. (e) Complete the derivation by using the results from part (c), the relation $K = \mathrm{e}^{-\Delta_r G^{\ominus}/RT}$, and assuming that all $\kappa v^{\ddagger}$ terms, which may be interpreted as collision frequencies, are identical.

94.2 Consider the reaction $\mathrm{D} + \mathrm{A} \rightarrow \mathrm{D}^+ + \mathrm{A}^-$. The rate constant k_r may be determined experimentally or may be predicted by the Marcus cross-relation (see Problem 94.1). It is common to make the assumption that $f \approx 1$. Use the approximate form of the Marcus cross-relation to estimate the rate constant for the reaction $\mathrm{Ru(bpy)}_3^{3+} + \mathrm{Fe(H_2O)}_6^{2+} \rightarrow \mathrm{Ru(bpy)}_3^{2+} + \mathrm{Fe(H_2O)}_6^{3+}$, where bpy stands for 4,4′ -bipyridine. The following data are useful (* denotes an excited state):

$\mathrm{Ru(bpy)}_3^{3+} + \mathrm{e}^- \rightarrow \mathrm{Ru(bpy)}_3^{2+}$	$E^{\ominus} = 1.26\,\mathrm{V}$
$\mathrm{Fe(H_2O)}_6^{3+} + \mathrm{e}^- \rightarrow \mathrm{Fe(H_2O)}_6^{2+}$	$E^{\ominus} = 0.77\,\mathrm{V}$
$^*\mathrm{Ru(bpy)}_3^{3+} + \mathrm{Ru(bpy)}_3^{2+} \rightarrow {}^*\mathrm{Ru(bpy)}_3^{2+} + \mathrm{Ru(bpy)}_3^{3+}$	$k_{\mathrm{Ru}} = 4.0 \times 10^8\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$
$^*\mathrm{Fe(H_2O)}_6^{3+} + \mathrm{Fe(H_2O)}_6^{2+} \rightarrow {}^*\mathrm{Fe(H_2O)}_6^{2+} + \mathrm{Fe(H_2O)}_6^{3+}$	$k_{\mathrm{Fe}} = 4.2\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$

94.3 A useful strategy for the study of electron transfer in proteins consists of attaching an electroactive species to the protein's surface and then measuring k_{et} between the attached species and an electroactive protein cofactor. J.W. Winkler and H.B. Gray (*Chem. Rev.* **92**, 369 (1992)) summarize data for cytochrome *c* modified by replacement of the haem iron by a zinc ion, resulting in a zinc–porphyrin (ZnP) group in the interior of the protein, and by attachment of a ruthenium ion complex to a surface histidine amino acid. The edge-to-edge distance between the electroactive species was thus fixed at 1.23 nm. A variety of ruthenium ion complexes with different standard potentials was used. For each ruthenium-modified protein, either the $\mathrm{Ru}^{2+} \rightarrow \mathrm{ZnP}^+$ or the $\mathrm{ZnP}^* \rightarrow \mathrm{Ru}^{3+}$, in which the electron donor is an electronically excited state of the zinc–porphyrin group formed by laser excitation, was monitored. This arrangement leads to different standard reaction Gibbs energies because the redox couples $\mathrm{ZnP}^+/\mathrm{ZnP}$ and $\mathrm{ZnP}^+/\mathrm{ZnP}^*$ have different standard potentials, with the electronically excited porphyrin being a more powerful reductant. Use the following data to estimate the reorganization energy for this system:

$-\Delta_r G^{\ominus}/\mathrm{eV}$	0.665	0.705	0.745	0.975	1.015	1.055
$k_{\mathrm{et}}/(10^6\,\mathrm{s^{-1}})$	0.657	1.52	1.12	8.99	5.76	10.1

94.4 The photosynthetic reaction centre of the purple photosynthetic bacterium *Rhodopseudomonas viridis* contains a number of bound cofactors that participate in electron transfer reactions. The following table shows data compiled by Moser, et al. (*Nature* **355**, 796 (1992)) on the rate constants for electron transfer between different cofactors and their edge-to-edge distances:

Reaction	$\mathrm{BChl^- \rightarrow BPh}$	$\mathrm{BPh^- \rightarrow BChl_2^+}$	$\mathrm{BPh^- \rightarrow Q_A}$	$\mathrm{cyt}\,c_{559} \rightarrow \mathrm{BChl_2^+}$
d/nm	0.48	0.95	0.96	1.23
$k_{\mathrm{et}}/\mathrm{s^{-1}}$	1.58×10^{12}	3.98×10^9	1.00×10^9	1.58×10^8

Reaction	$\mathrm{Q_A^- \rightarrow Q_B}$	$\mathrm{Q_A^- \rightarrow BChl_2^+}$
d/nm	1.35	2.24
$k_{\mathrm{et}}/\mathrm{s^{-1}}$	3.98×10^7	63.1

(BChl, bacteriochlorophyll; $\mathrm{BChl_2}$, bacteriochlorophyll dimer, functionally distinct from BChl; BPh, bacteriophaeophytin; $\mathrm{Q_A}$ and $\mathrm{Q_B}$, quinone molecules bound to two distinct sites; cyt c_{559}, a cytochrome bound to the reaction centre complex). Are these data in agreement with the behaviour predicted by eqn 94.9? If so, determine the value of β.

94.5 The rate constant for electron transfer between a cytochrome *c* and the bacteriochlorophyll dimer of the reaction centre of the purple bacterium *Rhodobacter sphaeroides* (Problem 94.4) decreases with decreasing temperature in the range 300 K to 130 K. Below 130 K, the rate constant becomes independent of temperature. Account for these results.

Integrated activities

F19.1 Autocatalysis is the catalysis of a reaction by the products. For example, for a reaction $\mathrm{A} \rightarrow \mathrm{P}$ it may be found that the rate law is $v = k_r[\mathrm{A}][\mathrm{P}]$ and the reaction rate is proportional to the concentration of P. The reaction gets started because there are usually other reaction routes for the formation of some P initially, which then takes part in the autocatalytic reaction proper. (a) Integrate the rate equation for an autocatalytic reaction of the form $\mathrm{A} \rightarrow \mathrm{P}$, with rate law $v = k_r[\mathrm{A}][\mathrm{P}]$, and show that

$$\frac{[\mathrm{P}]}{[\mathrm{P}]_0} = (b+1)\frac{\mathrm{e}^{at}}{1 + b\mathrm{e}^{at}}$$

where $a = ([\mathrm{A}]_0 + [\mathrm{P}]_0)k_r$ and $b = [\mathrm{P}]_0/[\mathrm{A}]_0$. *Hint*: Starting with the expression $v = -\mathrm{d}[\mathrm{A}]/\mathrm{d}t = k_r[\mathrm{A}][\mathrm{P}]$, write $[\mathrm{A}] = [\mathrm{A}]_0 - x$, $[\mathrm{P}] = [\mathrm{P}]_0 + x$, and then write the expression for the rate of change of either species in terms of x. To integrate the resulting expression, use the method of partial fractions (*The chemist's toolkit* 83.1), with

$$\frac{1}{([\mathrm{A}]_0 - x)([\mathrm{P}]_0 + x)} = \frac{1}{[\mathrm{A}]_0 + [\mathrm{P}]_0}\left(\frac{1}{[\mathrm{A}]_0 - x} + \frac{1}{[\mathrm{P}]_0 + x}\right)$$

(b) Plot $[\mathrm{P}]/[\mathrm{P}]_0$ against at for several values of b. Discuss the effect of autocatalysis on the shape of a plot of $[\mathrm{P}]/[\mathrm{P}]_0$ against t by comparing your results with those for a first-order process, in which $[\mathrm{P}]/[\mathrm{P}]_0 = 1 - \mathrm{e}^{-k_r t}$. (c) Show that, for the autocatalytic process discussed in parts (a) and (b), the reaction rate reaches a maximum at $t_{\max} = -(1/a)\ln b$. (d) An autocatalytic reaction $\mathrm{A} \rightarrow \mathrm{P}$ is observed to have the rate law $\mathrm{d}[\mathrm{P}]/\mathrm{d}t = k_r[\mathrm{A}]^2[\mathrm{P}]$. Solve the rate law for initial concentrations $[\mathrm{A}]_0$ and $[\mathrm{P}]_0$. Calculate the time at which the rate reaches a maximum. (e) Another reaction with the stoichiometry $\mathrm{A} \rightarrow \mathrm{P}$ has the rate law $\mathrm{d}[\mathrm{P}]/\mathrm{d}t = k_r[\mathrm{A}][\mathrm{P}]^2$; integrate the rate law for initial concentrations $[\mathrm{A}]_0$ and $[\mathrm{P}]_0$. Calculate the time at which the rate reaches a maximum.

F19.2 Many biological and biochemical processes involve autocatalytic steps (Problem F19.1). In the SIR model of the spread and decline of infectious diseases, the population is divided into three classes: the susceptibles, *S*, who can catch the disease; the infectives, *I*, who have the disease and can transmit it; and the removed class, *R*, who have either had the disease and recovered, are dead, are immune, or are isolated. The model mechanism for this process implies the following rate laws:

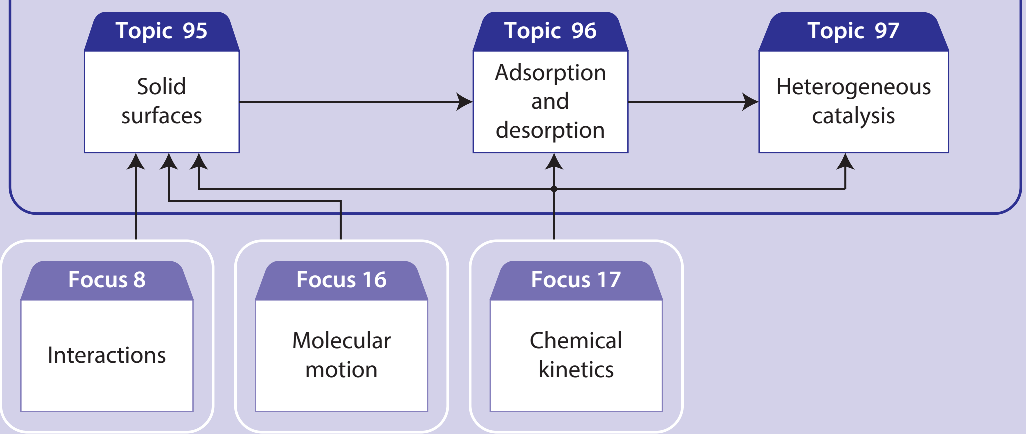
$$\frac{\mathrm{d}S}{\mathrm{d}t} = -rSI \qquad \frac{\mathrm{d}I}{\mathrm{d}t} = rSI - aI \qquad \frac{\mathrm{d}R}{\mathrm{d}t} = aI$$

What are the autocatalytic steps of this mechanism? Find the conditions on the ratio a/r that decide whether the disease will spread (an epidemic) or die out. Show that a constant population is built into this system, namely that $S+I+R=N$, meaning that the timescales of births, deaths by other causes, and migration are assumed large compared to that of the spread of the disease.

F19.3 Consult literature sources and list the observed ranges of timescales during which the following processes occur: radiative decay of excited electronic states, molecular rotational motion, molecular vibrational motion, proton transfer reactions, energy transfer between fluorescent molecules used in FRET analysis, electron transfer events between complex ions in solution, and collisions in liquids.

F19.4 Discuss the factors that govern the rates of photo-induced electron transfer according to Marcus theory and that govern the rates of resonance energy transfer according to Förster theory. Can you find similarities between the two theories?

FOCUS 20 ON Processes on solid surfaces



Processes at solid surfaces govern the viability of industry constructively, as in catalysis, and the permanence of its products destructively, as in corrosion. Chemical reactions at solid surfaces may differ sharply from reactions in the bulk, for reaction pathways of much lower activation energy may be provided by the surface, and hence result in catalysis. Here we extend the material introduced in *Chemical kinetics* by showing how to deal with processes on solid surfaces.

Topic 95 explores the structure of solid surfaces by drawing from knowledge of crystal structure (*Interactions*) and collisions in the gas phase (*Molecular motion*). We also describe a number of experimental techniques commonly used in surface science. Moving beyond a discussion of clean surfaces is important because for chemists the important aspects of a surface are the attachment of substances to it and the reactions that take place there. In **Topic 96** we discuss the extent to which a solid surface is covered and the variation of the extent of coverage with pressure and temperature. This material prepares us for a description of chemical reactions on solid surfaces. In **Topic 97** we focus on how surfaces affect the rate and course of chemical change by acting as the site of catalysis.

What is the impact of this material?

Almost the whole of modern chemical industry depends on the development, selection, and application of catalysts, with heterogeneous catalysts being particularly important. All we can hope to do in *Impact* 20.1 is to give a brief indication of some of the problems involved. Other than the ones we consider, these problems include the danger of the catalyst being poisoned by by-products or impurities, and economic considerations relating to cost and lifetime.

To read more about the impact of this material, scan the QR code or go to http://bcs.whfreeman.com/webpub/chemistry/qmc2e/impact/qchem_impact20.html.

TOPIC 95

Solid surfaces

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➤ Why do you need to know this material?

To understand the thermodynamics and kinetics of chemical reactions occurring on solid surfaces, which underlie much of catalysis and therefore the chemical industry, you need to understand their structure, composition, and growth.

➤ What is the key idea?

Structural features, including defects, play important roles in physical and chemical processes occurring on solid surfaces.

➤ What do you need to know already?

You need to be aware of the structure of solids (Topic 37), but not in detail. This Topic draws on results from the kinetic theory of gases (Topic 78).

A great deal of chemistry occurs at solid surfaces. Heterogeneous catalysis (Topic 97) is just one example, with the surface providing reactive sites where reactants can attach, be torn apart, and react with other reactants. Even as simple an act as dissolving is intrinsically a surface phenomenon, with the solid gradually escaping into the solvent from sites on the surface. Surface deposition, in which atoms are laid down on a surface to create layers, is crucial to the semiconductor industry, as it is the way in which integrated circuits are created.

95.1 Surface growth

Adsorption is the attachment of particles to a solid surface; **desorption** is the reverse process. The substance that adsorbs is the **adsorbate** and the material to which it adsorbs is the **adsorbent** or **substrate**.

A simple picture of a perfect crystal surface is as a tray of oranges in a grocery store (Fig. 95.1). A gas molecule that collides with the surface can be imagined as a ping-pong ball bouncing erratically over the oranges. The molecule loses energy as it bounces, but it is likely to escape from the surface before it has lost enough kinetic energy to be trapped. The same is true, to some extent, of an ionic crystal in contact with

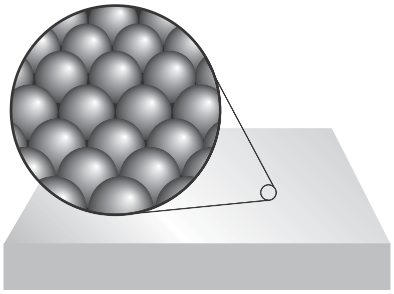


Figure 95.1 A schematic diagram of the flat surface of a solid. This primitive model is largely supported by scanning tunnelling microscope images.

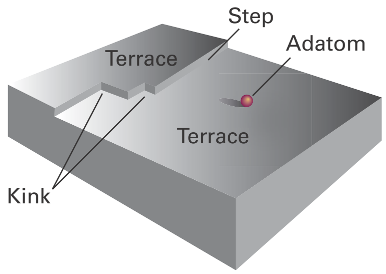


Figure 95.2 Some of the kinds of defects that may occur on otherwise perfect terraces. Defects play an important role in surface growth and catalysis.

a solution. There is little energy advantage for an ion in solution to discard some of its solvating molecules and stick at an exposed position on the surface.

The picture changes when the surface has defects, for then there are ridges of incomplete layers of atoms or ions. A common type of surface defect is a **step** between two otherwise flat layers of atoms called **terraces** (Fig. 95.2). A step defect might itself have defects, for it might have kinks. When an atom settles on a terrace it bounces across it under the influence of the intermolecular potential, and might come to a step or a corner formed by a kink. Instead of interacting with a single terrace atom, the molecule now interacts with several, and the interaction may be strong enough to trap it. Likewise, when ions deposit from solution, the loss of the solvation interaction is offset by a strong Coulombic interaction between the arriving ions and several ions at the surface defect.

The rapidity of growth depends on the crystal plane concerned, and the slowest-growing faces dominate the appearance of the crystal. This feature is explained in Fig. 95.3, where we see that, although the horizontal face grows forward most rapidly, it grows itself out of existence, and the slower-growing faces survive.

Under normal conditions, a surface exposed to a gas is constantly bombarded with molecules and a freshly prepared surface is covered very quickly. Just how quickly can be estimated using the kinetic model of gases and the following expression for the collision flux (eqn 78.13):

$$Z_W = \frac{p}{(2\pi mkT)^{1/2}} \qquad \text{Collision flux} \tag{95.1}$$

where p is the pressure, m is the molecular mass, k is Boltzmann's constant, and T is the temperature.

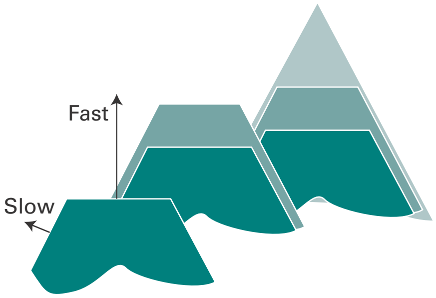


Figure 95.3 The slower-growing faces of a crystal dominate its final external appearance. Three successive stages of the growth are shown.

Brief illustration 95.1 The collision flux

If we write $m = M/N_A$, where M is the molar mass of the gas, eqn 95.1 becomes

$$Z_W = \frac{(N_A/2\pi k)^{1/2}\, p}{(TM)^{1/2}}$$

After inserting numerical values for the constants and selecting units for the variables, the practical form of this expression is

$$Z_W = \frac{Z_0(p/\text{Pa})}{\{(T/\text{K})(M/(\text{g mol}^{-1}))\}^{1/2}} \quad \text{with } Z_0 = 2.63\times10^{24}\,\text{m}^{-2}\,\text{s}^{-1}$$

For air, with $M \approx 29\,\text{g mol}^{-1}$, at $p = 1\,\text{atm} = 1.01325\times10^5\,\text{Pa}$ and $T = 298\,\text{K}$, we obtain $Z_W = 2.9\times10^{27}\,\text{m}^{-2}\,\text{s}^{-1}$. Because $1\,\text{m}^2$ of metal surface consists of about 10^{19} atoms, each atom is struck about 10^8 times each second. Even if only a few collisions leave a molecule adsorbed to the surface, the time for which a freshly prepared surface remains clean is very short.

Self-test 95.1 Calculate the collision flux with a surface of a vessel containing propane at 25 °C when the pressure is 100 Pa.

Answer: $Z_W = 2.30\times10^{20}\,\text{cm}^{-2}\,\text{s}^{-1}$

95.2 Physisorption and chemisorption

Molecules and atoms can attach to surfaces in two ways. In **physisorption** (an abbreviation of 'physical adsorption'), there is a van der Waals interaction (for example, a dispersion or a dipolar interaction, Topic 35) between the adsorbate and the substrate; van der Waals interactions have a long range but are weak, and the energy released when a particle is physisorbed is of the same order of magnitude as the enthalpy of condensation. Such small energies can be absorbed as vibrations of the lattice and dissipated as thermal motion, and a molecule bouncing across the surface will gradually lose its energy and finally adsorb to it in the process called **accommodation**.

The enthalpy of physisorption can be measured by monitoring the rise in temperature of a sample of known heat capacity,

Table 95.1* Maximum observed standard enthalpies of physisorption at 298 K

Adsorbate	$\Delta_{\text{ad}}H^{\ominus}/(\text{kJ mol}^{-1})$
CH_4	−21
H_2	−84
H_2O	−59
N_2	−21

* More values are given in the *Resource section*.

and typical values are in the region of $-20\,\text{kJ mol}^{-1}$ (Table 95.1). This small enthalpy change is insufficient to lead to bond breaking, so a physisorbed molecule retains its identity, although it might be distorted by the presence of the surface.

In **chemisorption** (an abbreviation of 'chemical adsorption'), the molecules (or atoms) stick to the surface by forming a chemical (usually covalent) bond, and tend to find sites that maximize their coordination number with the substrate. The enthalpy of chemisorption is very much greater than that for physisorption, and typical values are in the region of $-200\,\text{kJ mol}^{-1}$ (Table 95.2). The distance between the surface and the closest adsorbate atom is also typically shorter for chemisorption than for physisorption. A chemisorbed molecule may be torn apart at the demand of the unsatisfied valencies of the surface atoms, and the existence of molecular fragments on the surface as a result of chemisorption is one reason why solid surfaces catalyse reactions (Topic 97).

Except in special cases, chemisorption must be exothermic. A spontaneous process requires $\Delta G < 0$ at constant pressure and temperature. Because the translational freedom of the adsorbate is reduced when it is adsorbed, ΔS is negative. Therefore, in order for $\Delta G = \Delta H - T\Delta S$ to be negative, ΔH must be negative (that is, the process is exothermic). Exceptions may occur if the adsorbate dissociates and has high translational mobility on the surface. For example, H_2 adsorbs endothermically on glass because there is a large increase of translational entropy accompanying the dissociation of the molecules into atoms that move quite freely over the surface. In this case, the entropy change in the process $H_2(g) \rightarrow 2\,H(\text{glass})$ is sufficiently positive to overcome the small positive enthalpy change.

Table 95.2* Standard enthalpies of chemisorption, $\Delta_{\text{ad}}H^{\ominus}/(\text{kJ mol}^{-1})$ at 298 K

Adsorbate	Adsorbent (substrate)		
	Cr	Fe	Ni
C_2H_4	−427	−285	−243
CO		−192	
H_2	−188	−134	
NH_3		−188	−155

* More values are given in the *Resource section*.

The enthalpy of adsorption depends on the extent of surface coverage, mainly because the adsorbate particles interact. If the particles repel each other (as for CO on palladium) the adsorption becomes less exothermic (the enthalpy of adsorption less negative) as coverage increases. Moreover, studies show that such species settle on the surface in a disordered way until packing requirements demand order. If the adsorbate particles attract one another (as for O_2 on tungsten), then they tend to cluster together in islands, and growth occurs at the borders. These adsorbates also show order–disorder transitions when they are heated enough for thermal motion to overcome the particle–particle interactions, but not so much that they are desorbed.

Whether a result of physisorption or chemisorption, the extent of surface coverage is normally expressed as the **fractional coverage**, θ:

$$\theta = \frac{\text{number of adsorption sites occupied}}{\text{number of adsorption sites available}} \tag{95.2}$$

Definition Fractional coverage

The fractional coverage is often expressed in terms of the volume of adsorbate adsorbed by $\theta = V/V_\infty$, where V_∞ is the volume of adsorbate corresponding to complete monolayer coverage. In each case, the volumes in the definition of θ are those of the free gas measured under the same conditions of temperature and pressure, not the volume the adsorbed gas occupies when attached to the surface.

Brief illustration 95.2 Fractional coverage

For the adsorption of CO on charcoal at 273 K, $V_\infty = 111\,\text{cm}^3$, a value corrected to 1 atm. When the partial pressure of CO is 80.0 kPa, the value of V (also corrected to 1 atm) is $41.6\,\text{cm}^3$, so it follows that $\theta = (41.6\,\text{cm}^3)/(111\,\text{cm}^3) = 0.375$.

Self-test 95.2 It is commonly observed that θ increases sharply with the partial pressure of adsorbate at low pressures, but becomes increasingly less dependent on partial pressure at high pressures. Explain this behaviour.

Answer: See Topic 96

95.3 Experimental techniques

A vast array of experimental techniques are used to study the composition and structure of solid surfaces at the atomic level. Many of the arrangements allow for direct visualization of changes in the surface as adsorption and chemical reactions take place there.

Experimental procedures must begin with a clean surface. The obvious way to retain cleanliness of a surface is to reduce the pressure and thereby reduce the number of impacts on the surface. When the pressure is reduced to 0.1 mPa (as in a simple vacuum system) the collision flux falls to about $10^{18}\,\mathrm{m^{-2}\,s^{-1}}$, corresponding to one hit per surface atom in each 0.1 s. Even that is too frequent in most experiments, and in **ultrahigh vacuum** (UHV) techniques pressures as low as 0.1 μPa (when $Z_W = 10^{15}\,\mathrm{m^{-2}\,s^{-1}}$) are reached on a routine basis and as low as 1 nPa (when $Z_W = 10^{13}\,\mathrm{m^{-2}\,s^{-1}}$) are reached with special care. These collision fluxes correspond to each surface atom being hit once every 10^5 to 10^6 s, or about once a day.

(a) Microscopy

The basic approach of illuminating a small area of a sample and collecting light with a microscope has been used for many years to image small specimens. However, the resolution of a microscope, the minimum distance between two objects that leads to two distinct images, is on the order of the wavelength of the electromagnetic radiation being used. Therefore, conventional microscopes employing visible light have resolutions in the micrometre range and are blind to features on a scale of nanometres.

One technique that is often used to image nanometre-sized objects is **electron microscopy**, in which a beam of electrons with a well-defined de Broglie wavelength (Topic 4) replaces the lamp found in traditional light microscopes. Instead of glass or quartz lenses, magnetic fields are used to focus the beam. In **transmission electron microscopy** (TEM), the electron beam passes through the specimen and the image is collected on a screen. In **scanning electron microscopy** (SEM), electrons scattered back from a small irradiated area of the sample are detected and the electrical signal is sent to a video screen. An image of the surface is then obtained by scanning the electron beam across the sample.

As in traditional light microscopy, the wavelength of and the ability to focus the incident beam—in this case a beam of electrons—govern the resolution. Electron wavelengths in typical electron microscopes can be as short as 10 pm, but it is not possible to focus electrons well with magnetic lenses and in practice typical resolutions of TEM and SEM instruments are about 2 nm and 50 nm, respectively. It follows that electron microscopes cannot resolve individual atoms (which have diameters of about 0.2 nm). Furthermore, only particular kinds of samples can be observed under certain conditions. The measurements must be conducted under high vacuum. For TEM observations, the samples must be very thin cross-sections of a specimen and SEM observations must be made on dry samples.

Scanning probe microscopy (SPM) is a collection of techniques that can be used to visualize and manipulate objects as small as atoms on surfaces. One version of SPM is **scanning tunnelling microscopy** (STM), in which a platinum–rhodium or tungsten needle is scanned across the surface of a conducting solid. When the tip of the needle is brought very close to the surface, electrons tunnel across the intervening space (Fig. 95.4). In the 'constant-current mode' of operation, the stylus moves up and down corresponding to the form of the surface, and the topography of the surface, including any adsorbates, can therefore be mapped on an atomic scale. The vertical motion of the stylus is achieved by fixing it to a piezoelectric cylinder, which contracts or expands according to the potential difference it experiences. In the 'constant-*z* mode', the vertical position of the stylus is held constant and the current is monitored. Because the tunnelling probability is very sensitive to the size of the gap, the microscope can detect tiny, atom-scale variations in the height of the surface.

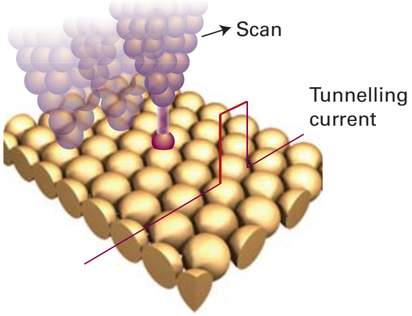


Figure 95.4 A scanning tunnelling microscope makes use of the current of electrons that tunnel between the surface and the tip. That current is very sensitive to the distance of the tip above the surface.

Figure 95.5 shows an example of the kind of image obtained with a surface, in this case of gallium arsenide that has been modified by addition of caesium atoms. Each 'bump' on the surface corresponds to an atom. In a further variation of the STM technique, the tip may be used to nudge single atoms around on the surface, making possible the fabrication of complex and yet very tiny nanometre-sized materials and devices.

In **atomic force microscopy** (AFM), a sharpened tip attached to a cantilever is scanned across the surface. The force exerted by the surface and any molecules attached to it pushes or pulls on the tip and deflects the cantilever (Fig. 95.6). The deflection is monitored by using a laser beam. Because no current needs

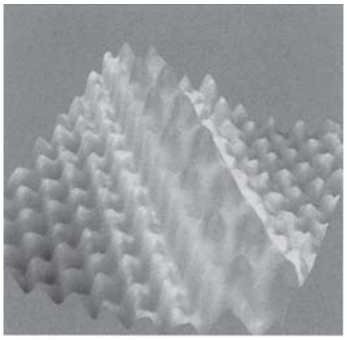


Figure 95.5 An STM image of caesium atoms on a gallium arsenide surface.

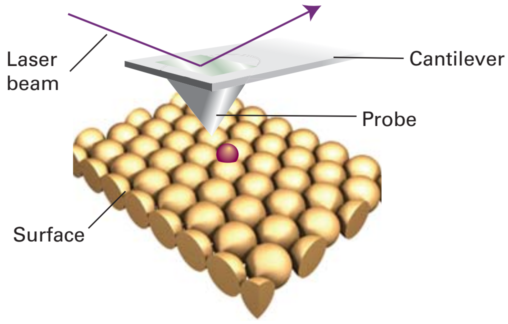


Figure 95.6 In atomic force microscopy, a laser beam is used to monitor the tiny changes in position of a probe as it is attracted to or repelled by atoms on a surface.

to pass between the sample and the probe, the technique can be applied to non-conducting surfaces and to liquid samples.

Two modes of operation of AFM are common. In 'contact mode', or 'constant-force mode', the force between the tip and surface is held constant and the tip makes contact with the surface. This mode of operation can damage fragile samples on the surface. In 'non-contact' or 'tapping mode', the tip bounces up and down with a specified frequency and never quite touches the surface. The amplitude of the tip's oscillation changes when it passes over a species adsorbed on the surface.

Figure 95.7 demonstrates the power of AFM, which shows germanium nanowires on a silicon surface. The wires are about 2 nm high, 10–32 nm wide, and 10–600 nm long.

(b) Ionization techniques

The chemical composition of a surface can be determined by a variety of ionization techniques. The same techniques can be used to detect any remaining contamination after cleaning and to detect layers of material adsorbed later in the experiment.

One technique is **photoemission spectroscopy**, a derivative of the photoelectric effect (Topic 4), in which X-rays (for XPS) or hard (short-wavelength) ultraviolet (for UPS) ionizing radiation is used, giving rise to ejected electrons from adsorbed species. The kinetic energies of the electrons ejected from their orbitals are measured and the pattern of energies is a fingerprint of the material present (Fig. 95.8). UPS, which examines electrons ejected from valence shells, is also used to establish the bonding characteristics and the details of valence-shell electronic structures of substances on the surface. Its usefulness is its ability to reveal which orbitals of the adsorbate are involved in the bond to the substrate.

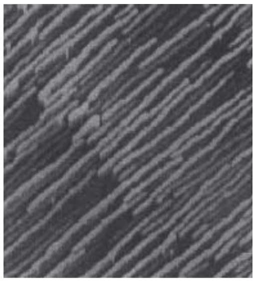


Figure 95.7 Germanium nanowires fabricated on to a silicon surface by molecular beam epitaxy. (Reproduced with permission from T. Ogino, et al., *Acc. Chem. Res.* **32**, 447 (1999).)

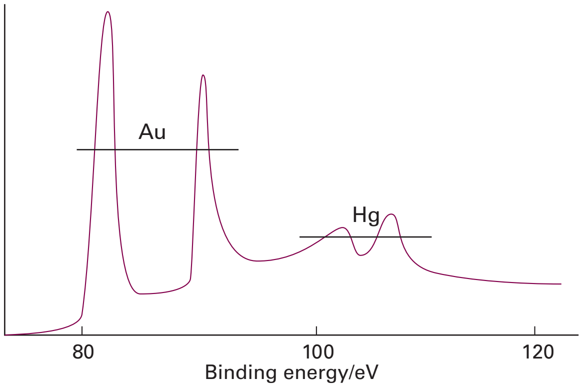


Figure 95.8 The X-ray photoelectron emission spectrum of a sample of gold contaminated with a surface layer of mercury (M.W. Roberts and C.S. McKee, *Chemistry of the metal–gas interface*, Oxford University Press (1978)).

Brief illustration 95.3 A UPS spectrum

The principal difference between the photoemission results on free benzene and benzene adsorbed on palladium is in the energies of the π electrons. This difference is interpreted as meaning that the C_6H_6 molecules lie parallel to the surface and are attached to it by their π orbitals.

Self-test 95.3 When adsorbed to palladium, pyridine (C_6H_5N) stands almost perpendicular to the surface. Suggest a mode of attachment of the molecule to palladium atoms on the surface.

Answer: Data are consistent with a σ bond formed by the nitrogen lone pair

A very important technique, which is widely used in the microelectronics industry, is **Auger electron spectroscopy** (AES). The **Auger effect** (pronounced oh-zhey) is the emission of a second electron after high-energy radiation has expelled another. The first electron to depart leaves a hole in a low-lying orbital, and an upper electron falls into it. The energy this transition releases may result either in the generation of radiation, which is called **X-ray fluorescence** (Fig. 95.9a), or in the ejection of another electron (Fig. 95.9b). The latter is the 'secondary electron' of the Auger effect. The energies of the secondary electrons are characteristic of the material present, so the Auger effect effectively takes a fingerprint of the sample. In practice, the Auger spectrum is normally obtained by irradiating the

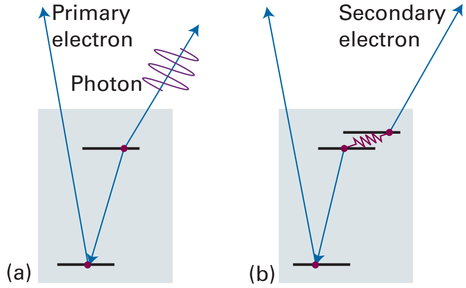


Figure 95.9 When an electron is expelled from a solid (a) an electron of higher energy may fall into the vacated orbital and emit an X-ray photon to produce X-ray fluorescence. Alternatively (b) the electron falling into the orbital may give up its energy to another electron, which is ejected in the Auger effect.

sample with an electron beam of energy in the range 1–5 keV rather than electromagnetic radiation. In **scanning Auger electron microscopy** (SAM), the finely focused electron beam is scanned over the surface and a map of composition is compiled; the resolution can reach below about 50 nm.

Diffusion characteristics of an adsorbate can be examined by using STM to follow the change in surface characteristics or by **field-ionization microscopy** (FIM), which portrays the electrical characteristics of a surface by using the ionization of noble gas atoms to probe the surface (Fig. 95.10). An individual atom is imaged and the temperature is raised, and then lowered after a definite interval. A new image is then recorded, and the new position of the atom measured (Fig. 95.11). A sequence of images shows that the atom makes a random walk across the surface, and the diffusion coefficient, D, can be inferred from the mean distance, d, travelled in an interval τ by using the two-dimensional random walk expression $d=(D\tau)^{1/2}$. The value of D for different crystal planes at different temperatures can be determined directly in this way, and the activation energy for migration over each plane obtained from the Arrhenius-like expression

$$D=D_0\mathrm{e}^{-E_{\mathrm{a,diff}}/RT} \qquad (95.3)$$

Temperature dependence of the diffusion coefficient

where $E_{\mathrm{a,diff}}$ is the activation energy for diffusion and D_0 is the diffusion coefficient in the limit of infinite temperature.

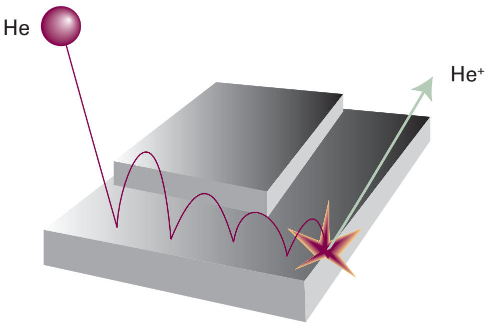


Figure 95.10 The events leading to an FIM image of a surface. The He atom migrates across the surface until it is ionized at an exposed atom, when it is pulled off by the externally applied potential. (The bouncing motion is due to the intermolecular potential, not gravity!)

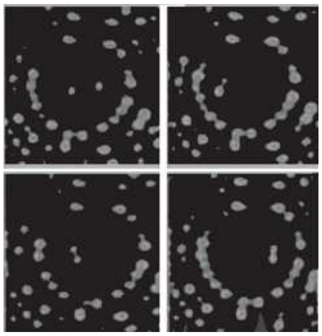


Figure 95.11 FIM micrographs showing the migration of Re atoms on rhenium during 3 s intervals at 375 K. (Photographs provided by Professor G. Ehrlich.)

Brief illustration 95.4 Diffusion coefficients

Typical values for W atoms on tungsten have $E_{\mathrm{a,diff}}$ in the range 57–87 kJ mol⁻¹ and $D_0\approx 3.8\times10^{-11}\ \mathrm{m^2\,s^{-1}}$. It follows from eqn 95.3 that at 800 K the diffusion coefficient varies approximately from

$$\begin{aligned}D&=(3.8\times10^{-11}\ \mathrm{m^2\,s^{-1}})\times\mathrm{e}^{-5.7\times10^{-4}\ \mathrm{J\,mol^{-1}}/(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}\times800\ \mathrm{K})}\\&=7.2\times10^{-15}\ \mathrm{m^2\,s^{-1}}\end{aligned}$$

to

$$\begin{aligned}D&=(3.8\times10^{-11}\ \mathrm{m^2\,s^{-1}})\times\mathrm{e}^{-8.7\times10^{-4}\ \mathrm{J\,mol^{-1}}/(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}\times800\ \mathrm{K})}\\&=7.9\times10^{-17}\ \mathrm{m^2\,s^{-1}}\end{aligned}$$

Self-test 95.4 For CO on tungsten, the activation energy falls from 144 kJ mol⁻¹ at low surface coverage to 88 kJ mol⁻¹ when the coverage is high. Calculate the ratio $D_{\mathrm{high}}/D_{\mathrm{low}}$ of diffusion coefficients at 800 K.

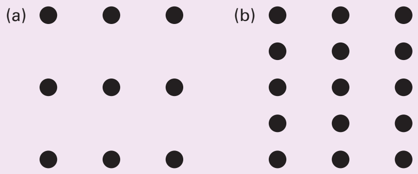
Answer: 4.5×10^3

(c) Diffraction techniques

A useful technique for determining the arrangement of the atoms close to the surface is **low-energy electron diffraction** (LEED). This technique is like X-ray diffraction (Topic 37) but uses the wave character of electrons, and the sample is now the surface of a solid. The use of low-energy electrons (with energies in the range 10–200 eV, corresponding to wavelengths in the range 100–400 pm) ensures that the diffraction is caused only by atoms on and close to the surface. The experimental arrangement is shown in Fig. 95.12, and typical LEED patterns, obtained by photographing the fluorescent screen through the viewing port, are shown in Fig. 95.13.

Example 95.1 Interpreting a LEED pattern

The LEED pattern from a clean (110) face of palladium is shown in (a) below. The reconstructed surface gives a LEED pattern shown as (b). What can be inferred about the structure of the surface?

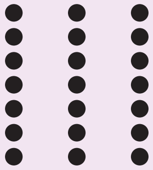


Method Recall from Bragg's law (Topic 37, $\lambda = 2d \sin \theta$) that, for a given wavelength, the greater the separation d of the layers, the smaller is the scattering angle (so that $2d \sin \theta$ remains constant). It follows that, in terms of the LEED pattern, the farther apart the atoms responsible for the pattern, the closer the spots appear in the pattern. Twice the separation between the atoms corresponds to half the separation between the spots, and vice versa. Therefore, inspect the two patterns and identify how the new pattern relates to the old.

Answer The horizontal separation between spots is unchanged, which indicates that the atoms remain in the same position in that dimension when reconstruction occurs. (Reconstruction refers to processes by which atoms on the surface achieve their equilibrium structures, which may differ from those of atoms in the bulk since surface and bulk atoms experience different forces.) However, the vertical spacing is halved, which suggests that the atoms are twice as far apart in that direction as they are in the unreconstructed surface.

Self-test 95.5 Sketch the LEED pattern for a surface that differs from that shown in (a) above by tripling the vertical separation.

Answer:



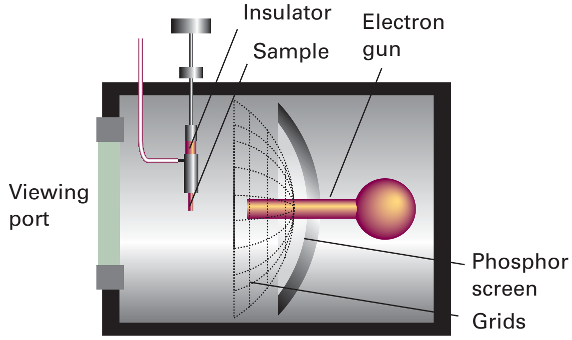


Figure 95.12 A schematic diagram of the apparatus used for a LEED experiment. The electrons diffracted by the surface layers are detected by the fluorescence they cause on the phosphor screen.

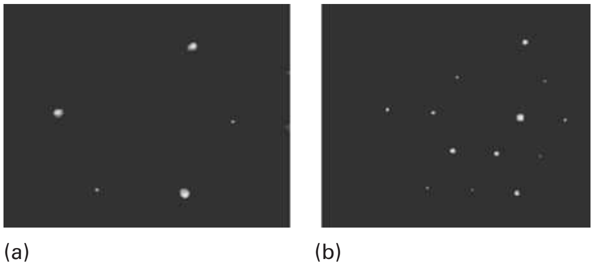

(a) (b)

Figure 95.13 LEED photographs of (a) a clean platinum surface and (b) after its exposure to propyne, $CH_3C{\equiv}CH$. (Photographs provided by Professor G.A. Somorjai.)

Observations using LEED show that the surface of a crystal rarely has exactly the same form as a slice through the bulk. As a general rule, it is found that metal surfaces are simply truncations of the bulk lattice, but the distance between the top layer of atoms and the one below is contracted by around 5 per cent. Semiconductors generally have surfaces reconstructed to a depth of several layers. Reconstruction occurs in ionic solids. For example, in lithium fluoride the Li^+ and F^- ions close to the surface apparently lie on slightly different planes. An actual example of the detail that can now be obtained from refined LEED techniques is shown in Fig. 95.14 for $CH_3C–$ adsorbed on a (111) plane of rhodium.

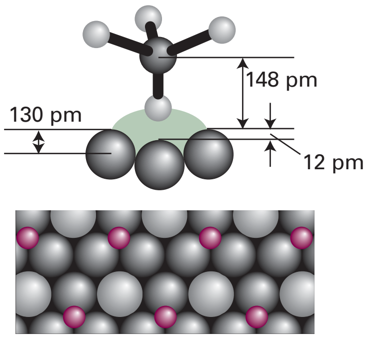


Figure 95.14 The structure of a surface close to the point of attachment of $CH_3C–$ to the (110) surface of rhodium at 300 K and the changes in positions of the metal atoms that accompany chemisorption.

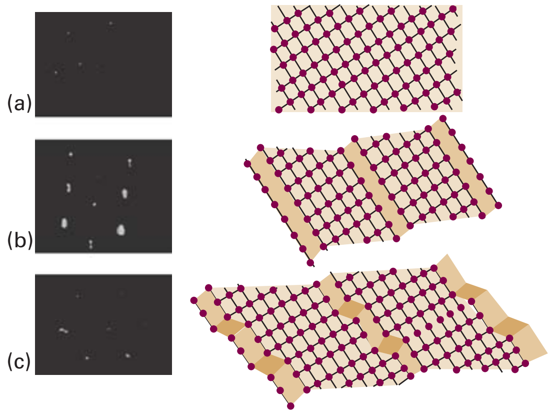


Figure 95.15 LEED patterns may be used to assess the defect density of a surface. The photographs correspond to a platinum surface with (a) low defect density, (b) regular steps separated by about six atoms, and (c) regular steps with kinks. (Photographs provided by Professor G.A. Samorjai.)

The presence of terraces, steps, and kinks in a surface shows up in LEED patterns, and their surface density (the number of defects in a region divided by the area of the region) can be estimated. Three examples of how steps and kinks affect the pattern are shown in Fig. 95.15. The samples used were obtained by cleaving a crystal at different angles to a plane of atoms. Only terraces are produced when the cut is parallel to the plane, and the density of steps increases as the angle of the cut increases. The observation of additional structure in the LEED patterns, rather than blurring, shows that the steps are arrayed regularly.

(d) The determination of adsorption and desorption rates

Among the principal techniques for measuring rates of processes on surfaces are flow methods. A common technique monitors the rates of flow of gas into and out of the system: the difference is the rate of gas uptake by the sample. Integration of this rate then gives the fractional coverage at any stage. In **flash desorption** the sample is suddenly heated (electrically) and the resulting rise of pressure is interpreted in terms of the amount of adsorbate originally on the sample. The interpretation may be confused by the desorption of a compound (for example, WO_3 from oxygen on tungsten).

Gravimetry, in which the sample is weighed on a microbalance during the experiment, can also be used. A common instrument for gravimetric measurements is the **quartz crystal microbalance** (QCM), in which the mass of a sample laid on the surface of a quartz crystal is related to changes in the latter's mechanical properties. The key principle behind the operation of a QCM is the ability of a quartz crystal to vibrate at a characteristic frequency when an oscillating electric field is applied. The vibrational frequency decreases when material is spread over the surface of the crystal and the change in frequency is proportional to the mass of material. Masses as small as a few nanograms can be measured reliably in this way.

Second harmonic generation (SHG) is very important for the study of all types of surfaces, including thin films and liquid–gas interfaces. Second harmonic generation is the conversion of an intense, pulsed laser beam to radiation with twice its initial frequency as it passes through a material. In addition to a number of crystals, surfaces are also suitable materials for SHG. For example, adsorption of gas molecules on to a surface alters the intensity of the SHG signal, allowing for characterization of physical and chemical processes. Because pulsed lasers are the excitation sources, time-resolved measurements of the kinetics and dynamics of surface processes are possible over timescales as short as femtoseconds.

Surface plasmon resonance (SPR) is a very sensitive technique now used routinely to measure the kinetics and thermodynamics of surface processes. An SPR instrument detects changes in the optical properties of a surface as it changes as a result of adsorption or desorption. Here we focus on its use in the study of interactions between biopolymers.

The mobility of delocalized valence electrons accounts for the electrical conductivity of metals and these mobile electrons form a **plasma**, a dense gas of charged particles. Bombardment of the plasma by light or an electron beam can cause transient changes in the distribution of electrons, with some regions becoming slightly more dense than others. Coulomb repulsion in the regions of high density causes electrons to move away from each other, so lowering their density. The resulting oscillations in electron density, called **plasmons,** can be excited both in the bulk and on the surface of a metal. Plasmons in the bulk may be visualized as waves that propagate through the solid. A surface plasmon also propagates away from the surface, but the amplitude of the wave, also called an **evanescent wave,** decreases sharply with distance from the surface.

Surface plasmon resonance is the absorption of energy from an incident beam of electromagnetic radiation by surface plasmons. Absorption, or 'resonance', can be observed with appropriate choice of the wavelength and angle of incidence of the excitation beam. It is common practice to use a monochromatic beam and to vary the angle of incidence, ϕ (Fig. 95.16). The beam passes through a prism that strikes one side of a thin film of gold or silver. The angle corresponding to light absorption depends on the refractive index of the medium in direct contact with the opposing side of the metallic film. This variation of the resonance angle with the state of the surface arises from the ability of the evanescent wave to interact with material a short distance away from the surface. For example, changing the identity and quantity of material on the surface changes the resonance angle. Hence, SPR can be used in the study of the

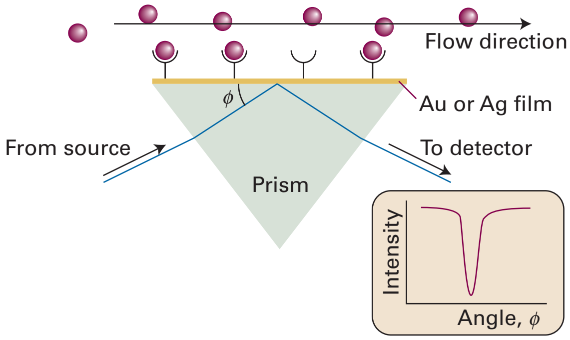


Figure 95.16 The experimental arrangement for the observation of surface plasmon resonance, as explained in the text.

binding of molecules to a surface or the binding of ligands to a biopolymer attached to the surface; this interaction mimics the biological recognition processes that occur in cells. Examples of complexes amenable to analysis include antibody–antigen and protein–DNA interactions. The most important advantage of SPR analysis is its sensitivity: it is possible to measure the deposition of nanograms of material on to a surface. The main disadvantage of the technique is its requirement for immobilization of at least one of the components of the system under study.

Example 95.2 Interpreting data from SPR analysis

Consider the association of two polymers, A and B, to form the complex AB. In a typical SPR analysis experiment, a stream of solution containing a known concentration of A flows above the surface to which B is chemisorbed. Then the time dependence of the surface plasmon resonance signal, with intensity $R \propto [\mathrm{AB}]$, is monitored until the system reaches equilibrium and the signal intensity is R_{eq}. Write an expression that relates the value of R_{eq} to the equilibrium constant K for the process $\mathrm{A}+\mathrm{B} \rightleftharpoons \mathrm{AB}$.

Method Follow the procedures shown in Topic 84 for relating kinetic data to equilibrium parameters. Begin by letting k_{on} and k_{off} be the rate constants for formation and dissociation of the AB complex; note that they have different units. Then the equilibrium constant K is

$$K = \frac{k_{\mathrm{on}}}{k_{\mathrm{off}}} \times c^{\ominus}$$

where $c^{\ominus} = 1\,\mathrm{mol\,dm^{-3}}$. As always, it is useful to make reasonable approximations, and in this case we assume that the flow rate of A is sufficiently high that at all times $[\mathrm{A}] = a_0$ is essentially constant.

Answer The concentration of the complex AB varies with time as

$$\frac{\mathrm{d[AB]}}{\mathrm{d}t} = k_{\mathrm{on}}[\mathrm{A}][\mathrm{B}] - k_{\mathrm{off}}[\mathrm{AB}]$$

with $[\mathrm{A}] = a_0$ and, from mass balance, $[\mathrm{B}] = b_0 - [\mathrm{AB}]$, where b_0 is the total concentration of B. The maximum value that R can have is $R_{\mathrm{max}} \propto b_0$, which would be measured if all B molecules were complexed with A. With $R \propto [\mathrm{AB}]$, it follows that $[\mathrm{B}] \propto R_{\mathrm{max}} - R$, and

$$\frac{\mathrm{d}R}{\mathrm{d}t} = k_{\mathrm{on}} a_0 (R_{\mathrm{max}} - R) - k_{\mathrm{off}} R \qquad (95.4)$$

At equilibrium $R = R_{\mathrm{eq}}$ and $\mathrm{d}R/\mathrm{d}t = 0$, and after some algebra (see Self-test 95.6), it follows that

$$R_{\mathrm{eq}} = R_{\mathrm{max}} \frac{C}{C+1} \qquad C = a_0 (k_{\mathrm{on}}/k_{\mathrm{off}}) \qquad (95.5)$$

Hence, the value of $K = k_{\mathrm{on}}/k_{\mathrm{off}} \times c^{\ominus}$ can be obtained from measurements of R_{eq} for a series of a_0.

Self-test 95.6 Provide the missing steps in the derivation of eqn 95.5 from eqn 95.4.

Checklist of concepts

☐ 1. **Adsorption** is the attachment of molecules to a surface; the substance that adsorbs is the adsorbate and the underlying material is the adsorbent or substrate. The reverse of adsorption is desorption.

☐ 2. Surface defects play an important role in surface growth and catalysis.

☐ 3. Techniques for studying surfaces include **scanning electron microscopy** (SEM), **scanning probe microscopy** (SPM), **field-ionization microscopy** (FIM), **photoemission spectroscopy**, **Auger electron spectroscopy** (AES), **low-energy electron diffraction** (LEED), **flash desorption**, **gravimetry**, **second harmonic generation** (SHG), and **surface plasmon resonance** (SPR).

Checklist of equations

Property	Equation	Comment	Equation number
Collision flux	$Z_\mathrm{W}=p/(2\pi mkT)^{1/2}$	KMT	95.1
Fractional coverage	$\theta=$(number of adsorption sites occupied)/(number of adsorption sites available)	Definition	95.2

TOPIC 96

Adsorption and desorption

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➤ Why do you need to know this material?

To understand how surfaces can affect the rates of chemical reactions, you need to know how to assess the extent of surface coverage and the factors that determine the rates at which molecules attach to and detach from solid surfaces.

➤ What is the key idea?

The extent of coverage of a solid surface by molecules can be measured and expressed by simple mathematical expressions.

➤ What do you need to know already?

You need to be familiar with the basic ideas of chemical kinetics (Topics 82–84), the Arrhenius equation (Topic 85), the manipulation of reaction mechanisms into rate laws (Topic 86), and the structure and coverage of surfaces (Topic 95).

Here we consider the extent to which a solid surface is covered and the variation of the extent of coverage with pressure and temperature. For simplicity, we consider only gas/solid systems. We use this material in Topic 97 to discuss how surfaces affect the rate and course of chemical change by acting as the site of catalysis.

96.1 Adsorption isotherms

In adsorption (Topic 95) the free gas and the adsorbed gas are in dynamic equilibrium, and the fractional coverage, θ, of the surface (eqn 95.2) depends on the pressure of the overlying gas. The variation of θ with pressure at a chosen temperature is called the **adsorption isotherm**.

(a) The Langmuir isotherm

The simplest physically plausible isotherm is based on three assumptions:

- Adsorption cannot proceed beyond monolayer coverage.
- All sites are equivalent and the surface is uniform (that is, the surface is perfectly flat on a microscopic scale).
- The ability of a molecule to adsorb at a given site is independent of the occupation of neighbouring sites (that is, there are no interactions between adsorbed molecules).

The dynamic equilibrium is

$$\mathrm{A(g)} + \mathrm{M(surface)} \rightleftharpoons \mathrm{AM(surface)}$$

with rate constants k_a for adsorption and k_d for desorption. The rate of change of the surface coverage, $\mathrm{d}\theta/\mathrm{d}t$, due to adsorption is proportional to the partial pressure p of A and the number of vacant sites $N(1-\theta)$, where N is the total number of sites:

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = k_\mathrm{a} pN(1-\theta) \qquad \text{Rate of adsorption} \qquad (96.1\mathrm{a})$$

The rate of change of θ due to desorption is proportional to the number of adsorbed species, $N\theta$:

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = -k_\mathrm{d} N\theta \tag{96.1b}$$

Rate of desorption

At equilibrium there is no net change (that is, the sum of these two rates is zero), and solving for θ gives the **Langmuir isotherm**:

$$\theta = \frac{\alpha p}{1+\alpha p} \qquad \alpha = \frac{k_\mathrm{a}}{k_\mathrm{d}} \tag{96.2}$$

Langmuir isotherm

where the dimensions of α are 1/pressure.

Example 96.1 Using the Langmuir isotherm

The data given below are for the adsorption of CO on charcoal at 273 K. Confirm that they fit the Langmuir isotherm, and find the constant α and the volume corresponding to complete coverage. In each case V has been corrected to 1 atm (101.325 kPa).

p/kPa	13.3	26.7	40.0	53.3	66.7	80.0	93.3
V/cm^3	10.2	18.6	25.5	31.5	36.9	41.6	46.1

Method From eqn 96.2,

$$\alpha p\theta + \theta = \alpha p$$

With $\theta = V/V_\infty$ (eqn 95.2), where V_∞ is the volume corresponding to complete coverage, this expression can be rearranged into

$$\frac{p}{V} = \frac{p}{V_\infty} + \frac{1}{\alpha V_\infty}$$

Hence, a plot of p/V against p should give a straight line of slope $1/V_\infty$ and intercept $1/\alpha V_\infty$.

Answer The data for the plot are as follows:

p/kPa	13.3	26.7	40.0	53.3	66.7	80.0	93.3
$(p/\mathrm{kPa})/(V/\mathrm{cm}^3)$	1.30	1.44	1.57	1.69	1.81	1.92	2.02

The points are plotted in Fig. 96.1. The (least-squares) slope is 0.009 00, so $V_\infty = 111\,\mathrm{cm}^3$. The intercept at $p = 0$ is 1.20, so

$$\alpha = \frac{1}{(111\,\mathrm{cm}^3)\times(1.20\,\mathrm{kPa\,cm}^3)} = 7.51\times10^{-3}\,\mathrm{kPa}^{-1}$$

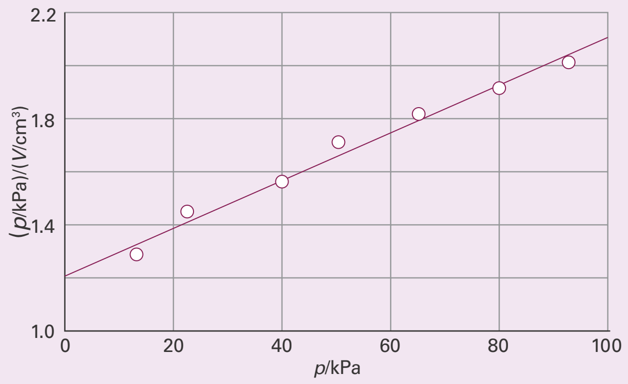

Figure 96.1 The plot of the data in Example 96.1. As illustrated here, the Langmuir isotherm predicts that a straight line should be obtained when p/V is plotted against p.

Self-test 96.1 Repeat the calculation for the following data:

p/kPa	13.3	26.7	40.0	53.3	66.7	80.0	93.3
V/cm^3	10.3	19.3	27.3	34.1	40.0	45.5	48.0

Answer: 128 cm^3, 6.69×10^{-3} kPa^{-1}

For adsorption with dissociation, the rate of adsorption is proportional to the pressure and to the probability that both atoms will find sites, which is proportional to the square of the number of vacant sites,

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = k_\mathrm{a} p\{N(1-\theta)\}^2 \tag{96.3a}$$

The rate of desorption is proportional to the frequency of encounters of atoms on the surface, and is therefore second-order in the number of atoms present:

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = -k_\mathrm{d}(N\theta)^2 \tag{96.3b}$$

The condition for no net change leads to the isotherm

$$\theta = \frac{(\alpha p)^{1/2}}{1+(\alpha p)^{1/2}} \tag{96.4}$$

Langmuir isotherm for adsorption with dissociation

The surface coverage now depends more weakly on pressure than for non-dissociative adsorption.

The shapes of the Langmuir isotherms with and without dissociation are shown in Figs 96.2 and 96.3. The fractional

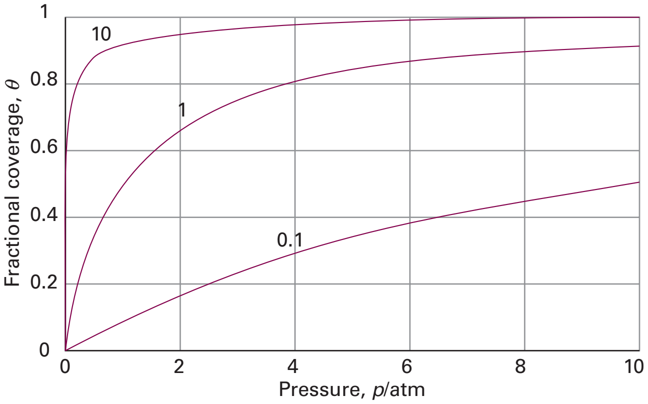

Figure 96.2 The Langmuir isotherm for dissociative adsorption, $X_2(g) \rightarrow 2\,X(\text{surface})$, for different values of α.

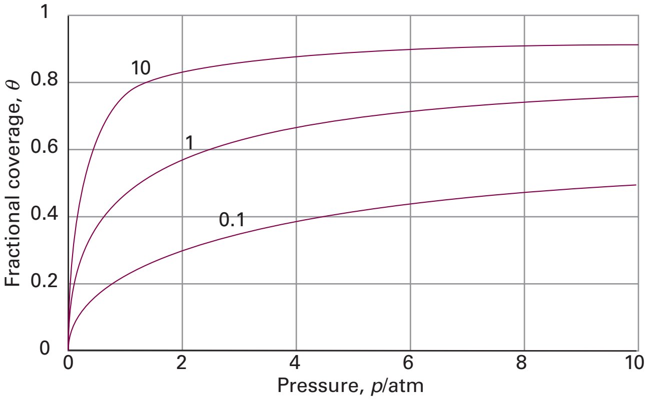

Figure 96.3 The Langmuir isotherm for non-dissociative adsorption for different values of α.

coverage increases with increasing pressure, and approaches 1 only at very high pressure, when the gas is forced on to every available site of the surface.

(b) The isosteric enthalpy of adsorption

The Langmuir isotherm is different for different temperatures. Because its form depends on the value of α, that parameter depends on the temperature. As we show in the following *Justification*, the temperature dependence of α can be used to determine the **isosteric enthalpy of adsorption**, $\Delta_{\text{ad}}H^{\ominus}$, the standard enthalpy of adsorption at a fixed surface coverage:

$$\left(\frac{\partial \ln(\alpha p^{\ominus})}{\partial T}\right)_{\theta} = \frac{\Delta_{\text{ad}}H^{\ominus}}{RT^2} \qquad (96.5)$$

Isosteric enthalpy of adsorption

Justification 96.1 The isosteric enthalpy of adsorption

According to the Arrhenius equation (Topic 85), the rate constants k_a and k_d may be written as

$$k_a = A_{\text{ad}}e^{-E_{\text{a,ad}}/RT} \qquad k_d = A_{\text{des}}e^{-E_{\text{a,des}}/RT}$$

where $E_{\text{a,ad}}$ and $E_{\text{a,des}}$ are, respectively, the activation energies of adsorption and desorption. It follows from eqn 96.2 that

$$\alpha = \frac{k_a}{k_d} = \frac{A_{\text{ad}}e^{-E_{\text{a,ad}}/RT}}{A_{\text{des}}e^{-E_{\text{a,des}}/RT}} = \frac{A_{\text{ad}}}{A_{\text{des}}}e^{-(E_{\text{a,ad}}-E_{\text{a,des}})/RT}$$

From Fig. 96.4 we see that $\Delta_{\text{ad}}H^{\ominus} = E_{\text{ad}} - E_{\text{des}}$. It follows that

$$\alpha = \frac{A_{\text{ad}}}{A_{\text{des}}}e^{-\Delta_{\text{ad}}H^{\ominus}/RT}$$

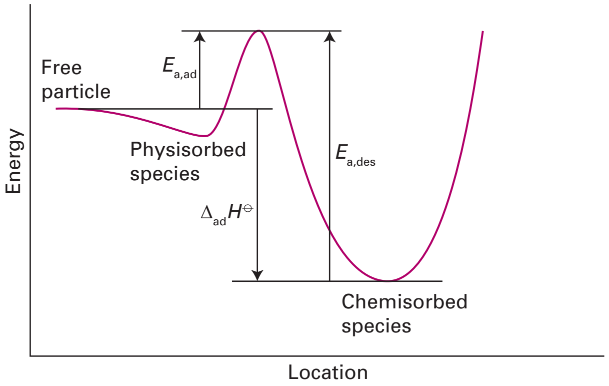

Figure 96.4 The reaction profile for adsorption (the process from left to right along the reaction coordinate) and desorption (the process from right to left). Note that $\Delta_{\text{ad}}H^{\ominus} = E_{\text{a,ad}} - E_{\text{a,des}}$.

Before manipulating this expression further, we need to pay attention to units, noting that α has dimensions of 1/pressure. To render both sides of the equation unitless, we multiply through by the standard pressure $p^{\ominus}$:

$$\alpha p^{\ominus} = \frac{A_{\text{ad}}}{A_{\text{des}}}p^{\ominus}e^{-\Delta_{\text{ad}}H^{\ominus}/RT}$$

Now we can write

$$\ln(\alpha p^{\ominus}) = \ln\left(\frac{A_{\text{ad}}}{A_{\text{des}}}p^{\ominus}\right) - \frac{\Delta_{\text{ad}}H^{\ominus}}{RT}$$

Because the term $(A_{\text{ad}}/A_{\text{des}})p^{\ominus}$ does not depend on temperature, differentiation of this expression with respect to T using $\mathrm{d}(1/T)/\mathrm{d}T = -1/T^2$, and treating $\Delta_{\text{ad}}H^{\ominus}$ as independent of temperature, while keeping the surface coverage constant, gives eqn 96.5.

Example 96.2 Measuring the isosteric enthalpy of adsorption

The data below show the pressures of CO needed for the volume of adsorption (corrected to 1 atm and 0 °C) to be 10.0 cm^3, using the same sample as in Example 96.1. In this case, there is no dissociation. Calculate the adsorption enthalpy at this surface coverage.

T/K	200	210	220	230	240	250
p/kPa	4.00	4.95	6.03	7.20	8.47	9.85

Method The Langmuir isotherm for adsorption without dissociation (eqn 96.2), can be rearranged to

$$\alpha p = \frac{\theta}{1-\theta}$$

which is a constant when θ is constant. Again we need to guard against problems with units as we manipulate expressions, and in this case it will prove useful to multiply and divide the left-hand side of the expression above by $p^\ominus$, then rearrange it to

$$(\alpha p^\ominus)(p/p^\ominus) = \text{constant}$$

and, using $\ln xy = \ln x + \ln y$, to

$$\ln\{(ap^\ominus)(p/p^\ominus)\} = \ln(ap^\ominus) + \ln(p/p^\ominus) = \text{constant}$$

It follows from eqn 96.5 that

$$\left(\frac{\partial \ln\left(p/p^\ominus\right)}{\partial T}\right)_\theta = -\left(\frac{\partial \ln\left(\alpha p^\ominus\right)}{\partial T}\right)_\theta = -\frac{\Delta_{\text{ad}}H^\ominus}{RT^2}$$

With $\mathrm{d}(1/T)/\mathrm{d}T = -1/T^2$, this expression rearranges to

$$\left(\frac{\partial \ln\left(p/p^\ominus\right)}{\partial (1/T)}\right)_\theta = \frac{\Delta_{\text{ad}}H^\ominus}{R}$$

Therefore, a plot of $\ln(p/p^\ominus)$ against $1/T$ should be a straight line of slope $\Delta_{\text{ad}}H^\ominus/R$.

Answer With $p^\ominus = 1\ \text{bar} = 10^2\ \text{kPa}$, we draw up the following table:

T/K	200	210	220	230	240	250
$10^3/(T/\text{K})$	5.00	4.76	4.55	4.35	4.17	4.00
$(p/p^\ominus)\times 10^2$	4.00	4.95	6.03	7.20	8.47	9.85
$\ln(p/p^\ominus)$	−3.22	−3.01	−2.81	−2.63	−2.47	−2.32

The points are plotted in Fig. 96.5. The slope (of the least-squares fitted line) is −0.904, so

$$\Delta_{\text{ad}}H^\ominus = -(0.904\times 10^3\ \text{K})\times R = -7.52\ \text{kJ mol}^{-1}$$

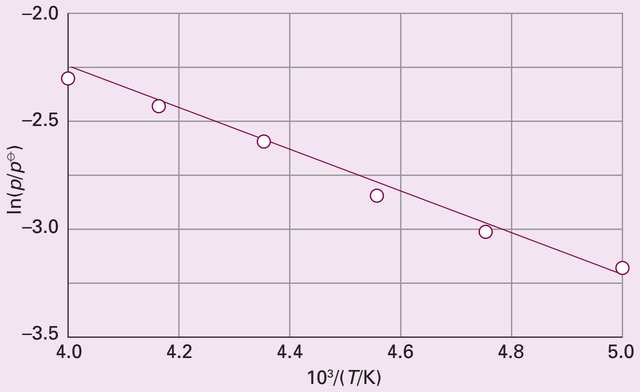

Figure 96.5 The isosteric enthalpy of adsorption can be obtained from the slope of the plot of $\ln(p/p^\ominus)$ against $1/T$, where p is the pressure needed to achieve the specified surface coverage. The data used are from Example 96.2.

Self-test 96.2 Repeat the calculation using the following data:

T/K	200	210	220	230	240	250
p/kPa	4.32	5.59	7.07	8.80	10.67	12.80

Answer: −9.0 kJ mol^{-1}

Two assumptions of the Langmuir isotherm are the independence and equivalence of the adsorption sites. Deviations from the isotherm can often be traced to the failure of these assumptions. For example, the enthalpy of adsorption often becomes less negative as θ increases, which suggests that the energetically most favourable sites are occupied first. Also, substrate–substrate interactions on the surface can be important. A number of isotherms have been developed to deal with cases where deviations from the Langmuir isotherm are important.

(c) The BET isotherm

If the initial adsorbed layer can act as a substrate for further (for example, physical) adsorption, then, instead of the isotherm levelling off to some saturated value at high pressures, it can be expected to rise indefinitely. The most widely used isotherm dealing with multilayer adsorption was derived by Stephen Brunauer, Paul Emmett, and Edward Teller and is called the **BET isotherm**:

$$\frac{V}{V_{\text{mon}}} = \frac{cz}{(1-z)\{1-(1-c)z\}} \quad \text{with} \quad z = \frac{p}{p^*} \qquad \text{BET isotherm} \qquad (96.6)$$

In this expression, which is obtained in the following *Justification*, p^* is the vapour pressure above a layer of adsorbate that is more than one molecule thick and which resembles a pure bulk liquid, V_{mon} is the volume corresponding

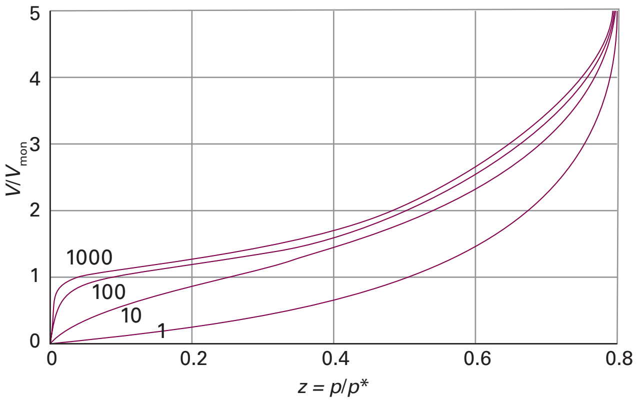

Figure 96.6 Plots of the BET isotherm for different values of *c*. The value of V/V_{mon} rises indefinitely because the adsorbate may condense on the covered substrate surface.

to monolayer coverage, and *c* is a constant which is large when the enthalpy of desorption from a monolayer is large compared with the enthalpy of vaporization of the liquid adsorbate:

$$c = \mathrm{e}^{(\Delta_{\text{des}}H^{\ominus} - \Delta_{\text{vap}}H^{\ominus})/RT} \tag{96.7}$$

Figure 96.6 illustrates the shapes of BET isotherms. They rise indefinitely as the pressure is increased because there is no limit to the amount of material that may condense when multilayer coverage is possible. A BET isotherm is not accurate at all pressures, but it is widely used in industry to determine the surface areas of solids.

Justification 96.2 The BET isotherm

We suppose that at equilibrium a fraction θ_0 of the surface sites are unoccupied, a fraction θ_1 is covered by a monolayer, a fraction θ_2 is covered by a bilayer, and so on. The number of adsorbed molecules is therefore

$$N = N_{\text{sites}}(\theta_1 + 2\theta_2 + 3\theta_3 + \cdots)$$

where N_{sites} is the total number of sites. We now follow the derivation that led to the Langmuir isotherm (eqn 96.2) but allow for different rates of desorption from the substrate and the various layers:

First layer:	Rate of adsorption $= Nk_{\text{a},0}p\theta_0$	Rate of desorption $= Nk_{\text{d},0}\theta_1$
	At equilibrium $k_{\text{a},0}p\theta_0 = k_{\text{d},0}\theta_1$	
Second layer:	Rate of adsorption $= Nk_{\text{a},1}p\theta_1$	Rate of desorption $= Nk_{\text{d},1}\theta_2$
	At equilibrium $k_{\text{a},1}p\theta_1 = k_{\text{d},1}\theta_2$	
Third layer:	Rate of adsorption $= Nk_{\text{a},2}p\theta_2$	Rate of desorption $= Nk_{\text{d},2}\theta_3$
	At equilibrium $k_{\text{a},2}p\theta_2 = k_{\text{d},2}\theta_3$	

and so on. We now suppose that once a monolayer has been formed, all the rate constants involving adsorption and desorption from the physisorbed layers are the same, and write these equations as

$$\begin{aligned}
&k_{\text{a},0}p\theta_0 = k_{\text{d},0}\theta_1, \text{ so}\\
&\qquad \theta_1 = (k_{\text{a},0}/k_{\text{d},0})p\theta_0 = \alpha_0 p\theta_0\\
&k_{\text{a},1}p\theta_1 = k_{\text{d},1}\theta_2, \text{ so}\\
&\qquad \theta_2 = (k_{\text{a},1}/k_{\text{d},1})p\theta_1 = (k_{\text{a},0}/k_{\text{d},0})(k_{\text{a},1}/k_{\text{d},1})p^2\theta_0 = \alpha_0\alpha_1 p^2\theta_0\\
&k_{\text{a},1}p\theta_2 = k_{\text{d},1}\theta_3, \text{ so}\\
&\qquad \theta_3 = (k_{\text{a},1}/k_{\text{d},1})p\theta_2 = (k_{\text{a},0}/k_{\text{d},0})(k_{\text{a},1}/k_{\text{d},1})^2 p^3\theta_0 = \alpha_0\alpha_1^2 p^3\theta_0
\end{aligned}$$

and so on, with $\alpha_0 = k_{\text{a},0}/k_{\text{d},0}$ and $\alpha_1 = k_{\text{a},1}/k_{\text{d},1}$ the ratios of rate constants for adsorption to the substrate and an overlayer, respectively. Now, because $\theta_0 + \theta_1 + \theta_2 + \cdots = 1$, it follows that

$$\begin{aligned}
&\theta_0 + \alpha_0 p\theta_0 + \alpha_0\alpha_1 p^2\theta_0 + \alpha_0\alpha_1^2 p^3\theta_0 + \cdots\\
&\quad = \theta_0 + \alpha_0 p\theta_0\{1 + \alpha_1 p + \alpha_1^2 p^2 + \cdots\} = \left\{1 + \frac{\alpha_0 p}{1-\alpha_1 p}\right\}\theta_0\\
&\quad = \left\{\frac{1-\alpha_1 p + \alpha_0 p}{1-\alpha_1 p}\right\}\theta_0
\end{aligned}$$

We have used $1 + x + x^2 + \cdots = 1/(1-x)$. Then, because this expression is equal to 1,

$$\theta_0 = \frac{1-\alpha_1 p}{1-(\alpha_1-\alpha_0)p}$$

In a similar way, we can write the number of adsorbed species as

$$\begin{aligned}
N &= N_{\text{sites}}\alpha_0 p\theta_0 + 2N_{\text{sites}}\alpha_0\alpha_1 p^2\theta_0 + \cdots\\
&= N_{\text{sites}}\alpha_0 p\theta_0(1 + 2\alpha_1 p + 3\alpha_1^2 p^2 + \cdots) = \frac{N_{\text{sites}}\alpha_0 p\theta_0}{(1-\alpha_1 p)^2}
\end{aligned}$$

In this case, we have used $1 + 2x + 3x^2 + \cdots = 1/(1-x)^2$. By combining the last two expressions, we obtain

$$N = \frac{N_{\text{sites}}\alpha_0 p}{(1-\alpha_1 p)^2} \times \frac{1-\alpha_1 p}{1-(\alpha_1-\alpha_0)p} = \frac{N_{\text{sites}}\alpha_0 p}{(1-\alpha_1 p)\{1-(\alpha_1-\alpha_0)p\}}$$

The ratio N/N_{sites} is equal to the ratio V/V_{mon}, where V is the total volume adsorbed and V_{mon} the volume adsorbed had there been complete monolayer coverage. The term $\alpha_1 = k_{\text{a},1}/k_{\text{d},1}$ can be interpreted as the (reciprocal of the) equilibrium constant for condensation and evaporation from the adsorbed layers, and hence can be equated with the reciprocal of the vapour pressure p^* of the liquid phase of the adsorbing substance. It follows that $\alpha_1 = 1/p^*$. With $z = p/p^*$, and $c = \alpha_0/\alpha_1$, the last equation becomes

$$\frac{V}{V_{\text{mon}}} = \frac{\alpha_0 p}{(1-p/p^*)\{1-(1-\alpha_0/\alpha_1)p/p^*\}} = \frac{cz}{(1-z)\{1-(1-c)z\}}$$

as in eqn 96.6.

The same model leads to eqn 96.7. As in *Justification* 96.1, the ratio α is related to the enthalpy of adsorption. So we can write

$$\alpha_0 = \frac{A_{\text{ad}}}{A_{\text{des}}}\mathrm{e}^{-\Delta_{\text{ad}}H^{\ominus}/RT} = \frac{A_{\text{ad}}}{A_{\text{des}}}\mathrm{e}^{\Delta_{\text{des}}H^{\ominus}/RT}$$

where we have used $\Delta_{\text{des}}H^{\ominus} = -\Delta_{\text{ad}}H^{\ominus}$. We handle desorption from a bilayer differently because adsorbate–adsorbate interactions (not surface–adsorbate interactions) are disrupted. Again modelling desorption from a bilayer as vaporization of a liquid, we use $\Delta_{\text{vap}}H^{\ominus} = -\Delta_{\text{ad}}H^{\ominus}$ and write

$$\alpha_1 = \frac{A_{\text{ad}}}{A_{\text{des}}}\mathrm{e}^{-\Delta_{\text{ad}}H^{\ominus}/RT} = \frac{A_{\text{ad}}}{A_{\text{des}}}\mathrm{e}^{\Delta_{\text{vap}}H^{\ominus}/RT}$$

The ratio c then becomes

$$c = \frac{\alpha_0}{\alpha_1} = \frac{\mathrm{e}^{\Delta_{\text{des}}H^{\ominus}/RT}}{\mathrm{e}^{\Delta_{\text{vap}}H^{\ominus}/RT}} = \mathrm{e}^{(\Delta_{\text{des}}H^{\ominus} - \Delta_{\text{vap}}H^{\ominus})/RT}$$

as in eqn 96.7.

Example 96.3 Using the BET isotherm

The data below relate to the adsorption of N_2 on rutile (TiO_2) at 75 K. Confirm that they fit a BET isotherm in the range of pressures reported, and determine V_{mon} and c.

p/kPa	0.160	1.87	6.11	11.67	17.02	21.92	27.29
V/mm^3	601	720	822	935	1046	1146	1254

At 75 K, $p^* = 76.0$ kPa. The volumes have been corrected to 1.00 atm and 273 K and refer to 1.00 g of substrate.

Method Equation 96.6 can be reorganized into

$$\frac{z}{(1-z)V} = \frac{1}{cV_{\text{mon}}} + \frac{(c-1)z}{cV_{\text{mon}}}$$

It follows that $(c-1)/cV_{\text{mon}}$ can be obtained from the slope of a plot of the expression on the left against z, and cV_{mon} can be found from the intercept at $z = 0$. The results can then be combined to give c and V_{mon}.

Answer We draw up the following table:

p/kPa	0.160	1.87	6.11	11.67	17.02	21.92	27.29
$10^3 z$	2.11	24.6	80.4	154	224	288	359
$10^4 z/((1-z)(V/\text{mm}^3))$	0.035	0.350	1.06	1.95	2.76	3.53	4.47

These points are plotted in Fig. 96.7. The least-squares best line has an intercept at 0.0398, so

$$\frac{1}{cV_{\text{mon}}} = 3.98 \times 10^{-6}\,\text{mm}^{-3}$$

The slope of the line is 1.23×10^{-2}, so

$$\frac{c-1}{cV_{\text{mon}}} = (1.23 \times 10^{-2}) \times 10^3 \times 10^{-4}\,\text{mm}^{-3} = 1.23 \times 10^{-3}\,\text{mm}^{-3}$$

The solutions of these equations are $c = 310$ and $V_{\text{mon}} = 811$ mm^3. At 1.00 atm and 273 K, 811 mm^3 corresponds to 3.6×10^{-5} mol, or 2.2×10^{19} atoms. Because each atom occupies an area of about 0.16 nm^2, the surface area of the sample is about 3.5 m^2.

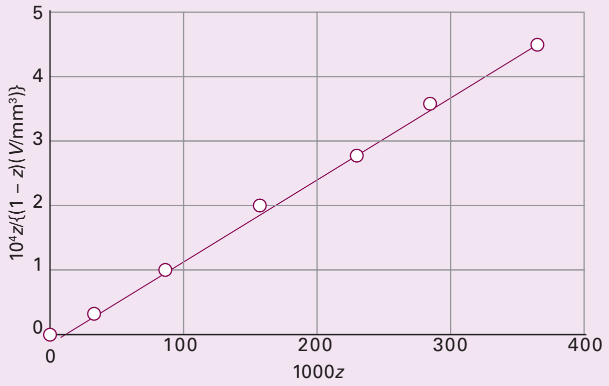

Figure 96.7 The BET isotherm can be tested, and the parameters determined, by plotting $z/(1-z)V$ against $z = p/p^*$. The data are from Example 96.3.

Self-test 96.3 Repeat the calculation for the following data:

p/kPa	0.160	1.87	6.11	11.67	17.02	21.92	27.29
V/cm^3	235	559	649	719	790	860	950

Answer: 370; 615 cm^3

When $c \gg 1$, the BET isotherm takes the simpler form

$$\frac{V}{V_{\text{mon}}} = \frac{1}{1-z} \qquad \text{BET isotherm when } c \gg 1 \qquad (96.8)$$

This expression is applicable to unreactive gases on polar surfaces, for which $c \approx 10^2$ because $\Delta_{\text{des}}H^{\ominus}$ is then significantly greater than $\Delta_{\text{vap}}H^{\ominus}$ (eqn 96.7). The BET isotherm fits experimental observations moderately well over restricted pressure ranges, but it errs by underestimating the extent of adsorption at low pressures and by overestimating it at high pressures.

Different isotherms agree with experiment more or less well over restricted ranges of pressure, but they remain largely empirical. Empirical, however, does not mean useless for, if the parameters of a reasonably reliable isotherm are known, reasonably reliable results can be obtained for the extent of surface coverage under various conditions. This kind of information is essential for any discussion of heterogeneous catalysis (Topic 97).

96.2 The rates of adsorption and desorption

We have noted that adsorption and desorption are activated processes, in the sense that they have an activation energy and follow Arrhenius behaviour. Now we are ready to look more closely at the origin of the activation energy in these processes, with a special focus on chemisorption.

(a) The precursor state

Figure 96.8 shows how the potential energy of a molecule varies with its distance from the substrate surface. As the molecule approaches the surface its energy falls as it becomes physisorbed into the **precursor state** for chemisorption (see Topic 95). Dissociation into fragments often takes place as a molecule moves into its chemisorbed state, and, after an initial increase of energy as the bonds stretch, there is a sharp decrease as the adsorbate–substrate bonds reach their full strength. Even if the molecule does not fragment, there is likely to be an initial increase of potential energy as the molecule approaches the surface and the bonds adjust.

In most cases, therefore, we can expect there to be a potential energy barrier separating the precursor and chemisorbed states. This barrier, though, might be low, and might not rise above the energy of a distant, stationary particle (as in Fig. 96.8a). In this case, chemisorption is not an activated process and can be expected to be rapid. Many gas adsorptions on clean metals appear to be non-activated. In some cases, however, the barrier rises above the zero axis (as in Fig. 96.8b); such chemisorptions are activated and slower than the non-activated kind. An example is H_2 on copper, which has an activation energy in the region of 20–40 kJ mol^{-1}.

One point that emerges from this discussion is that rates are not good criteria for distinguishing between physisorption and chemisorption. Chemisorption can be fast if the activation energy is small or zero, but it may be slow if the activation energy is large. Physisorption is usually fast, but it can appear to be slow if adsorption is taking place on a porous medium.

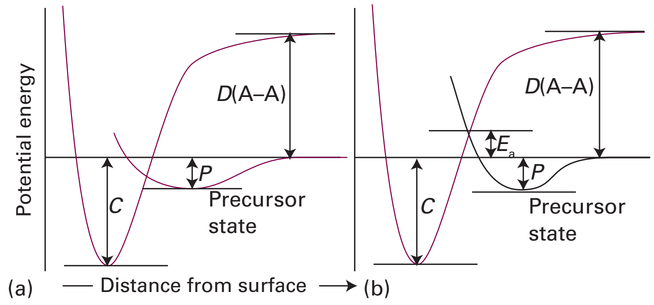

Figure 96.8 The potential energy profiles for the dissociative chemisorption of an A_2 molecule. In each case, P is the enthalpy of (non-dissociative) physisorption and C that for chemisorption (at $T=0$). The relative locations of the curves determine whether the chemisorption is (a) not activated or (b) activated.

Brief illustration 96.1 The rate of activated adsorption

Consider two adsorption experiments for hydrogen on different faces of a copper crystal. In one, Face 1, the activation energy is 28 kJ mol^{-1} and on the other, Face 2, the activation energy is 33 kJ mol^{-1}. The ratio of the rates of chemisorption on equal areas of the two faces at 250 K is

$$\frac{\text{Rate}(1)}{\text{Rate}(2)}=\frac{A\mathrm{e}^{-E_{\mathrm{a,ads}}(1)/RT}}{A\mathrm{e}^{-E_{\mathrm{a,ads}}(2)/RT}}=\mathrm{e}^{-\{E_{\mathrm{a,ads}}(1)-E_{\mathrm{a,ads}}(2)\}/RT}$$
$$=\mathrm{e}^{5\times10^{3}\,\mathrm{J\,mol^{-1}}/(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(250\,\mathrm{K})}=11$$

We have assumed that the A factor is the same for each face.

Self-test 96.4 What are the relative rates when the temperature is increased to 300 K?

Answer: 7

(b) Adsorption and desorption at the molecular level

The rate at which a surface is covered by adsorbate depends on the ability of the substrate to dissipate the energy of the incoming particle as thermal motion as it crashes on to the surface. If the energy is not dissipated quickly, the particle migrates over the surface until a vibration expels it into the overlying gas or it reaches an edge. The proportion of collisions with the surface that successfully lead to adsorption is called the **sticking probability**, s:

$$s=\frac{\text{rate of adsorption of particles by the surface}}{\text{rate of collision of particles with the surface}}$$

Definition Sticking probability (96.9)

The denominator can be calculated from the kinetic model, and the numerator can be measured by observing the rate of change of pressure.

Values of s vary widely. For example, at room temperature CO has s in the range 0.1–1.0 for several d-metal surfaces, but for N_2 on rhenium $s<10^{-2}$, indicating that more than a hundred collisions are needed before one molecule sticks successfully. Beam studies on specific crystal planes show a pronounced specificity: for N_2 on tungsten, s ranges from 0.74 on the (320) faces down to less than 0.01 on the (110) faces at room temperature. The sticking probability decreases as the surface coverage increases (Fig. 96.9). A simple assumption is that s is proportional to $1-\theta$, the fraction uncovered, and it is common to write

$$s=(1-\theta)s_0$$

Commonly used form of the sticking probability (96.10)

where s_0 is the sticking probability on a perfectly clean surface. The results in the illustration do not fit this expression because

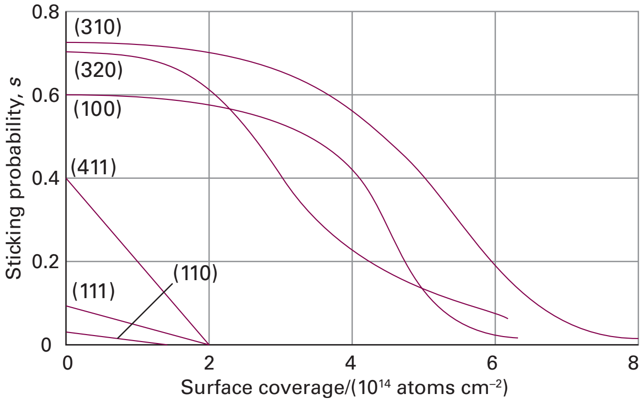

Figure 96.9 The sticking probability of N_2 on various faces of a tungsten crystal and its dependence on surface coverage. Note the very low sticking probability for the (110) and (111) faces. (Data provided by Professor D.A. King.)

they show that s remains close to s_0 until the coverage has risen to about 6×10^{13} molecules cm^{-2}, and then falls steeply. The explanation is probably that the colliding molecule does not enter the chemisorbed state at once, but moves over the surface until it encounters an empty site.

Desorption is always activated because the particles have to be lifted from the foot of a potential well. A physisorbed particle vibrates in its shallow potential well, and might shake itself off the surface after a short time. As we saw in *Justification* 96.1, the temperature dependence of the first-order rate of departure is given by $k_\mathrm{d}=A\mathrm{e}^{-E_\mathrm{a,des}/RT}$, with $E_\mathrm{a,des}$ the activation energy for desorption. Therefore, the half-life for remaining on the surface has a temperature dependence

$$t_{1/2}=\frac{\ln 2}{k_\mathrm{d}}=\tau_0\mathrm{e}^{E_\mathrm{a,des}/RT} \qquad \tau_0=\frac{\ln 2}{A} \qquad \text{Residence half-life} \qquad (96.11)$$

Note the positive sign in the exponent: the greater the activation energy for desorption, the larger the residence half-life.

Brief illustration 96.2 Residence half-lives

If we suppose that $1/\tau_0$ is approximately the same as the vibrational frequency of the weak particle–surface bond (about 10^{12} Hz) and $E_\mathrm{d}\approx25$ kJ mol^{-1}, then residence half-lives of around 10 ns are predicted at room temperature. Lifetimes close to 1 s are obtained only by lowering the temperature to about 100 K. For chemisorption, with $E_\mathrm{d}=100$ kJ mol^{-1} and guessing that $\tau_0=10^{-14}$ s (because the adsorbate–substrate bond is quite stiff), we expect a residence half-life of about 3×10^{3} s (about an hour) at room temperature, decreasing to 1 s at about 350 K.

Self-test 96.5 For how long on average would an atom remain on a surface at 800 K if its desorption activation energy is 200 kJ mol^{-1}? Take $\tau_0=0.10$ ps.

Answer: $t_{1/2}=1.3$ s

The desorption activation energy can be measured in several ways. However, we must be guarded in its interpretation because it often depends on the fractional coverage, and so may change as desorption proceeds. Moreover, the transfer of concepts such as 'reaction order' and 'rate constant' from bulk studies to surfaces is hazardous, and there are few examples of strictly first-order or second-order desorption kinetics (just as there are few integral-order reactions in the gas phase too).

If we disregard these complications, one way of measuring the desorption activation energy is to monitor the rate of increase in pressure when the sample is maintained at a series of temperatures, and to attempt to make an Arrhenius plot. A more sophisticated technique is **temperature-programmed desorption** (TPD) or **thermal desorption spectroscopy** (TDS). The basic observation is a surge in desorption rate (as monitored by a mass spectrometer) when the temperature is raised linearly to the temperature at which desorption occurs rapidly, but once the desorption has occurred there is no more adsorbate to escape from the surface, so the desorption flux falls again as the temperature continues to rise. The TPD spectrum, the plot of desorption flux against temperature, therefore shows a peak, the location of which depends on the desorption activation energy. There are three maxima in the example shown in Fig. 96.10, indicating the presence of three sites with different activation energies.

In many cases only a single activation energy (and a single peak in the TPD spectrum) is observed. When several peaks are observed they might correspond to adsorption on different crystal planes or to multilayer adsorption. For instance, Cd atoms on tungsten show two activation energies, one of 18 kJ mol^{-1} and the other of 90 kJ mol^{-1}. The explanation is that the more tightly bound Cd atoms are attached directly to the substrate, and the less strongly bound are in a layer

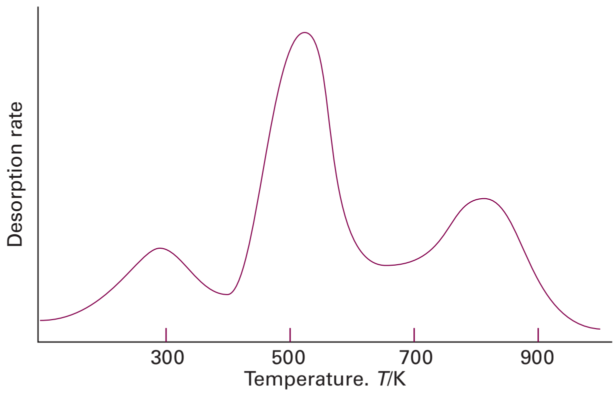

Figure 96.10 The flash desorption spectrum of H_2 on the (100) face of tungsten. The three peaks indicate the presence of three sites with different adsorption enthalpies and therefore different desorption activation energies (P.W. Tamm and L.D. Schmidt, *J. Chem. Phys.* **51**, 5352 (1969)).

(or layers) above the primary overlayer. Another example of a system showing two desorption activation energies is CO on tungsten, the values being 120 kJ mol^{-1} and 300 kJ mol^{-1}. The explanation is believed to be the existence of two types of metal–adsorbate binding site, one involving a simple M—CO bond, the other adsorption with dissociation into individually adsorbed C and O atoms.

(c) Mobility on surfaces

A further aspect of the strength of the interactions between adsorbate and substrate is the mobility of the adsorbate. Mobility is often a vital feature of a catalyst's activity, because a catalyst might be impotent if the reactant molecules adsorb so strongly that they cannot migrate. The activation energy for diffusion over a surface need not be the same as for desorption because the particles may be able to move through valleys between potential peaks without leaving the surface completely. In general, the activation energy for migration is about 10–20 per cent of the energy of the surface–adsorbate bond, but the actual value depends on the extent of coverage. The defect structure of the sample (which depends on the temperature) may also play a dominant role because the adsorbed molecules might find it easier to skip across a terrace than to roll along the foot of a step, and these molecules might become trapped in vacancies in an otherwise flat terrace. Diffusion may also be easier across one crystal face than another, and so the surface mobility depends on which lattice planes are exposed.

Checklist of concepts

☐ 1. An **adsorption isotherm** is the variation of the surface coverage θ with pressure at a chosen temperature.
☐ 2. Examples of adsorption isotherms include the **Langmuir** and **BET** isotherms.
☐ 3. The **sticking probability** is the proportion of collisions with the surface that successfully lead to adsorption.
☐ 4. Desorption is an activated process; the desorption activation energy is measured by **temperature-programmed desorption** or **thermal desorption spectroscopy**.
☐ 5. The mobility of adsorbates on a surface is dominated by diffusion.

Checklist of equations

Property	Equation	Comment	Equation number
Langmuir isotherm:		Independent and equivalent sites, monolayer coverage	
(a) without dissociation	$\theta = \alpha p/(1+\alpha p)$		96.2
(b) with dissociation	$\theta = (\alpha p)^{1/2}/\{1+(\alpha p)^{1/2}\}$		96.4
Isosteric enthalpy of adsorption	$(\partial \ln(\alpha p^{\ominus})/\partial T)_{\theta} = \Delta_{\mathrm{ad}}H^{\ominus}/RT^2$		96.5
BET isotherm	$V/V_{\mathrm{mon}} = cz/(1-z)\{1-(1-c)z\}$, $z = p/p^{*}, c = \mathrm{e}^{(\Delta_{\mathrm{des}}H^{\ominus}-\Delta_{\mathrm{vap}}H^{\ominus})/RT}$	Multilayer adsorption	96.6–96.7
Sticking probability	$s = (1-\theta)s_0$	Approximate form	96.10

TOPIC 97

Heterogeneous catalysis

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➤ Why do we need to know this material?

Catalysis is at the heart of the chemical industry, and an understanding of the concepts is essential for developing new catalysts.

➤ What is the key idea?

In heterogeneous catalysis, the pathway for lowering the activation energy of a reaction commonly involves chemisorption of one or more reactants.

➤ What do we need to know already?

Catalysis is introduced in Topics 85 and 92. This Topic builds on the discussion of reaction mechanisms (Topic 86), the Arrhenius equation (Topic 85), and adsorption isotherms (Topic 96).

A **heterogeneous catalyst** is a catalyst in a different phase from the reaction mixture. For example, the hydrogenation of ethene to ethane, a gas-phase reaction, is accelerated in the presence of a solid catalyst such as palladium, platinum, or nickel. The metal provides a surface to which the reactants bind; this binding facilitates encounters between reactants and increases the rate of the reaction. This Topic is an exploration of catalytic activity on surfaces, building on the concepts developed in Topic 96.

97.1 Mechanisms of heterogeneous catalysis

Many catalysts depend on **co-adsorption**, the adsorption of two or more species. One consequence of the presence of a second species may be the modification of the electronic structure at the surface of a metal. For instance, partial coverage of d-metal surfaces by alkali metals has a pronounced effect on the electron distribution at the surface and reduces the work function of the metal (the energy needed to remove an electron; see Topic 4). Such modifiers can act as promoters (to enhance the action of catalysts) or as poisons (to inhibit catalytic action).

Figure 97.1 shows the potential energy curve for a reaction influenced by the action of a heterogeneous catalyst. Differences between Fig. 97.1 and Fig. 92.1 arise from the fact that heterogeneous catalysis normally depends on at least one reactant being adsorbed (usually chemisorbed) and modified to an **active phase** in which it readily undergoes reaction, and desorption of products. Modification of the reactant often takes the form of a fragmentation of the reactant molecules. In practice, the active phase is dispersed as very small particles of linear dimension less than 2 nm on a porous oxide support. **Shape-selective catalysts**, such as the zeolites, which have a pore size that can distinguish shapes and sizes at a molecular scale, have high internal specific surface areas, in the range of 100–500 $m^2\ g^{-1}$.

Mechanisms of reactions catalysed by surfaces can be treated quantitatively by using the techniques of Topic 86 and the adsorption isotherms developed in Topic 96. Here we explore some simple mechanisms that can give significant insight into surface-catalysed reactions.

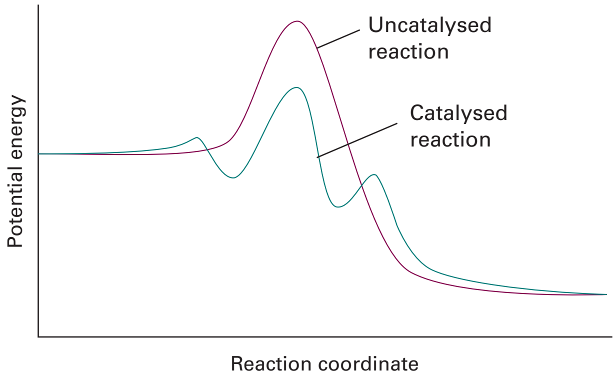


Figure 97.1 The reaction profile for catalysed and uncatalysed reactions. The catalysed reaction path includes activation energies for adsorption and desorption as well as an overall lower activation energy for the process.

(a) Unimolecular reactions

The rate law of a surface-catalysed unimolecular reaction, such as the decomposition of a substance on a surface, can be written in terms of an adsorption isotherm if the rate is supposed to be proportional to the surface coverage. For example, if θ is given by the Langmuir isotherm (eqn 96.2), we would write

$$v = k_r\theta = \frac{k_r\alpha p}{1+\alpha p} \qquad (97.1)$$

where p is the pressure of the adsorbing substance.

Brief illustration 97.1 Surface-catalysed unimolecular decomposition

Consider the decomposition of phosphine (PH_3) on tungsten, which is first-order at low pressures. We can use eqn 97.1 to account for this observation. When the pressure is so low that $\alpha p \ll 1$, we can neglect αp in the denominator of eqn 97.1 and obtain $v = k_r\alpha p$. The decomposition is predicted to be first-order, as observed experimentally.

Self-test 97.1 Write a rate law for the decomposition of PH_3 on tungsten at high pressures.

Answer: $v = k_r$; the reaction is zeroth-order at high pressures

(b) The Langmuir–Hinshelwood mechanism

In the **Langmuir–Hinshelwood mechanism** (LH mechanism) of surface-catalysed reactions, the reaction takes place by encounters between molecular fragments and atoms adsorbed on the surface. We therefore expect the rate law to be second-order in the extent of surface coverage:

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{P} \quad v = k_r\theta_A\theta_B \qquad (97.2)$$

Langmuir–Hinshelwood rate law

Insertion of the appropriate isotherms for A and B then gives the reaction rate in terms of the partial pressures of the reactants.

Example 97.1 Writing a rate law based on the Langmuir–Hinshelwood mechanism

Consider a reaction $\mathrm{A}+\mathrm{B}\rightarrow\mathrm{P}$ in which A and B follow Langmuir isotherms and adsorb without dissociation. Devise a rate law that is consistent with the Langmuir–Hinshelwood mechanism.

Method Begin by following the procedures outlined in Topic 96 for the derivation of the Langmuir isotherm to write expressions for θ_A and θ_B, the fractional coverages of A and B, respectively. However, note that, unlike the simple situation in Topic 96, two species compete for the same sites on the surface. Then, use equation 97.2 to express the rate law.

Answer Because two species compete for sites on the surface, the number of vacant sites is equal to $N(1-\theta_A-\theta_B)$, where N is the total number of sites. It follows from eqns 96.1a and 96.1b that the rates of adsorption and desorption are given by

$$\begin{aligned}\text{Rate of adsorption of A} &= k_{a,A}p_A N(1-\theta_A-\theta_B)\\ \text{Rate of desorption of A} &= k_{d,A}N\theta_A\\ \text{Rate of adsorption of B} &= k_{a,B}p_B N(1-\theta_A-\theta_B)\\ \text{Rate of desorption of B} &= k_{d,B}N\theta_B\end{aligned}$$

At equilibrium, the rates of adsorption and desorption for each species are equal, and, with $\alpha_A = k_{a,A}/k_{d,A}$ and $\alpha_B = k_{a,B}/k_{d,B}$, it follows that

$$\begin{aligned}\alpha_A p_A(1-\theta_A-\theta_B) &= \theta_A\\ \alpha_B p_B(1-\theta_A-\theta_B) &= \theta_B\end{aligned}$$

Solving this system of equations (see Self-test 97.2) gives

$$\theta_A = \frac{\alpha_A p_A}{1+\alpha_A p_A+\alpha_B p_B} \qquad \theta_B = \frac{\alpha_B p_B}{1+\alpha_A p_A+\alpha_B p_B} \qquad (97.3)$$

It follows from eqn 97.2 that the rate law is

$$v = \frac{k_r\alpha_A\alpha_B p_A p_B}{(1+\alpha_A p_A+\alpha_B p_B)^2} \qquad (97.4)$$

The parameters α in the isotherms and the rate constant k_r are all temperature-dependent, so the overall temperature dependence of the rate may be strongly non-Arrhenius (in the sense that the reaction rate is unlikely to be proportional to

$e^{-E_a/RT}$). The LH mechanism is dominant for the catalytic oxidation of CO to CO_2.

Self-test 97.2 Provide the missing steps in the derivation of eqn 97.3.

(c) The Eley–Rideal mechanism

In the **Eley–Rideal mechanism** (ER mechanism) of a surface-catalysed reaction, a gas-phase molecule collides with another molecule already adsorbed on the surface. The rate of formation of product is expected to be proportional to the partial pressure, p_B, of the non-adsorbed gas B and the extent of surface coverage, θ_A, of the adsorbed gas A. It follows that the rate law should be

$$A + B \rightarrow P \quad v = k_r p_B \theta_A \qquad \text{Eley–Rideal rate law} \tag{97.5}$$

The rate constant, k_r, might be much larger than for the uncatalysed gas-phase reaction because the reaction on the surface has a low activation energy and the adsorption itself is often not activated.

If we know the adsorption isotherm for A, we can express the rate law in terms of its partial pressure, p_A. For example, consider a reaction $A + B \rightarrow P$. If the adsorption of A follows a Langmuir isotherm in the pressure range of interest, then the rate law would be

$$v = \frac{k_r \alpha p_A p_B}{1 + \alpha p_A} \tag{97.6}$$

Brief illustration 97.2 The Eley–Rideal mechanism

According to eqn 97.6, when the partial pressure of A is high (in the sense $\alpha p_A \gg 1$) there is almost complete surface coverage, and the rate is equal to $k_r p_B$. Now the rate-determining step is the collision of B with the adsorbed fragments. When the pressure of A is low ($\alpha p_A \ll 1$), perhaps because of its reaction, the rate is equal to $k_r \alpha p_A p_B$; now the extent of surface coverage is important in the determination of the rate.

Self-test 97.3 Rewrite eqn 97.6 for cases where A is a diatomic molecule that adsorbs as atoms.

Answer: $v = k_r p_B (\alpha p_A)^{1/2}/(1 + (\alpha p_A)^{1/2})$

Almost all thermal surface-catalysed reactions are thought to take place by the LH mechanism, but a number of reactions with an ER mechanism have also been identified from molecular beam investigations. For example, the reaction between H(g) and D(ad) to form HD(g) is thought to be by an ER mechanism involving the direct collision and pick-up of the adsorbed D atom by the incident H atom. However, the two mechanisms should really be thought of as ideal limits, and all reactions lie somewhere between the two and show features of each one.

97.2 Catalytic activity at surfaces

It has become possible to investigate how the catalytic activity of a surface depends on its structure as well as its composition. For instance, the cleavage of C—H and H—H bonds appears to depend on the presence of steps and kinks, and a terrace often has only minimal catalytic activity. The reaction $H_2 + D_2 \rightarrow 2\,HD$ has been studied in detail. For this reaction, terrace sites are inactive but one molecule in ten reacts when it strikes a step. Although the step itself might be the important feature, it may be that the presence of the step merely exposes a more reactive crystal face (the step face itself). Likewise, the dehydrogenation of hexane to hexene depends strongly on the kink density, and it appears that kinks are needed to cleave C—C bonds. These observations suggest a reason why even small amounts of impurities may poison a catalyst: they are likely to attach to step and kink sites, and so impair the activity of the catalyst entirely. A constructive outcome is that the extent of dehydrogenation may be controlled relative to other types of reactions by seeking impurities that adsorb at kinks and act as specific poisons.

The activity of a catalyst depends on the strength of chemisorption, as indicated by the 'volcano' curve in Fig. 97.2 (which is so-called on account of its general shape). To be active, the catalyst should be extensively covered by adsorbate, which is

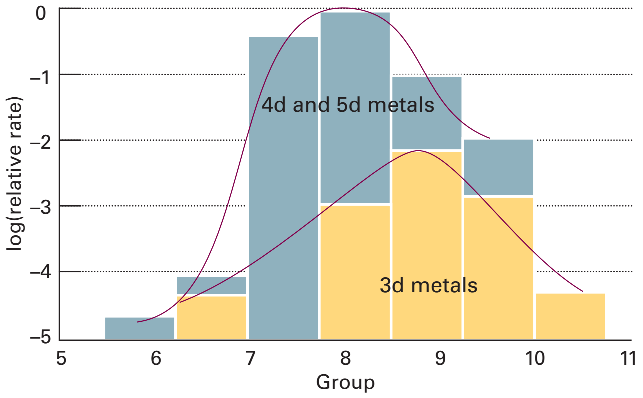


Figure 97.2 A volcano curve of catalytic activity arises because, although the reactants must adsorb reasonably strongly, they must not adsorb so strongly that they are immobilized. The lower curve refers to the first series of d-block metals, the upper curve to the second and third series of d-block metals. The group numbers relate to the periodic table inside the back cover.

Table 97.1 Chemisorption abilities*

	O_2	C_2H_2	C_2H_4	CO	H_2	CO_2	N_2
Ti, Cr, Mo, Fe	+	+	+	+	+	+	+
Ni, Co	+	+	+	+	+	+	–
Pd, Pt	+	+	+	+	+	–	–
Mn, Cu	+	+	+	+	±	–	–
Al, Au	+	+	+	–	–	–	–
Li, Na, K	+	+	–	–	–	–	–
Mg, Ag, Zn, Pb	+	–	–	–	–	–	–

* +, Strong chemisorption; ±, chemisorption; –, no chemisorption.

the case if chemisorption is strong. On the other hand, if the strength of the substrate–adsorbate bond becomes too great, the activity declines either because the other reactant molecules cannot react with the adsorbate or because the adsorbate molecules are immobilized on the surface. This pattern of behaviour suggests that the activity of a catalyst should initially increase with strength of adsorption (as measured, for instance, by the isosteric enthalpy of adsorption, Topic 96) and then decline, and that the most active catalysts should be those lying near the summit of the volcano. Most active metals are those that lie close to the middle of the d block. Many metals are suitable for adsorbing gases, and some trends are summarized in Table 97.1.

Brief illustration 97.3 Trends in chemisorption abilities

We see from Table 97.1 that for a number of metals the general order of adsorption strengths decreases along the series O_2, C_2H_2, C_2H_4, CO, H_2, CO_2, N_2. Some of these molecules adsorb dissociatively (for example, H_2). Elements from the d block, such as iron, titanium, and chromium, show a strong activity towards all these gases, but manganese and copper are unable to adsorb N_2 and CO_2. Metals towards the left of the periodic table (for example, magnesium) can adsorb (and, in fact, react with) only the most active gas (O_2).

Self-test 97.4 Why is iron a good catalyst for the formation of ammonia from N_2(g) and H_2(g)?

Answer: See Fig. 97.2 and Table 97.1

Checklist of concepts

☐ 1. A **heterogeneous catalyst** is a catalyst in a different phase from the reaction mixture.

☐ 2. In the **Langmuir–Hinshelwood mechanism** of surface-catalysed reactions, the reaction takes place by encounters between molecular fragments and atoms adsorbed on the surface.

☐ 3. In the **Eley–Rideal mechanism** of a surface-catalysed reaction, a gas-phase molecule collides with another molecule already adsorbed on the surface.

☐ 4. The activity of a catalyst depends on the strength of chemisorption.

Checklist of equations

Property	Equation	Comment	Equation number
Langmuir–Hinshelwood mechanism	$v=k_r\alpha_A\alpha_B p_A p_B/(1+\alpha_A p_A+\alpha_B p_B)^2$	Langmuir isotherm for adsorption of A and B; competitive adsorption	97.4
Eley–Rideal mechanism	$v=k_r\alpha p_A p_B/(1+\alpha p_A)$	Langmuir isotherm for adsorption of A	97.6

Focus 20 on Processes on solid surfaces

Topic 95 Solid surfaces

Discussion questions

95.1 (a) Distinguish between a step and a terrace. (b) Describe how steps and terraces can be formed by dislocations.

95.2 Drawing from knowledge you have acquired through the text, describe the advantages and limitations of each of the microscopy, diffraction, and scattering techniques designated by the acronyms AFM, FIM, LEED, SAM, SEM, and STM.

Exercises

95.1(a) Calculate the frequency of molecular collisions per square centimetre of surface in a vessel containing (i) hydrogen, (ii) propane at 25 °C when the pressure is 0.10 μTorr.

95.1(b) Calculate the frequency of molecular collisions per square centimetre of surface in a vessel containing (i) nitrogen, (ii) methane at 25 °C when the pressure is 10.0 Pa. Repeat the calculations for a pressure of 0.150 μTorr.

95.2(a) What pressure of argon gas is required to produce a collision rate of $4.5 \times 10^{20}\ \mathrm{s^{-1}}$ at 425 K on a circular surface of diameter 1.5 mm?

95.2(b) What pressure of nitrogen gas is required to produce a collision rate of $5.00 \times 10^{19}\ \mathrm{s^{-1}}$ at 525 K on a circular surface of diameter 2.0 mm?

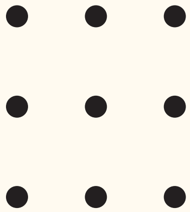
Problems

95.1 The movement of atoms and ions on a surface depends on their ability to leave one position and stick to another, and therefore on the energy changes that occur. As an illustration, consider a two-dimensional square lattice of univalent positive and negative ions separated by 200 pm, and consider a cation on the upper terrace of this array. Calculate, by direct summation, its Coulombic interaction when it is in an empty lattice point directly above an anion. Now consider a high step in the same lattice, and let the cation move into the corner formed by the step and the terrace. Calculate the Coulombic energy for this position, and decide on the likely settling point for the cation.

95.2 In a study of the catalytic properties of a titanium surface it was necessary to maintain the surface free from contamination. Calculate the collision frequency per square centimetre of surface made by O_2 molecules at (a) 100 kPa, (b) 1.00 Pa and 300 K. Estimate the number of collisions made with a single surface atom in each second. The conclusions underline the importance of working at very low pressures (much lower than 1 Pa, in fact) in order to study the properties of uncontaminated surfaces. Take the nearest neighbour distance as 291 pm.

95.3 Nickel is face-centred cubic with a unit cell of side 352 pm. What is the number of atoms per square centimetre exposed on a surface formed by (a) (100), (b) (110), (c) (111) planes? Calculate the frequency of molecular collisions per surface atom in a vessel containing (a) hydrogen, (b) propane at 25 °C when the pressure is (i) 100 Pa, (ii) 0.10 μTorr.

95.4 The LEED pattern from a clean, unreconstructed (110) face of a metal is shown below. Sketch the LEED pattern for a surface that was reconstructed by tripling the horizontal separation between the atoms.



95.5 Figure F20.1 shows the time dependence of the surface plasmon resonance signal, R. Adsorption leads to an increase in R until an equilibrium value, R_{eq}, is obtained. Desorption causes a decrease in R. Develop expressions for $R(t)$ that apply to the adsorption and desorption parts of the curve in Fig. F20.1.

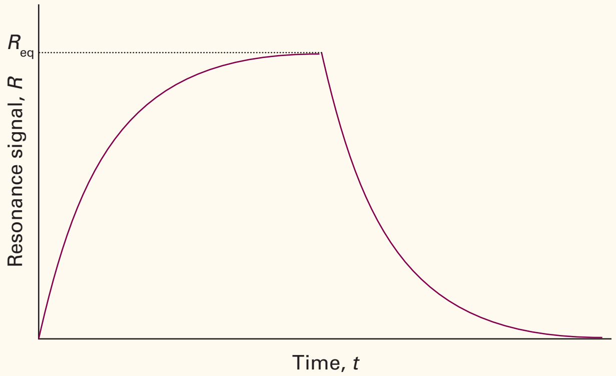


Figure F20.1 The time dependence of the surface plasmon resonance signal R.

Topic 96 Adsorption and desorption

Discussion question

96.1 Distinguish between the Langmuir and BET adsorption isotherms, and indicate when and why they are likely to be appropriate.

Exercises

96.1(a) The volume of oxygen gas at 0 °C and 104 kPa adsorbed on the surface of 1.00 g of a sample of silica at 0 °C was 0.286 cm^3 at 145.4 Torr and 1.443 cm^3 at 760 Torr. What is the value of V_{mon}?

96.1(b) The volume of gas at 20 °C and 1.00 bar adsorbed on the surface of 1.50 g of a sample of silica at 0 °C was 1.42 cm^3 at 56.4 kPa and 2.77 cm^3 at 108 kPa. What is the value of V_{mon}?

96.2(a) The enthalpy of adsorption of CO on a surface is found to be −120 kJ mol^{-1}. Estimate the mean lifetime of a CO molecule on the surface at 400 K.

96.2(b) The enthalpy of adsorption of ammonia on a nickel surface is found to be −155 kJ mol^{-1}. Estimate the mean lifetime of an NH_3 molecule on the surface at 500 K.

96.3(a) A certain solid sample adsorbs 0.44 mg of CO when the pressure of the gas is 26.0 kPa and the temperature is 300 K. The mass of gas adsorbed when the pressure is 3.0 kPa and the temperature is 300 K is 0.19 mg. The Langmuir isotherm is known to describe the adsorption. Find the fractional coverage of the surface at the two pressures.

96.3(b) A certain solid sample adsorbs 0.63 mg of CO when the pressure of the gas is 36.0 kPa and the temperature is 300 K. The mass of gas adsorbed when the pressure is 4.0 kPa and the temperature is 300 K is 0.21 mg. The Langmuir isotherm is known to describe the adsorption. Find the fractional coverage of the surface at the two pressures.

96.4(a) The adsorption of a gas is described by the Langmuir isotherm with $\alpha = 0.75$ kPa^{-1} at 25 °C. Calculate the pressure at which the fractional surface coverage is (a) 0.15, (b) 0.95.

96.4(b) The adsorption of a gas is described by the Langmuir isotherm with $\alpha = 0.548$ kPa^{-1} at 25 °C. Calculate the pressure at which the fractional surface coverage is (a) 0.20, (b) 0.75.

96.5(a) A solid in contact with a gas at 12 kPa and 25 °C adsorbs 2.5 mg of the gas and obeys the Langmuir isotherm. The enthalpy change when 1.00 mmol of the adsorbed gas is desorbed is +10.2 J. What is the equilibrium pressure for the adsorption of 2.5 mg of gas at 40 °C?

96.5(b) A solid in contact with a gas at 8.86 kPa and 25 °C adsorbs 4.67 mg of the gas and obeys the Langmuir isotherm. The enthalpy change when 1.00 mmol of the adsorbed gas is desorbed is +12.2 J. What is the equilibrium pressure for the adsorption of the same mass of gas at 45 °C?

96.6(a) Nitrogen gas adsorbed on charcoal to the extent of 0.921 cm^3 g^{-1} at 490 kPa and 190 K, but at 250 K the same amount of adsorption was achieved only when the pressure was increased to 3.2 MPa. What is the enthalpy of adsorption of nitrogen on charcoal?

96.6(b) Nitrogen gas adsorbed on a surface to the extent of 1.242 cm^3 g^{-1} at 350 kPa and 180 K, but at 240 K the same amount of adsorption was achieved only when the pressure was increased to 1.02 MPa. What is the enthalpy of adsorption of nitrogen on the surface?

96.7(a) In an experiment on the adsorption of oxygen on tungsten it was found that the same volume of oxygen was desorbed in 27 min at 1856 K and 2.0 min at 1978 K. What is the activation energy of desorption? How long would it take for the same amount to desorb at (a) 298 K, (b) 3000 K?

96.7(b) In an experiment on the adsorption of ethene on iron it was found that the same volume of the gas was desorbed in 1856 s at 873 K and 8.44 s at 1012 K. What is the activation energy of desorption? How long would it take for the same amount of ethene to desorb at (a) 298 K, (b) 1500 K?

96.8(a) The average time for which an oxygen atom remains adsorbed to a tungsten surface is 0.36 s at 2548 K and 3.49 s at 2362 K. What is the activation energy for chemisorption?

96.8(b) The average time for which a hydrogen atom remains adsorbed on a manganese surface is 35 per cent shorter at 1000 K than at 600 K. What is the activation energy for chemisorption?

96.9(a) For how long on average would an H atom remain on a surface at 400 K if its desorption activation energy is (a) 15 kJ mol^{-1}, (b) 150 kJ mol^{-1}? Take $\tau_0 = 0.10$ ps. For how long on average would the same atoms remain at 1000 K?

96.9(b) For how long on average would an atom remain on a surface at 298 K if its desorption activation energy is (a) 20 kJ mol^{-1}, (b) 200 kJ mol^{-1}? Take $\tau_0 = 0.12$ ps. For how long on average would the same atoms remain at 800 K?

96.10(a) Hydrogen iodide is very strongly adsorbed on gold but only slightly adsorbed on platinum. Assume the adsorption follows the Langmuir isotherm and predict the order of the HI decomposition reaction on each of the two metal surfaces.

96.10(b) Suppose it is known that ozone adsorbs on a particular surface in accord with a Langmuir isotherm. How could you use the pressure dependence of the fractional coverage to distinguish between adsorption (a) without dissociation, (b) with dissociation into $O + O_2$, (c) with dissociation into $O + O + O$?

Problems

96.1 Use mathematical software, a spreadsheet, or the *Living graphs* (labelled ^{LG}) on the website of this book to solve the following problems:

(a)^{LG} Use eqn 96.2 to generate a family of curves showing the dependence of $1/\theta$ on $1/p$ for several values of α.

(b)^{LG} Use eqn 96.4 to generate a family of curves showing the dependence of $1/\theta$ on $1/p$ for several values of α. On the basis of your results from parts (a) and (b), discuss how plots of $1/\theta$ against $1/p$ can be used to distinguish between adsorption with and without dissociation.

(c)$^{\mathrm{LG}}$ Use eqn 96.6 to generate a family of curves showing the dependence of $zV_{\mathrm{mon}}/(1-z)V$ on z for different values of c.

96.2 The data below are for the chemisorption of hydrogen on copper powder at 25 °C. Confirm that they fit the Langmuir isotherm at low coverages. Then find the value of α for the adsorption equilibrium and the adsorption volume corresponding to complete coverage.

p/Pa	25	129	253	540	1000	1593
V/cm^3	0.042	0.163	0.221	0.321	0.411	0.471

96.3 The data for the adsorption of ammonia on barium fluoride are reported below. Confirm that they fit a BET isotherm and find values of c and V_{mon}.

(a) $\theta = 0$ °C, $p^* = 429.6$ kPa:

p/kPa	14.0	37.6	65.6	79.2	82.7	100.7	106.4
V/cm^3	11.1	13.5	14.9	16.0	15.5	17.3	16.5

(b) $\theta = 18.6$ °C, $p^* = 819.7$ kPa:

p/kPa	5.3	8.4	14.4	29.2	62.1	74.0	80.1	102.0
V/cm^3	9.2	9.8	10.3	11.3	12.9	13.1	13.4	14.1

96.4 The following data have been obtained for the adsorption of H_2 on the surface of 1.00 g of copper at 0 °C. The volume of H_2 below is the volume that the gas would occupy at STP (0 °C and 1 atm).

p/atm	0.050	0.100	0.150	0.200	0.250
V/cm^3	23.8	13.3	8.70	6.80	5.71

Determine the volume of H_2 necessary to form a monolayer and estimate the surface area of the copper sample. The density of liquid hydrogen is 0.708 g cm^{-3}.

96.5‡ M.-G. Olivier and R. Jadot (*J. Chem. Eng. Data* **42**, 230 (1997)) studied the adsorption of butane on silica gel. They report the following amounts of absorption (in moles per kilogram of silica gel) at 303 K:

p/kPa	31.00	38.22	53.03	76.38	101.97
n/(mol kg^{-1})	1.00	1.17	1.54	2.04	2.49
p/kPa	130.47	165.06	182.41	205.75	219.91
n/(mol kg^{-1})	2.90	3.22	3.30	3.35	3.36

Fit these data to a Langmuir isotherm, and determine the value of n that corresponds to complete coverage and the constant α.

96.6 The designers of a new industrial plant wanted to use a catalyst code-named CR-1 in a step involving the fluorination of butadiene. As a first step in the investigation they determined the form of the adsorption isotherm. The volume of butadiene adsorbed per gram of CR-1 at 15 °C varied with pressure as given below. Is the Langmuir isotherm suitable at this pressure?

p/kPa	13.3	26.7	40.0	53.3	66.7	80.0
V/cm^3	17.9	33.0	47.0	60.8	75.3	91.3

Investigate whether the BET isotherm gives a better description of the adsorption of butadiene on CR-1. At 15 °C, p^*(butadiene) = 200 kPa. Find V_{mon} and c.

96.7‡ C. Huang and W.P. Cheng (*J. Colloid Interface Sci.* **188**, 270 (1997)) examined the adsorption of the hexacyanoferrate(III) ion, $[\mathrm{Fe(CN)_6}]^{3-}$, on γ-$\mathrm{Al_2O_3}$ from aqueous solution. They modelled the adsorption with a modified Langmuir isotherm, obtaining the following values of K at pH = 6.5:

T/K	283	298	308	318
$10^{-11}\alpha$	2.642	2.078	1.286	1.085

Determine the isosteric enthalpy of adsorption, $\Delta_{\mathrm{ads}}H^{\ominus}$, at this pH. The researchers also reported $\Delta_{\mathrm{ads}}S^{\ominus} = +146$ J mol^{-1} K^{-1} under these conditions. Determine $\Delta_{\mathrm{ads}}G^{\ominus}$.

96.8‡ In a study relevant to automobile catalytic converters, C.E. Wartnaby, et al. (*J. Phys. Chem.* **100**, 12483 (1996)) measured the enthalpy of adsorption of CO, NO, and O_2 on initially clean platinum (110) surfaces. They report $\Delta_{\mathrm{ads}}H^{\ominus}$ for NO to be −160 kJ mol^{-1}. How much more strongly adsorbed is NO at 500 °C than at 400 °C?

96.9‡ The removal or recovery of volatile organic compounds (VOCs) from exhaust gas streams is an important process in environmental engineering. Activated carbon has long been used as an adsorbent in this process, but the presence of moisture in the stream reduces its effectiveness. M.-S. Chou and J.-H. Chiou (*J. Envir. Engrg. ASCE* **123**, 437(1997)) have studied the effect of moisture content on the adsorption capacities of granular activated carbon (GAC) for normal hexane and cyclohexane in air streams. From their data for dry streams containing cyclohexane, shown in the table below, they conclude that GAC obeys a Langmuir-type model in which $\theta_{\mathrm{VOC,RH=0}} = abc_{\mathrm{VOC}}/(1+bc_{\mathrm{VOC}})$, where $\theta = m_{\mathrm{VOC}}/m_{\mathrm{GAC}}$, RH denotes relative humidity, a is the maximum adsorption capacity, b is an affinity parameter, and p is the abundance in parts per million (ppm). The following table gives values of $\theta_{\mathrm{VOC,\,RH=0}}$ for cyclohexane:

c/ppm	33.6 °C	41.5 °C	57.4 °C	76.4 °C	99 °C
200	0.080	0.069	0.052	0.042	0.027
500	0.093	0.083	0.072	0.056	0.042
1000	0.101	0.088	0.076	0.063	0.045
2000	0.105	0.092	0.083	0.068	0.052
3000	0.112	0.102	0.087	0.072	0.058

(a) By linear regression of $1/\theta_{\mathrm{VOC,\,RH=0}}$ against $1/c_{\mathrm{VOC}}$, test the goodness of fit and determine values of a and b. (b) The parameters a and b can be related to $\Delta_{\mathrm{ads}}H$, the enthalpy of adsorption, and $\Delta_{\mathrm{b}}H$, the difference in activation energy for adsorption and desorption of the VOC molecules, through Arrhenius-type equations of the form $a = k_{\mathrm{a}}\exp(-\Delta_{\mathrm{ads}}H/RT)$ and $b = k_{\mathrm{b}}\exp(-\Delta_{\mathrm{b}}H/RT)$. Test the goodness of fit of the data to these equations and obtain values for k_{a}, k_{b}, $\Delta_{\mathrm{ads}}H$, and $\Delta_{\mathrm{b}}H$. (c) What interpretation might you give to k_{a} and k_{b}?

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‡ These problems were supplied by Charles Trapp and Carmen Giunta.

Topic 97 Heterogeneous catalysis

Discussion questions

97.1 Describe the essential features of the Langmuir–Hinshelwood and Eley–Rideal mechanisms for surface-catalysed reactions.

97.2 Account for the dependence of catalytic activity of a surface on the strength of chemisorption, as shown in Fig. 96.8.

Exercises

97.1(a) A monolayer of N_2 molecules is adsorbed on the surface of 1.00 g of an Fe/Al_2O_3 catalyst at 77 K, the boiling point of liquid nitrogen. Upon warming, the nitrogen occupies 3.86 cm^3 at 0 °C and 760 Torr. What is the surface area of the catalyst?

97.1(b) A monolayer of CO molecules is adsorbed on the surface of 1.00 g of an Fe/Al_2O_3 catalyst at 77 K, the boiling point of liquid nitrogen. Upon warming, the carbon monoxide occupies 3.75 cm^3 at 0 °C and 1.00 bar. What is the surface area of the catalyst?

Problem

97.1 In some catalytic reactions the products may adsorb more strongly than the reacting gas. This is the case, for instance, in the catalytic decomposition of ammonia on platinum at 1000 °C. As a first step in examining the kinetics of this type of process, show that the rate of ammonia decomposition should follow

$$\frac{dp_{NH_3}}{dt} = -k_c \frac{p_{NH_3}}{p_{H_2}}$$

in the limit of very strong adsorption of hydrogen. Start by showing that when a gas J adsorbs very strongly, and its pressure is p_J, that the fraction of uncovered sites is approximately $1/Kp_J$. Solve the rate equation for the catalytic decomposition of NH_3 on platinum and show that a plot of $F(t) = (1/t)\ln(p/p_0)$ against $G(t) = (p - p_0)/t$, where p is the pressure of ammonia, should give a straight line from which k_c can be determined. Check the rate law on the basis of the data below, and find k_c for the reaction.

t/s	0	30	60	100	160	200	250
p/kPa	13.3	11.7	11.2	10.7	10.3	9.9	9.6

Integrated activities

F20.1 Although the attractive van der Waals interaction between individual molecules varies as R^{-6}, the interaction of a molecule with a nearby solid (a homogeneous collection of molecules) varies as R^{-3}, where R is its vertical distance above the surface. Confirm this assertion. Calculate the interaction energy between an Ar atom and the surface of solid argon on the basis of a Lennard-Jones (6,12) potential. Estimate the equilibrium distance of an atom above the surface.

F20.2 Electron microscopes can obtain images with several hundredfold higher resolution than optical microscopes because of the short wavelength obtainable from a beam of electrons. For electrons moving at speeds close to c, the speed of light, the expression for the de Broglie wavelength (eqn 4.6, $\lambda = h/p$) needs to be corrected for relativistic effects:

$$\lambda = \frac{h}{\left\{2m_e eV\left(1+\frac{eV}{2m_e c^2}\right)\right\}^{1/2}}$$

where c is the speed of light in vacuum and V is the potential difference through which the electrons are accelerated. (a) Use the expression above to calculate the de Broglie wavelength of electrons accelerated through 50 kV. (b) Is the relativistic correction important?

F20.3 The forces measured by AFM arise primarily from interactions between electrons of the stylus and on the surface. To get an idea of the magnitudes of these forces, calculate the force acting between two electrons separated by 2.0 nm. To calculate the force between the electrons, use $F = -dV/dr$, where V is their mutual Coulombic potential energy and r is their separation.

F20.4 To appreciate the distance dependence of the tunnelling current in scanning tunnelling microscopy, suppose that the electron in the gap between sample and needle has an energy 2.0 eV smaller than the barrier height. By what factor would the current drop if the needle is moved from $L_1 = 0.50$ nm to $L_2 = 0.60$ nm from the surface?

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PART 1 Common integrals

Algebraic functions

A.1 $$\int x^n \mathrm{d}x = \frac{x^{n+1}}{n+1} + \text{constant},\ n \neq -1$$

A.2 $$\int \frac{1}{x} \mathrm{d}x = \ln x + \text{constant}$$

Exponential functions

E.1 $$\int_0^\infty x^n \mathrm{e}^{-ax} \mathrm{d}x = \frac{n!}{a^{n+1}},\quad n! = n(n-1)\ldots 1;\ 0! \equiv 1$$

E.2 $$\int_0^\infty \frac{x^4 \mathrm{e}^x}{(\mathrm{e}^x - 1)^2} \mathrm{d}x = \frac{\pi^4}{15}$$

Gaussian functions

G.1 $$\int_0^\infty \mathrm{e}^{-ax^2} \mathrm{d}x = \frac{1}{2}\left(\frac{\pi}{a}\right)^{1/2}$$

G.2 $$\int_0^\infty x\mathrm{e}^{-ax^2} \mathrm{d}x = \frac{1}{2a}$$

G.3 $$\int_0^\infty x^2 \mathrm{e}^{-ax^2} \mathrm{d}x = \frac{1}{4}\left(\frac{\pi}{a^3}\right)^{1/2}$$

G.4 $$\int_0^\infty x^3 \mathrm{e}^{-ax^2} \mathrm{d}x = \frac{1}{2a^2}$$

G.5 $$\int_0^\infty x^4 \mathrm{e}^{-ax^2} \mathrm{d}x = \frac{3}{8a^2}\left(\frac{\pi}{a}\right)^{1/2}$$

G.6 $$\operatorname{erf} z = \frac{2}{\pi^{1/2}} \int_0^z \mathrm{e}^{-x^2} \mathrm{d}x \qquad \operatorname{erfc} z = 1 - \operatorname{erf} z$$

G.7 $$\int_0^\infty x^{2m+1} \mathrm{e}^{-ax^2} \mathrm{d}x = \frac{m!}{2a^{m+1}}$$

G.8 $$\int_0^\infty x^{2m} \mathrm{e}^{-ax^2} \mathrm{d}x = \frac{(2m-1)!!}{2^{m+1} a^m}\left(\frac{\pi}{a}\right)^{1/2}$$

$$(2m-1)!! = 1 \times 3 \times 5 \ldots \times (2m-1)$$

Trigonometric functions

T.1 $$\int \sin ax\, \mathrm{d}x = -\frac{1}{a} \cos ax + \text{constant}$$

T.2 $$\int \sin^2 ax\, \mathrm{d}x = \frac{1}{2}x - \frac{\sin 2ax}{4a} + \text{constant}$$

T.3 $$\int \sin^3 ax\, \mathrm{d}x = -\frac{(\sin^2 ax + 2)\cos ax}{3a} + \text{constant}$$

T.4 $$\int \sin^4 ax\, \mathrm{d}x = \frac{3x}{8} - \frac{3}{8a} \sin ax \cos ax - \frac{1}{4a} \sin^3 ax \cos ax + \text{constant}$$

T.5 $$\int \sin ax \sin bx\, \mathrm{d}x = \frac{\sin(a-b)x}{2(a-b)} - \frac{\sin(a+b)x}{2(a+b)} + \text{constant},\ a^2 \neq b^2$$

T.6 $$\int_0^L \sin nax \sin^2 ax\, \mathrm{d}x = -\frac{1}{2a}\left\{\frac{1}{n} - \frac{1}{2(n+2)} - \frac{1}{2(n-2)}\right\} \times \{(-1)^n - 1\}$$

T.7 $$\int \sin ax \cos ax\, \mathrm{d}x = \frac{1}{2a} \sin^2 ax + \text{constant}$$

T.8 $$\int \sin bx \cos ax\, \mathrm{d}x = \frac{\cos(a-b)x}{2(a-b)} - \frac{\cos(a+b)x}{2(a+b)} + \text{constant},\ a^2 \neq b^2$$

T.9 $$\int x \sin ax \sin bx\, \mathrm{d}x = -\frac{\mathrm{d}}{\mathrm{d}a} \int \sin bx \cos ax\, \mathrm{d}x$$

T.10 $$\int \cos^2 ax \sin ax\, \mathrm{d}x = -\frac{1}{3a} \cos^3 ax + \text{constant}$$

T.11 $$\int x \sin^2 ax\, \mathrm{d}x = \frac{x^2}{4} - \frac{x \sin 2ax}{4a} - \frac{\cos 2ax}{8a^2} + \text{constant}$$

T.12 $$\int x^2 \sin^2 ax\, \mathrm{d}x = \frac{x^3}{6} - \left(\frac{x^2}{4a} - \frac{1}{8a^3}\right) \sin 2ax - \frac{x \cos 2ax}{4a^2} + \text{constant}$$

T.13 $$\int x \cos ax\, \mathrm{d}x = \frac{1}{a^2} \cos ax + \frac{x}{a} \sin ax$$

PART 2 Quantum numbers and operators

A. Common quantum numbers

Symbol	Name or significance	Values
n (n_1, n_2, … in higher dimensions)	State of particle in a box. Principal quantum number of a hydrogenic atom	$1, 2, \ldots \infty$
v	Vibrational quantum number of a harmonic oscillator, a diatomic molecule, or a normal mode of a polyatomic molecule	$0, 1, 2, \ldots \infty$
l	Orbital angular momentum quantum number	$0, 1, 2, \ldots$; in an atom, terminates at $n-1$
m_l	Magnetic quantum number	$0, \pm 1, \pm 2, \ldots \pm l$
s	Spin quantum number of electron	$\frac{1}{2}$
m_s	Spin magnetic quantum number of electron	$\pm\frac{1}{2}$
j, m_j	Angular momenta in general	Integers or half-integers; $m_j=j, j-1, \ldots, -j$
L, M_L	Total orbital angular momentum quantum numbers	$L=l_1+l_2, l_1+l_2-1, \ldots, \lvert l_1-l_2\rvert$; $M_L=L, L-1, \ldots, -L$
S, M_S	Total spin angular momentum quantum numbers	$S=s_1+s_2, s_1+s_2-1, \ldots, \lvert s_1-s_2\rvert$; $M_S=S, S-1, \ldots, -S$
J, M_J	Total angular momentum quantum numbers Angular momentum quantum numbers of a rigid rotor	$J=L+S, L+S-1, \ldots, \lvert L-S\rvert$; $M_J=J, J-1, \ldots, -J$ $J=0, 1, 2, \ldots$; $M_J=0, \pm 1, \ldots, \pm J$
K	Quantum number for the component of angular momentum on the principal axis of a rigid rotor	$0, \pm 1, \ldots, \pm J$; for a linear rotor, $K\equiv 0$
λ	Quantum number for the component of the orbital angular momentum of an electron on the axis of a linear molecule	$0, \pm 1, \pm 2, \ldots$
Λ	Quantum number for the component of the total orbital angular momentum of electrons on the axis of a linear molecule	$0, \pm 1, \pm 2, \ldots$
Σ	Quantum number for the component of the total electron spin S of electrons on the axis of a linear molecule	$S, S-1, S-2, \ldots, -S$
Ω	Quantum number for the component of the total angular momentum of electrons on the axis of a linear molecule	$\Lambda+\Sigma$
I, m_I	Nuclear spin quantum numbers	Integers or half-integers; $m_I=I, I-1, \ldots, -I$

B. Common operators in quantum mechanics

Observable	Operator	Representation*
Energy	$\hat{H}$ (hamiltonian)	$\hat{H}=-\dfrac{\hbar^2}{2m}\nabla^2+\hat{V}$
Kinetic energy	$\hat{E}_\mathrm{k}$	$\hat{E}_\mathrm{k}=-\dfrac{\hbar^2}{2m}\nabla^2$
Potential energy	$\hat{V}$	$\hat{V}=V(\boldsymbol{r})\times$
Position (x-, y-, z-components)	$\hat{x}, \hat{y}, \hat{z}$; in general $\hat{q}$	$\hat{q}=q\times$
Radial distance	$\hat{r}$	$\hat{r}=r\times$

(continued)

Observable	**Operator**	**Representation***
Linear momentum (*x*-, *y*-, *z*-components)	$\hat{p}_x, \hat{p}_y, \hat{p}_z$; in general $\hat{p}_q$	$\hat{p}_q = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial q}$
Square of linear momentum	$\hat{p}^2 = \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2$	$\hat{p}^2 = -\hbar^2\nabla^2$
Electric dipole moment (*x*-, *y*-, *z*-components)	$\hat{\mu}_x, \hat{\mu}_y, \hat{\mu}_z$; in general $\hat{\mu}_q$	$\hat{\mu}_q = -eq\times$
Orbital angular momentum	$\hat{\boldsymbol{l}}$	$\hat{\boldsymbol{l}} = \hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}} = \frac{\hbar}{\mathrm{i}}\boldsymbol{r}\times\nabla$; $\hat{l}_z = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial\phi}$
Square of magnitude of the orbital angular momentum	$\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2$	$\hat{l}^2 = -\hbar^2\Lambda^2$
Square of magnitude of the spin angular momentum and its *z*-component	$\hat{s}^2, s_z$	
Energy of a magnetic moment $\boldsymbol{\mu}$ in a magnetic field $\mathcal{B}$	$\hat{H} = -\hat{\boldsymbol{\mu}}\cdot\boldsymbol{\mathcal{B}}$	
Nuclear magnetic moment	$\hat{\boldsymbol{\mu}} = \gamma_{\mathrm{N}}\hat{\boldsymbol{I}}$	
Spin magnetic moment	$\hat{\boldsymbol{\mu}} = \gamma_{\mathrm{e}}\hat{\boldsymbol{s}}$	

---

* In the ‘position representation’, in which the position operators have a simple multiplicative form.

PART 3 Units

Table 1.1 Some common units

Physical quantity	Name of unit	Symbol for unit	Value*
Time	minute	min	60 s
	hour	h	3600 s
	day	d	86 400 s
	year	a	31 556 952 s
Length	ångström	Å	10^{-10} m
Volume	litre	L, l	1 dm^3
Mass	tonne	t	10^3 kg
Pressure	bar	bar	10^5 Pa
	atmosphere	atm	101.325 kPa
Energy	electronvolt	eV	$1.602\ 177\ 33 \times 10^{-19}$ J 96.485 31 kJ mol^{-1}

* All values are exact, except for the definition of 1 eV, which depends on the measured value of *e*, and the year, which is not a constant and depends on a variety of astronomical assumptions.

Table 1.2 Common SI prefixes

Prefix	y	z	a	f	p	n	μ	m	c	d
Name	yocto	zepto	atto	femto	pico	nano	micro	milli	centi	deci
Factor	10^{-24}	10^{-21}	10^{-18}	10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}
Prefix	da	h	k	M	G	T	P	E	Z	Y
Name	deca	hecto	kilo	mega	giga	tera	peta	exa	zeta	yotta
Factor	10	10^2	10^3	10^6	10^9	10^{12}	10^{15}	10^{18}	10^{21}	10^{24}

Table 1.3 The SI base units

Physical quantity	Symbol for quantity	Base unit
Length	l	metre, m
Mass	m	kilogram, kg
Time	t	second, s
Electric current	I	ampere, A
Thermodynamic temperature	T	kelvin, K
Amount of substance	n	mole, mol
Luminous intensity	I_v	candela, cd

Table 1.4 A selection of derived units

Physical quantity	Derived unit*	Name of derived unit
Force	1 kg m s^{-2}	newton, N
Pressure	1 kg m^{-1} s^{-2} 1 N m^{-2}	pascal, Pa
Energy	1 kg m^2 s^{-2} 1 N m 1 Pa m^3	joule, J
Power	1 kg m^2 s^{-3} 1 J s^{-1}	watt, W

* Equivalent definitions in terms of derived units are given following the definition in terms of base units.

PART 4 Data

The following is a directory of all tables in the text; those included in this *Resource section* are marked with an asterisk. The remainder will be found on the pages indicated. These tables reproduce and expand the data given in the short tables in the text, and follow their numbering. Standard states refer to a pressure of $p^{\ominus} = 1$ bar. The general references are as follows:

AIP: D.E. Gray (ed.), *American Institute of Physics handbook*. McGraw-Hill, New York (1972).

E: J. Emsley, *The elements*. Oxford University Press, Oxford (1991).

HCP: D.R. Lide (ed.), *Handbook of chemistry and physics*. CRC Press, Boca Raton (2000).

JL: A.M. James and M.P. Lord, *Macmillan's chemical and physical data*. Macmillan, London (1992).

KL: G.W.C. Kaye and T.H. Laby (ed.), *Tables of physical and chemical constants*. Longman, London (1973).

LR: G.N. Lewis and M. Randall, revised by K.S. Pitzer and L. Brewer, *Thermodynamics*. McGraw-Hill, New York (1961).

NBS: *NBS tables of chemical thermodynamic properties*, published as *J. Phys. Chem. Reference Data*, **11**, Supplement 2 (1982).

RS: R.A. Robinson and R.H. Stokes, *Electrolyte solutions*, Butterworth, London (1959).

TDOC: J.B. Pedley, J.D. Naylor, and S.P. Kirby, *Thermochemical data of organic compounds*. Chapman & Hall, London (1986).

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Table 0.1 Physical properties of selected materials

	ρ/(g cm^{-3}) at 293 K†	T_f/K	T_b/K		ρ/(g cm^{-3}) at 293 K†	T_f/K	T_b/K
Elements				**Inorganic compounds**			
Aluminium(s)	2.698	933.5	2740	$CaCO_3$(s, calcite)	2.71	1612	1171^d
Argon(g)	1.381	83.8	87.3	$CuSO_4\cdot 5H_2O$(s)	2.284	383($-H_2O$)	423($-5H_2O$)
Boron(s)	2.340	2573	3931	HBr(g)	2.77	184.3	206.4
Bromine(l)	3.123	265.9	331.9	HCl(g)	1.187	159.0	191.1
Carbon(s, gr)	2.260	3700^s		HI(g)	2.85	222.4	237.8
Carbon(s, d)	3.513			H_2O(l)	0.997	273.2	373.2

(*continued*)

Table 0.1 (Continued)

	ρ/(g cm^{-3}) at 293 K†	T_f/K	T_b/K		ρ/(g cm^{-3}) at 293 K†	T_f/K	T_b/K
Elements (continued)				**Inorganic compounds (continued)**			
Chlorine(g)	1.507	172.2	239.2	D_2O(l)	1.104	277.0	374.6
Copper(s)	8.960	1357	2840	NH_3(g)	0.817	195.4	238.8
Fluorine(g)	1.108	53.5	85.0	KBr(s)	2.750	1003	1708
Gold(s)	19.320	1338	3080	KCl(s)	1.984	1049	1773^{s}
Helium(g)	0.125		4.22	NaCl(s)	2.165	1074	1686
Hydrogen(g)	0.071	14.0	20.3	H_2SO_4(l)	1.841	283.5	611.2
Iodine(s)	4.930	386.7	457.5				
Iron(s)	7.874	1808	3023	**Organic compounds**			
Krypton(g)	2.413	116.6	120.8	Acetaldehyde, CH_3CHO(l)	0.788	152	293
Lead(s)	11.350	600.6	2013	Acetic acid, CH_3COOH(l)	1.049	289.8	391
Lithium(s)	0.534	453.7	1620	Acetone, $(CH_3)_2CO$(l)	0.787	178	329
Magnesium(s)	1.738	922.0	1363	Aniline, $C_6H_5NH_2$(l)	1.026	267	457
Mercury(l)	13.546	234.3	629.7	Anthracene, $C_{14}H_{10}$(s)	1.243	490	615
Neon(g)	1.207	24.5	27.1	Benzene, C_6H_6(l)	0.879	278.6	353.2
Nitrogen(g)	0.880	63.3	77.4	Carbon tetrachloride, CCl_4(l)	1.63	250	349.9
Oxygen(g)	1.140	54.8	90.2	Chloroform, $CHCl_3$(l)	1.499	209.6	334
Phosphorus(s, α)	1.820	317.3	553	Ethanol, C_2H_5OH(l)	0.789	156	351.4
Potassium(s)	0.862	336.8	1047	Formaldehyde, HCHO(g)		181	254.0
Silver(s)	10.500	1235	2485	Glucose, $C_6H_{12}O_6$(s)	1.544	415	
Sodium(s)	0.971	371.0	1156	Methane, CH_4(g)		90.6	111.6
Sulfur(s, α)	2.070	386.0	717.8	Methanol, CH_3OH(l)	0.791	179.2	337.6
Uranium(s)	18.950	1406	4018	Naphthalene, $C_{10}H_8$(s)	1.145	353.4	491
Xenon(g)	2.939	161.3	166.1	Octane, C_8H_{18}(l)	0.703	216.4	398.8
Zinc(s)	7.133	692.7	1180	Phenol, C_6H_5OH(s)	1.073	314.1	455.0
				Sucrose, $C_{12}H_{22}O_{11}$(s)	1.588	457d	

d: decomposes; s: sublimes; Data: AIP, E, HCP, KL. † For gases, at their boiling points.

Table 0.2 Masses and natural abundances of selected nuclides

Nuclide		m/m_u	**Abundance/%**
H	^{1}H	1.0078	99.985
	^{2}H	2.0140	0.015
He	^{3}He	3.0160	0.000 13
	^{4}He	4.0026	100
Li	^{6}Li	6.0151	7.42
	^{7}Li	7.0160	92.58
B	^{10}B	10.0129	19.78
	^{11}B	11.0093	80.22
C	^{12}C	12*	98.89
	^{13}C	13.0034	1.11
N	^{14}N	14.0031	99.63
	^{15}N	15.0001	0.37
O	^{16}O	15.9949	99.76
	^{17}O	16.9991	0.037
	^{18}O	17.9992	0.204
F	^{19}F	18.9984	100
P	^{31}P	30.9738	100
S	^{32}S	31.9721	95.0
	^{33}S	32.9715	0.76

Table 0.2 (Continued)

	Nuclide	m/m_u	Abundance/%
	^{34}S	33.9679	4.22
Cl	^{35}Cl	34.9688	75.53
	^{37}Cl	36.9651	24.4
Br	^{79}Br	78.9183	50.54
	^{81}Br	80.9163	49.46
I	^{127}I	126.9045	100

* Exact value.

Table 19.1 Effective nuclear charge, $Z_{\text{eff}}=Z-\sigma$

	H							**He**
1s	1							1.6875
	Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
1s	2.6906	3.6848	4.6795	5.6727	6.6651	7.6579	8.6501	9.6421
2s	1.2792	1.9120	2.5762	3.2166	3.8474	4.4916	5.1276	5.7584
2p			2.4214	3.1358	3.8340	4.4532	5.1000	5.7584
	Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
1s	10.6259	11.6089	12.5910	13.5745	14.5578	15.5409	16.5239	17.5075
2s	6.5714	7.3920	8.3736	9.0200	9.8250	10.6288	11.4304	12.2304
2p	6.8018	7.8258	8.9634	9.9450	10.9612	11.9770	12.9932	14.0082
3s	2.5074	3.3075	4.1172	4.9032	5.6418	6.3669	7.0683	7.7568
3p			4.0656	4.2852	4.8864	5.4819	6.1161	6.7641

Data: E. Clementi and D.L. Raimondi, *Atomic screening constants from SCF functions.* IBM Res. Note NJ-27 (1963). *J. Chem. Phys.* **38**, 2686 (1963).

Table 20.2 First and second ionization energies, I/(kJ mol^{-1})

H							**He**
1312.0							2372.3
							5250.4
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
513.3	899.4	800.6	1086.2	1402.3	1313.9	1681	2080.6
7298.0	1757.1	2427	2352	2856.1	3388.2	3374	3952.2
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
495.8	737.7	577.4	786.5	1011.7	999.6	1251.1	1520.4
4562.4	1450.7	1816.6	1577.1	1903.2	2251	2297	2665.2
		2744.6		2912			
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
418.8	589.7	578.8	762.1	947.0	940.9	1139.9	1350.7
3051.4	1145	1979	1537	1798	2044	2104	2350
		2963	2735				
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
403.0	549.5	558.3	708.6	833.7	869.2	1008.4	1170.4
2632	1064.2	1820.6	1411.8	1794	1795	1845.9	2046
		2704	2943.0	2443			
Cs	**Ba**	**Tl**	**Pb**	**Bi**	**Po**	**At**	**Rn**
375.5	502.8	589.3	715.5	703.2	812	930	1037
2420	965.1	1971.0	1450.4	1610			
		2878	3081.5	2466			

Data: E.

Table 20.3 Electron affinities, $E_{ea}/(\mathrm{kJ\ mol^{-1}})$

H							**He**
72.8							−21
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
59.8	≤0	23	122.5	−7	141	322	−29
					−844		
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
52.9	≤0	44	133.6	71.7	200.4	348.7	−35
					−532		
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
48.3	2.37	36	116	77	195.0	324.5	−39
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
46.9	5.03	34	121	101	190.2	295.3	−41
Cs	**Ba**	**Tl**	**Pb**	**Bi**	**Po**	**At**	**Rn**
45.5	13.95	30	35.2	101	186	270	−41

Data: E.

Table 24.1 Bond lengths, R_e/pm

(a) Bond lengths in specific molecules

Br_2	228.3
Cl_2	198.75
CO	112.81
F_2	141.78
H_2^+	106
H_2	74.138
HBr	141.44
HCl	127.45
HF	91.680
HI	160.92
N_2	109.76
O_2	120.75

(b) Mean bond lengths from covalent radii*

H	37						
C	77(1)	N	74(1)	O	66(1)	F	64
	67(2)		65(2)		57(2)		
	60(3)						
Si	118	P	110	S	104(1)	Cl	99
					95(2)		
Ge	122	As	121	Se	104	Br	114
		Sb	141	Te	137	I	133

* Values are for single bonds except where indicated otherwise (values in parentheses). The length of an A–B covalent bond (of given order) is the sum of the corresponding covalent radii.

Table 24.2a Bond dissociation enthalpies, $\Delta H^{\ominus}(\mathrm{A{-}B})/(\mathrm{kJ\ mol^{-1}})$ at 298 K*

Diatomic molecules

H–H	436	F–F	155	Cl–Cl	242	Br–Br	193	I–I	151
O=O	497	C=O	1076	N≡N	945				
H–O	428	H–F	565	H–Cl	431	H–Br	366	H–I	299

Polyatomic molecules

$H{-}CH_3$	435	$H{-}NH_2$	460	H–OH	492	$H{-}C_6H_5$	469
$H_3C{-}CH_3$	368	$H_2C{=}CH_2$	720	HC≡CH	962		
$HO{-}CH_3$	377	$Cl{-}CH_3$	352	$Br{-}CH_3$	293	$I{-}CH_3$	237
O=CO	531	HO–OH	213	$O_2N{-}NO_2$	54		

* To a good approximation bond dissociation enthalpies and dissociation energies are related by $\Delta H^{\ominus} = D_e + \frac{3}{2}RT$ with $D_e = D_0 + \frac{1}{2}\hbar\omega$.
For precise values of D_0 for diatomic molecules, see Table 43.1.
Data: HCP, KL.

Table 24.2b Mean bond enthalpies, $\Delta H^{\ominus}(\mathrm{A{-}B})/(\mathrm{kJ\ mol^{-1}})$*

	H	C	N	O	F	Cl	Br	I	S	P	Si
H	436										
C	412	348(i) 612(ii) 838(iii) 518(a)									
N	388	305(i) 613(ii) 890(iii)	163(i) 409(ii) 946(iii)								
O	463	360(i) 743(ii)	157	146(i) 497(ii)							
F	565	484	270	185	155						
Cl	431	338	200	203	254	242					
Br	366	276				219	193				
I	299	238				210	178	151			
S	338	259			496	250	212		264		
P	322									201	
Si	318		374	466							226

* Mean bond enthalpies are such a crude measure of bond strength that they need not be distinguished from dissociation energies.
(i) Single bond, (ii) double bond, (iii) triple bond, (a) aromatic.
Data: HCP and L. Pauling, *The nature of the chemical bond*. Cornell University Press (1960).

Table 25.1 Pauling (*italics*) and Mulliken electronegativities

H							**He**
2.20							
3.06							
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
0.98	*1.57*	*2.04*	*2.55*	*3.04*	*3.44*	*3.98*	
1.28	1.99	1.83	2.67	3.08	3.22	4.43	4.60
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
0.93	*1.31*	*1.61*	*1.90*	*2.19*	*2.58*	*3.16*	
1.21	1.63	1.37	2.03	2.39	2.65	3.54	3.36
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
0.82	*1.00*	*1.81*	*2.01*	*2.18*	*2.55*	*2.96*	*3.0*
1.03	1.30	1.34	1.95	2.26	2.51	3.24	2.98
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
0.82	*0.95*	*1.78*	*1.96*	*2.05*	*2.10*	*2.66*	*2.6*
0.99	1.21	1.30	1.83	2.06	2.34	2.88	2.59
Cs	**Ba**	**Tl**	**Pb**	**Bi**			
0.79	*0.89*	*2.04*	*2.33*	*2.02*			

Data: Pauling values: A.L. Allred, *J. Inorg. Nucl. Chem.* **17**, 215 (1961); L.C. Allen and J.E. Huheey, ibid., **42**, 1523 (1980). Mulliken values: L.C. Allen, *J. Am. Chem. Soc.* **111**, 9003 (1989). The Mulliken values have been scaled to the range of the Pauling values.

Table 34.1 Magnitudes of dipole moments (μ), polarizabilities (α), and polarizability volumes (α')

	$\mu/(10^{-30}\ \mathrm{C\ m})$	μ/D	$\alpha'/(10^{-30}\ \mathrm{m}^3)$	$\alpha/(10^{-40}\ \mathrm{J}^{-1}\ \mathrm{C}^2\ \mathrm{m}^2)$
Ar	0	0	1.66	1.85
C_2H_5OH	5.64	1.69		
$C_6H_5CH_3$	1.20	0.36		
C_6H_6	0	0	10.4	11.6
CCl_4	0	0	10.3	11.7
CH_2Cl_2	5.24	1.57	6.80	7.57
CH_3Cl	6.24	1.87	4.53	5.04
CH_3OH	5.70	1.71	3.23	3.59
CH_4	0	0	2.60	2.89
$CHCl_3$	3.37	1.01	8.50	9.46
CO	0.390	0.117	1.98	2.20
CO_2	0	0	2.63	2.93
H_2	0	0	0.819	0.911
H_2O	6.17	1.85	1.48	1.65
HBr	2.67	0.80	3.61	4.01
HCl	3.60	1.08	2.63	2.93
He	0	0	0.20	0.22
HF	6.37	1.91	0.51	0.57
HI	1.40	0.42	5.45	6.06
N_2	0	0	1.77	1.97
NH_3	4.90	1.47	2.22	2.47
1,2-$C_6H_4(CH_3)_2$	2.07	0.62		

Data: HCP and C.J.F. Böttcher and P. Bordewijk, *Theory of electric polarization*. Elsevier, Amsterdam (1978).

Table 35.2 Lennard-Jones (12,6) potential parameters

	(ε/k)/K	r_0/pm
Ar	111.84	362.3
C_2H_2	209.11	463.5
C_2H_4	200.78	458.9
C_2H_6	216.12	478.2
C_6H_6	377.46	617.4
CCl_4	378.86	624.1
Cl_2	296.27	448.5
CO_2	201.71	444.4
F_2	104.29	357.1
Kr	154.87	389.5
N_2	91.85	391.9
O_2	113.27	365.4
Xe	213.96	426.0

Source: F. Cuadros, I. Cachadiña, and W. Ahamuda, *Molec. Engineering* **6**, 319 (1996).

Table 36.1 Second virial coefficients, $B/(\text{cm}^3\ \text{mol}^{-1})$

	100 K	273 K	373 K	600 K
Air	−167.3	−13.5	3.4	19.0
Ar	−187.0	−21.7	−4.2	11.9
CH_4		−53.6	−21.2	8.1
CO_2		−142	−72.2	−12.4
H_2	−2.0	13.7	15.6	
He	11.4	12.0	11.3	10.4
Kr		−62.9	−28.7	1.7
N_2	−160.0	−10.5	6.2	21.7
Ne	−6.0	10.4	12.3	13.8
O_2	−197.5	−22.0	−3.7	12.9
Xe		−153.7	−81.7	−19.6

Data: AIP, JL. The values relate to the expansion in eqn 36.4b of Topic 36; convert to eqn 36.4a using $B' = B/RT$.
For Ar at 273 K, $C = 1200\ \text{cm}^6\ \text{mol}^{-1}$.

Table 36.2 Boyle temperatures of gases

	T_B/K
Ar	411.5
CH_4	510.0
CO_2	714.8
H_2	110.0
He	22.64
Kr	575.0
N_2	327.2
Ne	122.1
O_2	405.9
Xe	768.0

Data: AIP, KL.

Table 36.3 van der Waals parameters

	$a/(\text{atm dm}^6\ \text{mol}^{-2})$	$b/(10^{-2}\ \text{dm}^3\ \text{mol}^{-1})$		$a/(\text{atm dm}^6\ \text{mol}^{-2})$	$b/(10^{-2}\ \text{dm}^3\ \text{mol}^{-1})$
Ar	1.337	3.20	H_2S	4.484	4.34
C_2H_4	4.552	5.82	He	0.0341	2.38
C_2H_6	5.507	6.51	Kr	5.125	1.06
C_6H_6	18.57	11.93	N_2	1.352	3.87
CH_4	2.273	4.31	Ne	0.205	1.67
Cl_2	6.260	5.42	NH_3	4.169	3.71
CO	1.453	3.95	O_2	1.364	3.19
CO_2	3.610	4.29	SO_2	6.775	5.68
H_2	0.2420	2.65	Xe	4.137	5.16
H_2O	5.464	3.05			

Data: HCP.

Table 36.5 Critical constants of gases

	p_c/atm	V_c/(cm^3 mol^{-1})	T_c/K
Ar	48.0	75.3	150.7
Br_2	102	135	584
C_2H_4	50.50	124	283.1
C_2H_6	48.20	148	305.4
C_6H_6	48.6	260	562.7
CH_4	45.6	98.7	190.6
Cl_2	76.1	124	417.2
CO_2	72.9	94.0	304.2
F_2	55	144	
H_2	12.8	34.99	33.23
H_2O	218.3	55.3	647.4
HBr	84.0	363.0	
HCl	81.5	81.0	324.7
He	2.26	57.8	5.2
HI	80.8	423.2	
Kr	54.27	92.24	209.39
N_2	33.54	90.10	126.3
Ne	26.86	41.74	44.44
O_2	50.14	78.0	154.8
Xe	58.0	118.8	289.75

Table 38.2 Ionic radii, *r*/pm*

Li^+(4)	Be^{2+}(4)	B^{3+}(4)	N^{3-}	O^{2-}(6)	F^-(6)		
59	27	12	171	140	133		
Na^+(6)	Mg^{2+}(6)	Al^{3+}(6)	P^{3-}	S^{2-}(6)	Cl^-(6)		
102	72	53	212	184	181		
K^+(6)	Ca^{2+}(6)	Ga^{3+}(6)	As^{3-}(6)	Se^{2-}(6)	Br^-(6)		
138	100	62	222	198	196		
Rb^+(6)	Sr^{2+}(6)	In^{3+}(6)		Te^{2-}(6)	I^-(6)		
149	116	79		221	220		
Cs^+(6)	Ba^{2+}(6)	Tl^{3+}(6)					
167	136	88					
d-block elements (high-spin ions)							
Sc^{3+}(6)	Ti^{4+}(6)	Cr^{3+}(6)	Mn^{3+}(6)	Fe^{2+}(6)	Co^{3+}(6)	Cu^{2+}(6)	Zn^{2+}(6)
73	60	61	65	63	61	73	75

* Numbers in parentheses are the coordination numbers of the ions. Values for ions without a coordination number stated are estimates.

Data: R.D. Shannon and C.T. Prewitt, *Acta Cryst.* **B25**, 925 (1969).

Table 38.4 Lattice enthalpies, $\Delta H_{\mathrm{L}}^{\ominus}$/(kJ mol^{-1}) at 298 K

	F	Cl	Br	I
Halides				
Li	1037	852	815	761
Na	926	787	752	705
K	821	717	689	649
Rb	789	695	668	632
Cs	750	676	654	620
Ag	969	912	900	886
Be		3017		
Mg		2524		
Ca		2255		
Sr		2153		

Oxides							
MgO	3850	CaO	3461	SrO	3283	BaO	3114
Sulfides							
MgS	3406	CaS	3119	SrS	2974	BaS	2832

Entries refer to $MX(s) \rightarrow M^+(g) + X^-(g)$.
Data: Principally D. Cubicciotti, et al., *J. Chem. Phys.* **31**, 1646 (1959).

Table 39.1 Magnetic susceptibilities at 298 K

	$\chi/10^{-6}$	$\chi_m/(10^{-10}\ \mathrm{m^3\ mol^{-1}})$
$H_2O(l)$	−9.02	−1.63
$C_6H_6(l)$	−8.8	−7.8
$C_6H_{12}(l)$	−10.2	−11.1
$CCl_4(l)$	−5.4	−5.2
NaCl(s)	−16	−3.8
Cu(s)	−9.7	−0.69
S(rhombic)	−12.6	−1.95
Hg(l)	−28.4	−4.21
Al(s)	+20.7	+2.07
Pt(s)	+267.3	+24.25
Na(s)	+8.48	+2.01
K(s)	+5.94	+2.61
$CuSO_4 \cdot 5H_2O(s)$	+167	+183
$MnSO_4 \cdot 4H_2O(s)$	+1859	+1835
$NiSO_4 \cdot 7H_2O(s)$	+355	+503
$FeSO_4(s)$	+3743	+1558

Source: Principally HCP, with $\chi_m = \chi V_m = \chi\rho/M$.

Table 43.1 Properties of diatomic molecules

	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\theta^{\mathrm{V}}/\mathrm{K}$	$\tilde{B}/\mathrm{cm}^{-1}$	$\theta^{\mathrm{R}}/\mathrm{K}$	R_e/pm	$k_f/(\mathrm{N\ m^{-1}})$	$D_0/(\mathrm{kJ\ mol^{-1}})$	σ
$^{1}\mathrm{H}_2^+$	2321.8	3341	29.8	42.9	106	160	255.8	2
$^{1}\mathrm{H}_2$	4400.39	6332	60.864	87.6	74.138	574.9	432.1	2
$^{2}\mathrm{H}_2$	3118.46	4487	30.442	43.8	74.154	577.0	439.6	2
$^{1}\mathrm{H}^{19}\mathrm{F}$	4138.32	5955	20.956	30.2	91.680	965.7	564.4	1
$^{1}\mathrm{H}^{35}\mathrm{Cl}$	2990.95	4304	10.593	15.2	127.45	516.3	427.7	1
$^{1}\mathrm{H}^{81}\mathrm{Br}$	2648.98	3812	8.465	12.2	141.44	411.5	362.7	1
$^{1}\mathrm{H}^{127}\mathrm{I}$	2308.09	3321	6.511	9.37	160.92	313.8	294.9	1
$^{14}\mathrm{N}_2$	2358.07	3393	1.9987	2.88	109.76	2293.8	941.7	2
$^{16}\mathrm{O}_2$	1580.36	2274	1.4457	2.08	120.75	1176.8	493.5	2
$^{19}\mathrm{F}_2$	891.8	1283	0.8828	1.27	141.78	445.1	154.4	2
$^{35}\mathrm{Cl}_2$	559.71	805	0.2441	0.351	198.75	322.7	239.3	2
$^{12}\mathrm{C}^{16}\mathrm{O}$	2170.21	3122	1.9313	2.78	112.81	1903.17	1071.8	1
$^{79}\mathrm{Br}^{81}\mathrm{Br}$	323.2	465	0.0809	0.116	283.3	245.9	190.2	1

Data: AIP.

Table 44.1 Typical vibrational wavenumbers, $\tilde{\nu}/\mathrm{cm}^{-1}$

C–H stretch	2850–2960
C–H bend	1340–1465
C–C stretch, bend	700–1250
C=C stretch	1620–1680
C≡C stretch	2100–2260
O–H stretch	3590–3650
H-bonds	3200–3570
C=O stretch	1640–1780
C≡N stretch	2215–2275
N–H stretch	3200–3500
C–F stretch	1000–1400
C–Cl stretch	600–800
C–Br stretch	500–600
C–I stretch	500
CO_3^{2-}	1410–1450
NO_3^-	1350–1420
NO_2^-	1230–1250
SO_4^{2-}	1080–1130
Silicates	900–1100

Data: L.J. Bellamy, *The infrared spectra of complex molecules*. Chapman and Hall (1975). *Advances in infrared group frequencies*. Chapman and Hall (1968).

Table 45.1 Colour, wavelength, frequency, and energy of light

Colour	λ/nm	$\nu/(10^{14}\ \mathrm{Hz})$	$\tilde{\nu}/(10^{4}\ \mathrm{cm^{-1}})$	E/eV	$E/(\mathrm{kJ\ mol^{-1}})$
Infrared	>1000	<3.00	<1.00	<1.24	<120
Red	700	4.28	1.43	1.77	171
Orange	620	4.84	1.61	2.00	193
Yellow	580	5.17	1.72	2.14	206
Green	530	5.66	1.89	2.34	226
Blue	470	6.38	2.13	2.64	254
Violet	420	7.14	2.38	2.95	285
Ultraviolet	<400	>7.5	>2.5	>3.10	>300

Data: J.G. Calvert and J.N. Pitts, *Photochemistry*. Wiley, New York (1966).

Table 45.2 Absorption characteristics of some groups and molecules

Group	$\tilde{\nu}_{\max}/(10^4\ \mathrm{cm}^{-1})$	$\lambda_{\max}$/nm	$\varepsilon/(\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-1})$
C=C ($\pi^* \leftarrow \pi$)	6.10	163	1.5×10^4
	5.73	174	5.5×10^3
C=O ($\pi^* \leftarrow$ n)	3.7–3.5	270–290	10–20
–N=N–	2.9	350	15
	>3.9	<260	Strong
$-NO_2$	3.6	280	10
	4.8	210	1.0×10^4
C_6H_5-	3.9	255	200
	5.0	200	6.3×10^3
	5.5	180	1.0×10^5
$[Cu(OH_2)_6]^{2+}$(aq)	1.2	810	10
$[Cu(NH_3)_4]^{2+}$(aq)	1.7	600	50
H_2O ($\pi^* \leftarrow$ n)	6.0	167	7.0×10^3

Table 47.2 Nuclear spin properties

Nuclide	Natural abundance, %	Spin, I	Magnetic Moment, μ/μ_N	g-value	$\gamma/(10^7\ \mathrm{T}^{-1}\mathrm{s}^{-1})$	NMR frequency at 1 T, ν/MHz
^{1}n*		$\frac{1}{2}$	−1.9130	−3.8260	−18.324	29.164
^{1}H	99.9844	$\frac{1}{2}$	2.792 85	5.5857	26.752	42.576
^{2}H	0.0156	1	0.857 44	0.857 44	4.1067	6.536
^{3}H*		$\frac{1}{2}$	2.978 96	−4.2553	−20.380	45.414
^{10}B	19.6	3	1.8006	0.6002	2.875	4.575
^{11}B	80.4	$\frac{3}{2}$	2.6886	1.7923	8.5841	13.663
^{13}C	1.108	$\frac{1}{2}$	0.7024	1.4046	6.7272	10.708
^{14}N	99.635	1	0.403 56	0.403 56	1.9328	3.078
^{17}O	0.037	$\frac{5}{2}$	−1.893 79	−0.7572	−3.627	5.774
^{19}F	100	$\frac{1}{2}$	2.628 87	5.2567	25.177	40.077
^{31}P	100	$\frac{1}{2}$	1.1316	2.2634	10.840	17.251
^{33}S	0.74	$\frac{3}{2}$	0.6438	0.4289	2.054	3.272
^{35}Cl	75.4	$\frac{3}{2}$	0.8219	0.5479	2.624	4.176
^{37}Cl	24.6	$\frac{3}{2}$	0.6841	0.4561	2.184	3.476

* Radioactive.

μ is the magnetic moment of the spin state with the largest value of m_I: $\mu = g_I \mu_N I$ and μ_N is the nuclear magneton (see inside front cover).

Data: KL and HCP.

Table 50.1 Hyperfine coupling constants for atoms, *a*/mT

Nuclide	Spin	Isotropic coupling	Anisotropic coupling
^{1}H	$\frac{1}{2}$	50.8(1s)	
^{2}H	1	7.8(1s)	
^{13}C	$\frac{1}{2}$	113.0(2s)	6.6(2p)
^{14}N	1	55.2(2s)	4.8(2p)
^{19}F	$\frac{1}{2}$	1720(2s)	108.4(2p)
^{31}P	$\frac{1}{2}$	364(3s)	20.6(3p)
^{35}Cl	$\frac{3}{2}$	168(3s)	10.0(3p)
^{37}Cl	$\frac{3}{2}$	140(3s)	8.4(3p)

Data: P.W. Atkins and M.C.R. Symons, *The structure of inorganic radicals*. Elsevier, Amsterdam (1967).

Table 52.1 Rotational and vibrational temperatures: see Table 43.1

Table 52.2 Symmetry numbers: see Table 43.1

Table 56.1 Temperature variation of molar heat capacities†

	a	*b*/(10^{-3} K^{-1})	*c*/(10^{5} K^{2})
Monatomic gases			
	20.78	0	0
Other gases			
Br_2	37.32	0.50	−1.26
Cl_2	37.03	0.67	−2.85
CO_2	44.22	8.79	−8.62
F_2	34.56	2.51	−3.51
H_2	27.28	3.26	0.50
I_2	37.40	0.59	−0.71
N_2	28.58	3.77	−0.50
NH_3	29.75	25.1	−1.55
O_2	29.96	4.18	−1.67
Liquids (from melting to boiling)			
$C_{10}H_8$, naphthalene	79.5	0.4075	0
I_2	80.33	0	0
H_2O	75.29	0	0
Solids			
Al	20.67	12.38	0
C (graphite)	16.86	4.77	−8.54
$C_{10}H_8$, naphthalene	−110	936	0
Cu	22.64	6.28	0
I_2	40.12	49.79	0
NaCl	45.94	16.32	0
Pb	22.13	11.72	0.96

† For $C_{p,\mathrm{m}}/(\mathrm{J\,K^{-1}\,mol^{-1}}) = a + bT + c/T^2$.
Source: Mostly LR.

Table 56.2 Inversion temperatures, normal freezing and boiling points, and Joule–Thomson coefficients at 1 atm and 298 K

	T_I/K	T_f/K	T_b/K	μ/(K atm^{-1})
Air	603			0.189 at 50 °C
Argon	723	83.8	87.3	
Carbon dioxide	1500	194.7^s		1.11 at 300 K
Helium	40		4.22	−0.062
Hydrogen	202	14.0	20.3	−0.03
Krypton	1090	116.6	120.8	
Methane	968	90.6	111.6	
Neon	231	24.5	27.1	
Nitrogen	621	63.3	77.4	0.27
Oxygen	764	54.8	90.2	0.31

s: sublimes.
Data: AIP, JL, and M.W. Zemansky, *Heat and thermodynamics*. McGraw-Hill, New York (1957).

Table 57.2 Standard enthalpies of fusion and vaporization at the transition temperature, $\Delta_{trs}H^{\ominus}$/(kJ mol^{-1})

	T_f/K	Fusion	T_b/K	Vaporization		T_f/K	Fusion	T_b/K	Vaporization
Elements					**Inorganic compounds**				
Ag	1234	11.30	2436	250.6	CO_2	217.0	8.33	194.6	25.23^s
Ar	83.81	1.188	87.29	6.506	CS_2	161.2	4.39	319.4	26.74
Br_2	265.9	10.57	332.4	29.45	H_2O	273.15	6.008	373.15	40.656
Cl_2	172.1	6.41	239.1	20.41					44.016 at 298 K
F_2	53.6	0.26	85.0	3.16	H_2S	187.6	2.377	212.8	18.67
H_2	13.96	0.117	20.38	0.916	H_2SO_4	283.5	2.56		
He	3.5	0.021	4.22	0.084	NH_3	195.4	5.652	239.7	23.35
Hg	234.3	2.292	629.7	59.30					
I_2	386.8	15.52	458.4	41.80					
					Organic compounds				
N_2	63.15	0.719	77.35	5.586	CH_4	90.68	0.941	111.7	8.18
Na	371.0	2.601	1156	98.01	CCl_4	250.3	2.47	349.9	30.00
O_2	54.36	0.444	90.18	6.820	C_2H_6	89.85	2.86	184.6	14.7
Xe	161	2.30	165	12.6	C_6H_6	278.61	10.59	353.2	30.8
K	336.4	2.35	1031	80.23	C_6H_{14}	178	13.08	342.1	28.85
					$C_{10}H_8$	354	18.80	490.9	51.51
					CH_3OH	175.2	3.16	337.2	35.27
									37.99 at 298 K
					C_2H_5OH	158.7	4.60	352	43.5

Data: AIP; s denotes sublimation.

Table 57.3 Thermodynamic data for organic compounds at 298 K

	$M/(\mathrm{g\ mol^{-1}})$	$\Delta_f H^\ominus/(\mathrm{kJ\ mol^{-1}})$	$\Delta_f G^\ominus/(\mathrm{kJ\ mol^{-1}})$	$S_m^\ominus/(\mathrm{J\,K^{-1}\ mol^{-1}})$	$C_{p,m}^\ominus/(\mathrm{J\,K^{-1}\ mol^{-1}})$	$\Delta_c H^\ominus/(\mathrm{kJ\ mol^{-1}})$
C(s) (graphite)	12.011	0	0	5.740	8.527	−393.51
C(s) (diamond)	12.011	+1.895	+2.900	2.377	6.113	−395.40
CO_2(g)	44.040	−393.51	−394.36	213.74	37.11	
Hydrocarbons						
CH_4(g), methane	16.04	−74.81	−50.72	186.26	35.31	−890
CH_3(g), methyl	15.04	+145.69	+147.92	194.2	38.70	
C_2H_2(g), ethyne	26.04	+226.73	+209.20	200.94	43.93	−1300
C_2H_4(g), ethene	28.05	+52.26	+68.15	219.56	43.56	−1411
C_2H_6(g), ethane	30.07	−84.68	−32.82	229.60	52.63	−1560
C_3H_6(g), propene	42.08	+20.42	+62.78	267.05	63.89	−2058
C_3H_6(g), cyclopropane	42.08	+53.30	+104.45	237.55	55.94	−2091
C_3H_8(g), propane	44.10	−103.85	−23.49	269.91	73.5	−2220
C_4H_8(g), 1-butene	56.11	−0.13	+71.39	305.71	85.65	−2717
C_4H_8(g), *cis*-2-butene	56.11	−6.99	+65.95	300.94	78.91	−2710
C_4H_8(g), *trans*-2-butene	56.11	−11.17	+63.06	296.59	87.82	−2707
C_4H_{10}(g), butane	58.13	−126.15	−17.03	310.23	97.45	−2878
C_5H_{12}(g), pentane	72.15	−146.44	−8.20	348.40	120.2	−3537
C_5H_{12}(l)	72.15	−173.1				
C_6H_6(l), benzene	78.12	+49.0	+124.3	173.3	136.1	−3268
C_6H_6(g)	78.12	+82.93	+129.72	269.31	81.67	−3302
C_6H_{12}(l), cyclohexane	84.16	−156	+26.8	204.4	156.5	−3920
C_6H_{14}(l), hexane	86.18	−198.7		204.3		−4163
$C_6H_5CH_3$(g), methylbenzene (toluene)	92.14	+50.0	+122.0	320.7	103.6	−3953
C_7H_{16}(l), heptane	100.21	−224.4	+1.0	328.6	224.3	
C_8H_{18}(l), octane	114.23	−249.9	+6.4	361.1		−5471
C_8H_{18}(l), iso-octane	114.23	−255.1				−5461
$C_{10}H_8$(s), naphthalene	128.18	+78.53				−5157
Alcohols and phenols						
CH_3OH(l), methanol	32.04	−238.66	−166.27	126.8	81.6	−726
CH_3OH(g)	32.04	−200.66	−161.96	239.81	43.89	−764
C_2H_5OH(l), ethanol	46.07	−277.69	−174.78	160.7	111.46	−1368
C_2H_5OH(g)	46.07	−235.10	−168.49	282.70	65.44	−1409
C_6H_5OH(s), phenol	94.12	−165.0	−50.9	146.0		−3054
Carboxylic acids, hydroxy acids, and esters						
HCOOH(l), formic	46.03	−424.72	−361.35	128.95	99.04	−255
CH_3COOH(l), acetic	60.05	−484.5	−389.9	159.8	124.3	−875
CH_3COOH(aq)	60.05	−485.76	−396.46	178.7		
$CH_3CO_2^-$(aq)	59.05	−486.01	−369.31	+86.6†	−6.3	
$(COOH)_2$(s), oxalic	90.04	−827.2			117	−254
C_6H_5COOH(s), benzoic	122.13	−385.1	−245.3	167.6	146.8	−3227
$CH_3CH(OH)COOH$(s), lactic	90.08	−694.0				−1344
$CH_3COOC_2H_5$(l), ethyl acetate	88.11	−479.0	−332.7	259.4	170.1	−2231

Table 57.3 (Continued)

	M/(g mol^{-1})	$\Delta_f H^\ominus$/(kJ mol^{-1})	$\Delta_f G^\ominus$/(kJ mol^{-1})	$S_m^\ominus$ /(J K^{-1} mol^{-1})	$C_{p,m}^\ominus$ /(J K^{-1} mol^{-1})	$\Delta_c H^\ominus$/(kJ mol^{-1})
Alkanals and alkanones						
HCHO(g), methanal	30.03	−108.57	−102.53	218.77	35.40	−571
CH_3CHO(l), ethanal	44.05	−192.30	−128.12	160.2		−1166
CH_3CHO(g)	44.05	−166.19	−128.86	250.3	57.3	−1192
CH_3COCH_3(l), propanone	58.08	−248.1	−155.4	200.4	124.7	−1790
Sugars						
$C_6H_{12}O_6$(s), α-ᴅ-glucose	180.16	−1274				−2808
$C_6H_{12}O_6$(s), β-ᴅ-glucose	180.16	−1268	−910	212		
$C_6H_{12}O_6$(s), β-ᴅ-fructose	180.16	−1266				−2810
$C_{12}H_{22}O_{11}$(s), sucrose	342.30	−2222	−1543	360.2		−5645
Nitrogen compounds						
$CO(NH_2)_2$(s), urea	60.06	−333.51	−197.33	104.60	93.14	−632
CH_3NH_2(g), methylamine	31.06	−22.97	+32.16	243.41	53.1	−1085
$C_6H_5NH_2$(l), aniline	93.13	+31.1				−3393
$CH_2(NH_2)COOH$(s), glycine	75.07	−532.9	−373.4	103.5	99.2	−969

Data: NBS, TDOC. † Standard entropies of ions may be either positive or negative because the values are relative to the entropy of the hydrogen ion.

Table 57.4 Thermodynamic data for elements and inorganic compounds at 298 K

	M/(g mol^{-1})	$\Delta_f H^\ominus$/(kJ mol^{-1})	$\Delta_f G^\ominus$/(kJ mol^{-1})	$S_m^\ominus$ /(J K^{-1} mol^{-1})†	$C_{p,m}^\ominus$ /(J K^{-1} mol^{-1})
Aluminium (aluminum)					
Al(s)	26.98	0	0	28.33	24.35
Al(l)	26.98	+10.56	+7.20	39.55	24.21
Al(g)	26.98	+326.4	+285.7	164.54	21.38
Al^{3+}(g)	26.98	+5483.17			
Al^{3+}(aq)	26.98	−531	−485	−321.7	
Al_2O_3(s, α)	101.96	−1675.7	−1582.3	50.92	79.04
$AlCl_3$(s)	133.24	−704.2	−628.8	110.67	91.84
Argon					
Ar(g)	39.95	0	0	154.84	20.786
Antimony					
Sb(s)	121.75	0	0	45.69	25.23
SbH_3(g)	124.77	+145.11	+147.75	232.78	41.05
Arsenic					
As(s, α)	74.92	0	0	35.1	24.64
As(g)	74.92	+302.5	+261.0	174.21	20.79
As_4(g)	299.69	+143.9	+92.4	314	
AsH_3(g)	77.95	+66.44	+68.93	222.78	38.07
Barium					
Ba(s)	137.34	0	0	62.8	28.07
Ba(g)	137.34	+180	+146	170.24	20.79
Ba^{2+}(aq)	137.34	−537.64	−560.77	+9.6	
BaO(s)	153.34	−553.5	−525.1	70.43	47.78
$BaCl_2$(s)	208.25	−858.6	−810.4	123.68	75.14

(continued)

Table 57.4 (Continued)

	$M/(\mathrm{g\ mol^{-1}})$	$\Delta_f H^\ominus/(\mathrm{kJ\ mol^{-1}})$	$\Delta_f G^\ominus/(\mathrm{kJ\ mol^{-1}})$	$S_m^\ominus/(\mathrm{J\,K^{-1}\ mol^{-1}})^\dagger$	$C_{p,m}^\ominus/(\mathrm{J\,K^{-1}\ mol^{-1}})$
Beryllium					
Be(s)	9.01	0	0	9.50	16.44
Be(g)	9.01	+324.3	+286.6	136.27	20.79
Bismuth					
Bi(s)	208.98	0	0	56.74	25.52
Bi(g)	208.98	+207.1	+168.2	187.00	20.79
Bromine					
Br_2(l)	159.82	0	0	152.23	75.689
Br_2(g)	159.82	+30.907	+3.110	245.46	36.02
Br(g)	79.91	+111.88	+82.396	175.02	20.786
Br^-(g)	79.91	−219.07			
Br^-(aq)	79.91	−121.55	−103.96	+82.4	−141.8
HBr(g)	90.92	−36.40	−53.45	198.70	29.142
Cadmium					
Cd(s, γ)	112.40	0	0	51.76	25.98
Cd(g)	112.40	+112.01	+77.41	167.75	20.79
Cd^{2+}(aq)	112.40	−75.90	−77.612	−73.2	
CdO(s)	128.40	−258.2	−228.4	54.8	43.43
$CdCO_3$(s)	172.41	−750.6	−669.4	92.5	
Caesium (cesium)					
Cs(s)	132.91	0	0	85.23	32.17
Cs(g)	132.91	+76.06	+49.12	175.60	20.79
Cs^+(aq)	132.91	−258.28	−292.02	+133.05	−10.5
Calcium					
Ca(s)	40.08	0	0	41.42	25.31
Ca(g)	40.08	+178.2	+144.3	154.88	20.786
Ca^{2+}(aq)	40.08	−542.83	−553.58	−53.1	
CaO(s)	56.08	−635.09	−604.03	39.75	42.80
$CaCO_3$(s) (calcite)	100.09	−1206.9	−1128.8	92.9	81.88
$CaCO_3$(s) (aragonite)	100.09	−1207.1	−1127.8	88.7	81.25
CaF_2(s)	78.08	−1219.6	−1167.3	68.87	67.03
$CaCl_2$(s)	110.99	−795.8	−748.1	104.6	72.59
$CaBr_2$(s)	199.90	−682.8	−663.6	130	
Carbon (for 'organic' compounds of carbon, see Table 57.3)					
C(s) (graphite)	12.011	0	0	5.740	8.527
C(s) (diamond)	12.011	+1.895	+2.900	2.377	6.113
C(g)	12.011	+716.68	+671.26	158.10	20.838
C_2(g)	24.022	+831.90	+775.89	199.42	43.21
CO(g)	28.011	−110.53	−137.17	197.67	29.14
CO_2(g)	44.010	−393.51	−394.36	213.74	37.11
CO_2(aq)	44.010	−413.80	−385.98	117.6	
H_2CO_3(aq)	62.03	−699.65	−623.08	187.4	
HCO_3^-(aq)	61.02	−691.99	−586.77	+91.2	
CO_3^{2-}(aq)	60.01	−677.14	−527.81	−56.9	

Table 57.4 (Continued)

	$M/(\text{g mol}^{-1})$	$\Delta_f H^\ominus/(\text{kJ mol}^{-1})$	$\Delta_f G^\ominus/(\text{kJ mol}^{-1})$	$S_m^\ominus/(\text{J K}^{-1}\text{ mol}^{-1})^\dagger$	$C_{p,m}^\ominus/(\text{J K}^{-1}\text{ mol}^{-1})$
Carbon (for 'organic' compounds of carbon, see Table 57.3) (continued)					
$CCl_4(l)$	153.82	−135.44	−65.21	216.40	131.75
$CS_2(l)$	76.14	+89.70	+65.27	151.34	75.7
HCN(g)	27.03	+135.1	+124.7	201.78	35.86
HCN(l)	27.03	+108.87	+124.97	112.84	70.63
$CN^-(aq)$	26.02	+150.6	+172.4	+94.1	
Chlorine					
$Cl_2(g)$	70.91	0	0	223.07	33.91
Cl(g)	35.45	+121.68	+105.68	165.20	21.840
$Cl^-(g)$	34.45	−233.13			
$Cl^-(aq)$	35.45	−167.16	−131.23	+56.5	−136.4
HCl(g)	36.46	−92.31	−95.30	186.91	29.12
HCl(aq)	36.46	−167.16	−131.23	56.5	−136.4
Chromium					
Cr(s)	52.00	0	0	23.77	23.35
Cr(g)	52.00	+396.6	+351.8	174.50	20.79
$CrO_4^{2-}(aq)$	115.99	−881.15	−727.75	+50.21	
$Cr_2O_7^{2-}(aq)$	215.99	−1490.3	−1301.1	+261.9	
Copper					
Cu(s)	63.54	0	0	33.150	24.44
Cu(g)	63.54	+338.32	+298.58	166.38	20.79
$Cu^+(aq)$	63.54	+71.67	+49.98	+40.6	
$Cu^{2+}(aq)$	63.54	+64.77	+65.49	−99.6	
$Cu_2O(s)$	143.08	−168.6	−146.0	93.14	63.64
CuO(s)	79.54	−157.3	−129.7	42.63	42.30
$CuSO_4(s)$	159.60	−771.36	−661.8	109	100.0
$CuSO_4{\cdot}H_2O(s)$	177.62	−1085.8	−918.11	146.0	134
$CuSO_4{\cdot}5H_2O(s)$	249.68	−2279.7	−1879.7	300.4	280
Deuterium					
$D_2(g)$	4.028	0	0	144.96	29.20
HD(g)	3.022	+0.318	−1.464	143.80	29.196
$D_2O(g)$	20.028	−249.20	−234.54	198.34	34.27
$D_2O(l)$	20.028	−294.60	−243.44	75.94	84.35
HDO(g)	19.022	−245.30	−233.11	199.51	33.81
HDO(l)	19.022	−289.89	−241.86	79.29	
Fluorine					
$F_2(g)$	38.00	0	0	202.78	31.30
F(g)	19.00	+78.99	+61.91	158.75	22.74
$F^-(aq)$	19.00	−332.63	−278.79	−13.8	−106.7
HF(g)	20.01	−271.1	−273.2	173.78	29.13
Gold					
Au(s)	196.97	0	0	47.40	25.42
Au(g)	196.97	+366.1	+326.3	180.50	20.79
Helium					
He(g)	4.003	0	0	126.15	20.786

(continued)

Table 57.4 (Continued)

	$M/(\mathrm{g\ mol^{-1}})$	$\Delta_f H^\ominus/(\mathrm{kJ\ mol^{-1}})$	$\Delta_f G^\ominus/(\mathrm{kJ\ mol^{-1}})$	$S_m^\ominus/(\mathrm{J\,K^{-1}\ mol^{-1}})^\dagger$	$C_{p,m}^\ominus/(\mathrm{J\,K^{-1}\ mol^{-1}})$
Hydrogen (see also deuterium)					
$H_2(g)$	2.016	0	0	130.684	28.824
H(g)	1.008	+217.97	+203.25	114.71	20.784
$H^+(aq)$	1.008	0	0	0	0
$H^+(g)$	1.008	+1536.20			
$H_2O(s)$	18.015			37.99	
$H_2O(l)$	18.015	−285.83	−237.13	69.91	75.291
$H_2O(g)$	18.015	−241.82	−228.57	188.83	33.58
$H_2O_2(l)$	34.015	−187.78	−120.35	109.6	89.1
Iodine					
$I_2(s)$	253.81	0	0	116.135	54.44
$I_2(g)$	253.81	+62.44	+19.33	260.69	36.90
I(g)	126.90	+106.84	+70.25	180.79	20.786
$I^-(aq)$	126.90	−55.19	−51.57	+111.3	−142.3
HI(g)	127.91	+26.48	+1.70	206.59	29.158
Iron					
Fe(s)	55.85	0	0	27.28	25.10
Fe(g)	55.85	+416.3	+370.7	180.49	25.68
$Fe^{2+}(aq)$	55.85	−89.1	−78.90	−137.7	
$Fe^{3+}(aq)$	55.85	−48.5	−4.7	−315.9	
$Fe_3O_4(s)$ (magnetite)	231.54	−1118.4	−1015.4	146.4	143.43
$Fe_2O_3(s)$ (haematite)	159.69	−824.2	−742.2	87.40	103.85
FeS(s, α)	87.91	−100.0	−100.4	60.29	50.54
$FeS_2(s)$	119.98	−178.2	−166.9	52.93	62.17
Krypton					
Kr(g)	83.80	0	0	164.08	20.786
Lead					
Pb(s)	207.19	0	0	64.81	26.44
Pb(g)	207.19	+195.0	+161.9	175.37	20.79
$Pb^{2+}(aq)$	207.19	−1.7	−24.43	+10.5	
PbO(s, yellow)	223.19	−217.32	−187.89	68.70	45.77
PbO(s, red)	223.19	−218.99	−188.93	66.5	45.81
$PbO_2(s)$	239.19	−277.4	−217.33	68.6	64.64
Lithium					
Li(s)	6.94	0	0	29.12	24.77
Li(g)	6.94	+159.37	+126.66	138.77	20.79
$Li^+(aq)$	6.94	−278.49	−293.31	+13.4	68.6
Magnesium					
Mg(s)	24.31	0	0	32.68	24.89
Mg(g)	24.31	+147.70	+113.10	148.65	20.786
$Mg^{2+}(aq)$	24.31	−466.85	−454.8	−138.1	
MgO(s)	40.31	−601.70	−569.43	26.94	37.15
$MgCO_3(s)$	84.32	−1095.8	−1012.1	65.7	75.52
$MgCl_2(s)$	95.22	−641.32	−591.79	89.62	71.38

Table 57.4 (Continued)

	$M/(\mathrm{g\ mol^{-1}})$	$\Delta_f H^\ominus/(\mathrm{kJ\ mol^{-1}})$	$\Delta_f G^\ominus/(\mathrm{kJ\ mol^{-1}})$	$S_m^\ominus/(\mathrm{J\,K^{-1}\ mol^{-1}})^\dagger$	$C_{p,m}^\ominus/(\mathrm{J\,K^{-1}\ mol^{-1}})$
Mercury					
Hg(l)	200.59	0	0	76.02	27.983
Hg(g)	200.59	+61.32	+31.82	174.96	20.786
Hg^{2+}(aq)	200.59	+171.1	+164.40	−32.2	
Hg_2^{2+}(aq)	401.18	+172.4	+153.52	+84.5	
HgO(s)	216.59	−90.83	−58.54	70.29	44.06
Hg_2Cl_2(s)	472.09	−265.22	−210.75	192.5	102
$HgCl_2$(s)	271.50	−224.3	−178.6	146.0	
HgS(s, black)	232.65	−53.6	−47.7	88.3	
Neon					
Ne(g)	20.18	0	0	146.33	20.786
Nitrogen					
N_2(g)	28.013	0	0	191.61	29.125
N(g)	14.007	+472.70	+455.56	153.30	20.786
NO(g)	30.01	+90.25	+86.55	210.76	29.844
N_2O(g)	44.01	+82.05	+104.20	219.85	38.45
NO_2(g)	46.01	+33.18	+51.31	240.06	37.20
N_2O_4(g)	92.1	+9.16	+97.89	304.29	77.28
N_2O_5(s)	108.01	−43.1	+113.9	178.2	143.1
N_2O_5(g)	108.01	+11.3	+115.1	355.7	84.5
HNO_3(l)	63.01	−174.10	−80.71	155.60	109.87
HNO_3(aq)	63.01	−207.36	−111.25	146.4	−86.6
NO_3^-(aq)	62.01	−205.0	−108.74	+146.4	−86.6
NH_3(g)	17.03	−46.11	−16.45	192.45	35.06
NH_3(aq)	17.03	−80.29	−26.50	111.3	
NH_4^+(aq)	18.04	−132.51	−79.31	+113.4	79.9
NH_2OH(s)	33.03	−114.2			
HN_3(l)	43.03	+264.0	+327.3	140.6	43.68
HN_3(g)	43.03	+294.1	+328.1	238.97	98.87
N_2H_4(l)	32.05	+50.63	+149.43	121.21	139.3
NH_4NO_3(s)	80.04	−365.56	−183.87	151.08	84.1
NH_4Cl(s)	53.49	−314.43	−202.87	94.6	
Oxygen					
O_2(g)	31.999	0	0	205.138	29.355
O(g)	15.999	+249.17	+231.73	161.06	21.912
O_3(g)	47.998	+142.7	+163.2	238.93	39.20
OH^-(aq)	17.007	−229.99	−157.24	−10.75	−148.5
Phosphorus					
P(s, wh)	30.97	0	0	41.09	23.840
P(g)	30.97	+314.64	+278.25	163.19	20.786
P_2(g)	61.95	+144.3	+103.7	218.13	32.05
P_4(g)	123.90	+58.91	+24.44	279.98	67.15
PH_3(g)	34.00	+5.4	+13.4	210.23	37.11
PCl_3(g)	137.33	−287.0	−267.8	311.78	71.84

(*continued*)

Table 57.4 (Continued)

	$M/(\mathrm{g\ mol^{-1}})$	$\Delta_f H^\ominus/(\mathrm{kJ\ mol^{-1}})$	$\Delta_f G^\ominus/(\mathrm{kJ\ mol^{-1}})$	$S_\mathrm{m}^\ominus/(\mathrm{J\,K^{-1}\,mol^{-1}})^\dagger$	$C_{p,\mathrm{m}}^\ominus/(\mathrm{J\,K^{-1}\,mol^{-1}})$
Phosphorus (continued)					
PCl_3(l)	137.33	−319.7	−272.3	217.1	
PCl_5(g)	208.24	−374.9	−305.0	364.6	112.8
PCl_5(s)	208.24	−443.5			
H_3PO_3(s)	82.00	−964.4			
H_3PO_3(aq)	82.00	−964.8			
H_3PO_4(s)	94.97	−1279.0	−1119.1	110.50	106.06
H_3PO_4(l)	94.97	−1266.9			
H_3PO_4(aq)	94.97	−1277.4	−1018.7	−222	
PO_4^{3-}(aq)	94.97	−1277.4	−1018.7	−221.8	
P_4O_{10}(s)	283.89	−2984.0	−2697.0	228.86	211.71
P_4O_6(s)	219.89	−1640.1			
Potassium					
K(s)	39.10	0	0	64.18	29.58
K(g)	39.10	+89.24	+60.59	160.336	20.786
K^+(g)	39.10	+514.26			
K^+(aq)	39.10	−252.38	−283.27	+102.5	21.8
KOH(s)	56.11	−424.76	−379.08	78.9	64.9
KF(s)	58.10	−576.27	−537.75	66.57	49.04
KCl(s)	74.56	−436.75	−409.14	82.59	51.30
KBr(s)	119.01	−393.80	−380.66	95.90	52.30
KI(s)	166.01	−327.90	−324.89	106.32	52.93
Silicon					
Si(s)	28.09	0	0	18.83	20.00
Si(g)	28.09	+455.6	+411.3	167.97	22.25
SiO_2(s, α)	60.09	−910.94	−856.64	41.84	44.43
Silver					
Ag(s)	107.87	0	0	42.55	25.351
Ag(g)	107.87	+284.55	+245.65	173.00	20.79
Ag^+(aq)	107.87	+105.58	+77.11	+72.68	21.8
AgBr(s)	187.78	−100.37	−96.90	107.1	52.38
AgCl(s)	143.32	−127.07	−109.79	96.2	50.79
Ag_2O(s)	231.74	−31.05	−11.20	121.3	65.86
$AgNO_3$(s)	169.88	−129.39	−33.41	140.92	93.05
Sodium					
Na(s)	22.99	0	0	51.21	28.24
Na(g)	22.99	+107.32	+76.76	153.71	20.79
Na^+(aq)	22.99	−240.12	−261.91	+59.0	46.4
NaOH(s)	40.00	−425.61	−379.49	64.46	59.54
NaCl(s)	58.44	−411.15	−384.14	72.13	50.50
NaBr(s)	102.90	−361.06	−348.98	86.82	51.38
NaI(s)	149.89	−287.78	−286.06	98.53	52.09

Table 57.4 (Continued)

	$M/(\mathrm{g\ mol^{-1}})$	$\Delta_f H^{\ominus}/(\mathrm{kJ\ mol^{-1}})$	$\Delta_f G^{\ominus}/(\mathrm{kJ\ mol^{-1}})$	$S_m^{\ominus}/(\mathrm{J\,K^{-1}\ mol^{-1}})^{\dagger}$	$C_{p,m}^{\ominus}/(\mathrm{J\,K^{-1}\ mol^{-1}})$
Sulfur					
S(s, α) (rhombic)	32.06	0	0	31.80	22.64
S(s, β) (monoclinic)	32.06	+0.33	+0.1	32.6	23.6
S(g)	32.06	+278.81	+238.25	167.82	23.673
S_2(g)	64.13	+128.37	+79.30	228.18	32.47
S^{2-}(aq)	32.06	+33.1	+85.8	−14.6	
SO_2(g)	64.06	−296.83	−300.19	248.22	39.87
SO_3(g)	80.06	−395.72	−371.06	256.76	50.67
H_2SO_4(l)	98.08	−813.99	−690.00	156.90	138.9
H_2SO_4(aq)	98.08	−909.27	−744.53	20.1	−293
SO_4^{2-}(aq)	96.06	−909.27	−744.53	+20.1	−293
HSO_4^{-}(aq)	97.07	−887.34	−755.91	+131.8	−84
H_2S(g)	34.08	−20.63	−33.56	205.79	34.23
H_2S(aq)	34.08	−39.7	−27.83	121	
HS^{-}(aq)	33.072	−17.6	+12.08	+62.08	
SF_6(g)	146.05	−1209	−1105.3	291.82	97.28
Tin					
Sn(s, β)	118.69	0	0	51.55	26.99
Sn(g)	118.69	+302.1	+267.3	168.49	20.26
Sn^{2+}(aq)	118.69	−8.8	−27.2	−17	
SnO(s)	134.69	−285.8	−256.9	56.5	44.31
SnO_2(s)	150.69	−580.7	−519.6	52.3	52.59
Xenon					
Xe(g)	131.30	0	0	169.68	20.786
Zinc					
Zn(s)	65.37	0	0	41.63	25.40
Zn(g)	65.37	+130.73	+95.14	160.98	20.79
Zn^{2+}(aq)	65.37	−153.89	−147.06	−112.1	46
ZnO(s)	81.37	−348.28	−318.30	43.64	40.25

Source: NBS. † Standard entropies of ions may be either positive or negative because the values are relative to the entropy of the hydrogen ion.

Table 58.1 Expansion coefficients, α, and isothermal compressibilities, κ_T

	$\alpha/(10^{-4}\ \mathrm{K}^{-1})$	$\kappa_T/(10^{-6}\ \mathrm{atm}^{-1})$
Liquids		
Benzene	12.4	92.1
Carbon tetrachloride	12.4	90.5
Ethanol	11.2	76.8
Mercury	1.82	38.7
Water	2.1	49.6
Solids		
Copper	0.501	0.735
Diamond	0.030	0.187
Iron	0.354	0.589
Lead	0.861	2.21

The values refer to 20 °C.
Data: AIP(α), KL(κ_T).

Table 62.1 Standard entropies (and temperatures) of phase transitions, $\Delta_{\mathrm{trs}}S^{\ominus}/(\mathrm{J\ K^{-1}\ mol^{-1}})$

	Fusion (at T_f)	Vaporization (at T_b)
Ar	14.17 (at 83.8 K)	74.53 (at 87.3 K)
Br_2	39.76 (at 265.9 K)	88.61 (at 332.4 K)
C_6H_6	38.00 (at 278.6 K)	87.19 (at 353.2 K)
CH_3COOH	40.4 (at 289.8 K)	61.9 (at 391.4 K)
CH_3OH	18.03 (at 175.2 K)	104.6 (at 337.2 K)
Cl_2	37.22 (at 172.1 K)	85.38 (at 239.0 K)
H_2	8.38 (at 14.0 K)	44.96 (at 20.38 K)
H_2O	22.00 (at 273.2 K)	109.1 (at 373.2 K)
H_2S	12.67 (at 187.6 K)	87.75 (at 212.0 K)
He	4.8 (at 1.8 K and 30 bar)	19.9 (at 4.22 K)
N_2	11.39 (at 63.2 K)	75.22 (at 77.4 K)
NH_3	28.93 (at 195.4 K)	97.41 (at 239.73 K)
O_2	8.17 (at 54.4 K)	75.63 (at 90.2 K)

Data: AIP.

Table 62.2 The standard enthalpies and entropies of vaporization of liquids at their normal boiling point

	$\Delta_{\mathrm{vap}}H^{\ominus}/(\mathrm{kJ\ mol^{-1}})$	$\theta_b/°\mathrm{C}$	$\Delta_{\mathrm{vap}}S^{\ominus}/(\mathrm{J\ K^{-1}\ mol^{-1}})$
Benzene	30.8	80.1	+87.2
Carbon disulfide	26.74	46.25	+83.7
Carbon tetrachloride	30.00	76.7	+85.8
Cyclohexane	30.1	80.7	+85.1
Decane	38.75	174	+86.7
Dimethyl ether	21.51	−23	+86
Ethanol	38.6	78.3	+110.0
Hydrogen sulfide	18.7	−60.4	+87.9
Mercury	59.3	356.6	+94.2
Methane	8.18	−161.5	+73.2
Methanol	35.21	65.0	+104.1
Water	40.7	100.0	+109.1

Data: JL.

Table 63.1 Standard Third-Law entropies at 298 K: see Tables 57.3 and 57.4

Table 65.1 Standard Gibbs energies of formation at 298 K: see Tables 57.3 and 57.4

Table 70.1 Henry's law constants for gases at 298 K, $K/(\mathrm{kPa\ kg\ mol^{-1}})$

	Water	Benzene
CH_4	7.55×10^4	44.4×10^3
CO_2	3.01×10^3	8.90×10^2
H_2	1.28×10^5	2.79×10^4
N_2	1.56×10^5	1.87×10^4
O_2	7.92×10^4	

Data: converted from R.J. Silbey and R.A. Alberty, *Physical chemistry*. Wiley, New York (2001).

Table 72.3 Mean activity coefficients in water at 298 K

$b/b^{\ominus}$	HCl	KCl	$CaCl_2$	H_2SO_4	$LaCl_3$	$In_2(SO_4)_3$
0.001	0.966	0.966	0.888	0.830	0.790	
0.005	0.929	0.927	0.789	0.639	0.636	0.16
0.01	0.905	0.902	0.732	0.544	0.560	0.11
0.05	0.830	0.816	0.584	0.340	0.388	0.035
0.10	0.798	0.770	0.524	0.266	0.356	0.025
0.50	0.769	0.652	0.510	0.155	0.303	0.014
1.00	0.811	0.607	0.725	0.131	0.387	
2.00	1.011	0.577	1.554	0.125	0.954	

Data: RS, HCP, and S. Glasstone, *Introduction to electrochemistry*. Van Nostrand (1942).

Table 77.1A Standard potentials at 298 K. (a) In electrochemical order

Reduction half-reaction	$E^{\ominus}/V$
Strongly oxidizing	
$H_4XeO_6 + 2 H^+ + 2 e^- \rightarrow XeO_3 + 3 H_2O$	+3.0
$F_2 + 2 e^- \rightarrow 2F^-$	+2.87
$O_3 + 2 H^+ + 2 e^- \rightarrow O_2 + H_2O$	+2.07
$S_2O_8^{2-} + 2 e^- \rightarrow 2 SO_4^{2-}$	+2.05
$Ag^{2+} + e^- \rightarrow Ag^+$	+1.98
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.81
$H_2O_2 + 2 H^+ + 2 e^- \rightarrow 2 H_2O$	+1.78
$Au^+ + e^- \rightarrow Au$	+1.69
$Pb^{4+} + 2 e^- \rightarrow Pb^{2+}$	+1.67
$2 HClO + 2 H^+ + 2 e^- \rightarrow Cl_2 + 2 H_2O$	+1.63
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61
$2 HBrO + 2 H^+ + 2 e^- \rightarrow Br_2 + 2 H_2O$	+1.60
$MnO_4^- + 8 H^+ + 5e^- \rightarrow Mn^{2+} + 4 H_2O$	+1.51
$Mn^{3+} + e^- \rightarrow Mn^{2+}$	+1.51
$Au^{3+} + 3 e^- \rightarrow Au$	+1.40
$Cl_2 + 2 e^- \rightarrow 2 Cl^-$	+1.36
$Cr_2O_7^{2-} + 14 H^+ + 6 e^- \rightarrow 2 Cr^{3+} + 7 H_2O$	+1.33
$O_3 + H_2O + 2 e^- \rightarrow O_2 + 2 OH^-$	+1.24
$O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O$	+1.23
$ClO_4^- + 2 H^+ + 2 e^- \rightarrow ClO_3^- + H_2O$	+1.23
$MnO_2 + 4 H^+ + 2 e^- \rightarrow Mn^{2+} + 2 H_2O$	+1.23
$Pt^{2+} + 2 e^- \rightarrow Pt$	+1.20
$Br_2 + 2 e^- \rightarrow 2Br^-$	+1.09
$Pu^{4+} + e^- \rightarrow Pu^{3+}$	+0.97
$NO_3^- + 4 H^+ + 3 e^- \rightarrow NO + 2 H_2O$	+0.96
$2 Hg^{2+} + 2 e^- \rightarrow Hg_2^{2+}$	+0.92
$ClO^- + H_2O + 2 e^- \rightarrow Cl^- + 2 OH^-$	+0.89
$Hg^{2+} + 2 e^- \rightarrow Hg$	+0.86
$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$	+0.80
$Ag^+ + e^- \rightarrow Ag$	+0.80
$Hg_2^{2+} + 2 e^- \rightarrow 2 Hg$	+0.79
$AgF + e^- \rightarrow Ag + F^-$	+0.78
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77
$BrO^- + H_2O + 2 e^- \rightarrow Br^- + 2 OH^-$	+0.76
$Hg_2SO_4 + 2 e^- \rightarrow 2 Hg + SO_4^{2-}$	+0.62
$MnO_4^{2-} + 2 H_2O + 2 e^- \rightarrow MnO_2 + 4 OH^-$	+0.60
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	+0.56
$I_2 + 2 e^- \rightarrow 2 I^-$	+0.54
$I_3^- + 2 e^- \rightarrow 3 I^-$	+0.53
$Cu^+ + e^- \rightarrow Cu$	+0.52
$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$	+0.49
$Ag_2CrO_4 + 2 e^- \rightarrow 2 Ag + CrO_4^{2-}$	+0.45
$O_2 + 2 H_2O + 4 e^- \rightarrow 4 OH^-$	+0.40
$ClO_4^- + H_2O + 2 e^- \rightarrow ClO_3^- + 2OH^-$	+0.36
$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$	+0.36
$Cu^{2+} + 2 e^- \rightarrow Cu$	+0.34
$Hg_2Cl_2 + 2 e^- \rightarrow 2 Hg + 2 Cl^-$	+0.27
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.22
$Bi^{3+} + 3 e^- \rightarrow Bi$	+0.20
$Cu^{2+} + e^- \rightarrow Cu^+$	+0.16
$Sn^{4+} + 2 e^- \rightarrow Sn^{2+}$	+0.15
$NO_3^- + H_2O + 2 e^- \rightarrow NO_2^- + 2 OH^-$	+0.10
$AgBr + e^- \rightarrow Ag + Br^-$	+0.0713
$Ti^{4+} + e^- \rightarrow Ti^{3+}$	0.00
$2 H^+ + 2 e^- \rightarrow H_2$	0, by definition

(continued)

Table 77.1 (Continued)

Reduction half-reaction	$E^\ominus$/V	Reduction half-reaction	$E^\ominus$/V
$\mathrm{Fe^{3+}+3\,e^-\rightarrow Fe}$	−0.04	$\mathrm{Zn^{2+}+2\,e^-\rightarrow Zn}$	−0.76
$\mathrm{O_2+H_2O+2\,e^-\rightarrow HO_2^-+OH^-}$	−0.08	$\mathrm{Cd(OH)_2+2e^-\rightarrow Cd+2OH^-}$	−0.81
$\mathrm{Pb^{2+}+2\,e^-\rightarrow Pb}$	−0.13	$\mathrm{2\,H_2O+2\,e^-\rightarrow H_2+2\,OH^-}$	−0.83
$\mathrm{In^++e^-\rightarrow In}$	−0.14	$\mathrm{Cr^{2+}+2e^-\rightarrow Cr}$	−0.91
$\mathrm{Sn^{2+}+2\,e^-\rightarrow Sn}$	−0.14	$\mathrm{Mn^{2+}+2\,e^-\rightarrow Mn}$	−1.18
$\mathrm{AgI+e^-\rightarrow Ag+I^-}$	−0.15	$\mathrm{V^{2+}+2\,e^-\rightarrow V}$	−1.19
$\mathrm{Ni^{2+}+2\,e^-\rightarrow Ni}$	−0.23	$\mathrm{Ti^{2+}+2\,e^-\rightarrow Ti}$	−1.63
$\mathrm{V^{3+}+e^-\rightarrow V^{2+}}$	−0.26	$\mathrm{Al^{3+}+3\,e^-\rightarrow Al}$	−1.66
$\mathrm{Co^{2+}+2\,e^-\rightarrow Co}$	−0.28	$\mathrm{U^{3+}+3\,e^-\rightarrow U}$	−1.79
$\mathrm{In^{3+}+3\,e^-\rightarrow In}$	−0.34	$\mathrm{Be^{2+}+2\,e^-\rightarrow Be}$	−1.85
$\mathrm{Tl^++e^-\rightarrow Tl}$	−0.34	$\mathrm{Sc^{3+}+3\,e^-\rightarrow Sc}$	−2.09
$\mathrm{PbSO_4+2\,e^-\rightarrow Pb+SO_4^{2-}}$	−0.36	$\mathrm{Mg^{2+}+2\,e^-\rightarrow Mg}$	−2.36
$\mathrm{Ti^{3+}+e^-\rightarrow Ti^{2+}}$	−0.37	$\mathrm{Ce^{3+}+3\,e^-\rightarrow Ce}$	−2.48
$\mathrm{Cd^{2+}+2\,e^-\rightarrow Cd}$	−0.40	$\mathrm{La^{3+}+3\,e^-\rightarrow La}$	−2.52
$\mathrm{In^{2+}+e^-\rightarrow In^+}$	−0.40	$\mathrm{Na^++e^-\rightarrow Na}$	−2.71
$\mathrm{Cr^{3+}+e^-\rightarrow Cr^{2+}}$	−0.41	$\mathrm{Ca^{2+}+2\,e^-\rightarrow Ca}$	−2.87
$\mathrm{Fe^{2+}+2\,e^-\rightarrow Fe}$	−0.44	$\mathrm{Sr^{2+}+2\,e^-\rightarrow Sr}$	−2.89
$\mathrm{In^{3+}+2\,e^-\rightarrow In^+}$	−0.44	$\mathrm{Ba^{2+}+2\,e^-\rightarrow Ba}$	−2.91
$\mathrm{S+2\,e^-\rightarrow S^{2-}}$	−0.48	$\mathrm{Ra^{2+}+2\,e^-\rightarrow Ra}$	−2.92
$\mathrm{In^{3+}+e^-\rightarrow In^{2+}}$	−0.49	$\mathrm{Cs^++e^-\rightarrow Cs}$	−2.92
$\mathrm{O_2+e^-\rightarrow O_2^-}$	−0.56	$\mathrm{Rb^++e^-\rightarrow Rb}$	−2.93
$\mathrm{U^{4+}+e^-\rightarrow U^{3+}}$	−0.61	$\mathrm{K^++e^-\rightarrow K}$	−2.93
$\mathrm{Cr^{3+}+3\,e^-\rightarrow Cr}$	−0.74	$\mathrm{Li^++e^-\rightarrow Li}$	−3.05
		Strongly reducing	

Table 77.1 Standard potentials at 298 K. (b) In alphabetical order

Reduction half-reaction	$E^\ominus$/V	Reduction half-reaction	$E^\ominus$/V
$\mathrm{Ag^++e^-\rightarrow Ag}$	+0.80	$\mathrm{Ca^{2+}+2\,e^-\rightarrow Ca}$	−2.87
$\mathrm{Ag^{2+}+e^-\rightarrow Ag^+}$	+1.98	$\mathrm{Cd(OH)_2+2\,e^-\rightarrow Cd+2\,OH^-}$	−0.81
$\mathrm{AgBr+e^-\rightarrow Ag+Br^-}$	+0.0713	$\mathrm{Cd^{2+}+2\,e^-\rightarrow Cd}$	−0.40
$\mathrm{AgCl+e^-\rightarrow Ag+Cl^-}$	+0.22	$\mathrm{Ce^{3+}+3\,e^-\rightarrow Ce}$	−2.48
$\mathrm{Ag_2CrO_4+2\,e^-\rightarrow 2Ag+CrO_4^{2-}}$	+0.45	$\mathrm{Ce^{4+}+e^-\rightarrow Ce^{3+}}$	+1.61
$\mathrm{AgF+e^-\rightarrow Ag+F^-}$	+0.78	$\mathrm{Cl_2+2\,e^-\rightarrow 2\,Cl^-}$	+1.36
$\mathrm{AgI+e^-\rightarrow Ag+I^-}$	−0.15	$\mathrm{ClO^-+H_2O+2\,e^-\rightarrow Cl^-+2\,OH^-}$	+0.89
$\mathrm{Al^{3+}+3\,e^-\rightarrow Al}$	−1.66	$\mathrm{ClO_4^-+2\,H^++2\,e^-\rightarrow ClO_3^-+H_2O}$	+1.23
$\mathrm{Au^++e^-\rightarrow Au}$	+1.69	$\mathrm{ClO_4^-+H_2O+2\,e^-\rightarrow ClO_3^-+2\,OH^-}$	+0.36
$\mathrm{Au^{3+}+3\,e^-\rightarrow Au}$	+1.40	$\mathrm{Co^{2+}+2\,e^-\rightarrow Co}$	−0.28
$\mathrm{Ba^{2+}+2\,e^-\rightarrow Ba}$	−2.91	$\mathrm{Co^{3+}+e^-\rightarrow Co^{2+}}$	+1.81
$\mathrm{Be^{2+}+2\,e^-\rightarrow Be}$	−1.85	$\mathrm{Cr^{2+}+2\,e^-\rightarrow Cr}$	−0.91
$\mathrm{Bi^{3+}+3\,e^-\rightarrow Bi}$	+0.20	$\mathrm{Cr_2O_7^{2-}+14\,H^++6\,e^-\rightarrow 2\,Cr^{3+}+7H_2O}$	+1.33
$\mathrm{Br_2+2\,e^-\rightarrow 2Br^-}$	+1.09	$\mathrm{Cr^{3+}+3\,e^-\rightarrow Cr}$	−0.74
$\mathrm{BrO^-+H_2O+2\,e^-\rightarrow Br^-+2\,OH^-}$	+0.76	$\mathrm{Cr^{3+}+e^-\rightarrow Cr^{2+}}$	−0.41

Table 77.1 (Continued)

Reduction half-reaction	$E^\ominus$/V	Reduction half-reaction	$E^\ominus$/V
$Cs^+ + e^- \rightarrow Cs$	−2.92	$MnO_4^{2-} + 2\ H_2O + 2\ e^- \rightarrow MnO_2 + 4\ OH^-$	+0.60
$Cu^+ + e^- \rightarrow Cu$	+0.52	$Na^+ + e^- \rightarrow Na$	−2.71
$Cu^{2+} + 2\ e^- \rightarrow Cu$	+0.34	$Ni^{2+} + 2\ e^- \rightarrow Ni$	−0.23
$Cu^{2+} + e^- \rightarrow Cu^+$	+0.16	$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$	+0.49
$F_2 + 2\ e^- \rightarrow 2F^-$	+2.87	$NO_3^- + 2\ H^+ + e^- \rightarrow NO_2 + H_2O$	+0.80
$Fe^{2+} + 2\ e^- \rightarrow Fe$	−0.44	$NO_3^- + 4\ H^+ + 3\ e^- \rightarrow NO + 2\ H_2O$	+0.96
$Fe^{3+} + 3\ e^- \rightarrow Fe$	−0.04	$NO_3^- + H_2O + 2\ e^- \rightarrow NO_2^- + 2\ OH^-$	+0.10
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77	$O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$	+0.40
$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$	+0.36	$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$	+1.23
$2\ H^+ + 2\ e^- \rightarrow H_2$	0, by definition	$O_2 + e^- \rightarrow O_2^-$	−0.56
$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$	−0.83	$O_2 + H_2O + 2\ e^- \rightarrow HO_2^- + OH^-$	−0.08
$2\ HBrO + 2\ H^+ + 2\ e^- \rightarrow Br_2 + 2\ H_2O$	+1.60	$O_3 + 2\ H^+ + 2\ e^- \rightarrow O_2 + H_2O$	+2.07
$2\ HClO + 2\ H^+ + 2\ e^- \rightarrow Cl_2 + 2\ H_2O$	+1.63	$O_3 + H_2O + 2\ e^- \rightarrow O_2 + 2\ OH^-$	+1.24
$H_2O_2 + 2\ H^+ + 2\ e^- \rightarrow 2\ H_2O$	+1.78	$Pb^{2+} + 2\ e^- \rightarrow Pb$	−0.13
$H_4XeO_6 + 2\ H^+ + 2\ e^- \rightarrow XeO_3 + 3\ H_2O$	+3.0	$Pb^{4+} + 2\ e^- \rightarrow Pb^{2+}$	+1.67
$Hg_2^{2+} + 2\ e^- \rightarrow 2\ Hg$	+0.79	$PbSO_4 + 2\ e^- \rightarrow Pb + SO_4^{2-}$	−0.36
$Hg_2Cl_2 + 2\ e^- \rightarrow 2\ Hg + 2\ Cl^-$	+0.27	$Pt^{2+} + 2\ e^- \rightarrow Pt$	+1.20
$Hg^{2+} + 2\ e^- \rightarrow Hg$	+0.86	$Pu^{4+} + e^- \rightarrow Pu^{3+}$	+0.97
$2\ Hg^{2+} + 2\ e^- \rightarrow Hg_2^{2+}$	+0.92	$Ra^{2+} + 2\ e^- \rightarrow Ra$	−2.92
$Hg_2SO_4 + 2\ e^- \rightarrow 2\ Hg + SO_4^{2-}$	+0.62	$Rb^+ + e^- \rightarrow Rb$	−2.93
$I_2 + 2\ e^- \rightarrow 2\ I^-$	+0.54	$S + 2\ e^- \rightarrow S^{2-}$	−0.48
$I_3^- + 2\ e^- \rightarrow 3\ I^-$	+0.53	$S_2O_8^{2-} + 2e^- \rightarrow 2\ SO_4^{2-}$	+2.05
$In^+ + e^- \rightarrow In$	−0.14	$Sc^{3+} + 3\ e^- \rightarrow Sc$	−2.09
$In^{2+} + e^- \rightarrow In^+$	−0.40	$Sn^{2+} + 2\ e^- \rightarrow Sn$	−0.14
$In^{3+} + 2\ e^- \rightarrow In^+$	−0.44	$Sn^{4+} + 2\ e^- \rightarrow Sn^{2+}$	+0.15
$In^{3+} + 3\ e^- \rightarrow In$	−0.34	$Sr^{2+} + 2\ e^- \rightarrow Sr$	−2.89
$In^{3+} + e^- \rightarrow In^{2+}$	−0.49	$Ti^{2+} + 2\ e^- \rightarrow Ti$	−1.63
$K^+ + e^- \rightarrow K$	−2.93	$Ti^{3+} + e^- \rightarrow Ti^{2+}$	−0.37
$La^{3+} + 3\ e^- \rightarrow La$	−2.52	$Ti^{4+} + e^- \rightarrow Ti^{3+}$	0.00
$Li^+ + e^- \rightarrow Li$	−3.05	$Tl^+ + e^- \rightarrow Tl$	−0.34
$Mg^{2+} + 2\ e^- \rightarrow Mg$	−2.36	$U^{3+} + 3\ e^- \rightarrow U$	−1.79
$Mn^{2+} + 2\ e^- \rightarrow Mn$	−1.18	$U^{4+} + e^- \rightarrow U^{3+}$	−0.61
$Mn^{3+} + e^- \rightarrow Mn^{2+}$	+1.51	$V^{2+} + 2\ e^- \rightarrow V$	−1.19
$MnO_2 + 4\ H^+ + 2\ e^- \rightarrow Mn^{2+} + 2\ H_2O$	+1.23	$V^{3+} + e^- \rightarrow V^{2+}$	−0.26
$MnO_4^{2-} + 8\ H^+ + 5\ e^- \rightarrow Mn^{2+} + 4H_2O$	+1.51	$Zn^{2+} + 2\ e^- \rightarrow Zn$	−0.76
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	+0.56		

Table 78.1 Collision cross-sections, σ/nm^2

Ar	0.36
C_2H_4	0.64
C_6H_6	0.88
CH_4	0.46
Cl_2	0.93
CO_2	0.52
H_2	0.27
He	0.21
N_2	0.43
Ne	0.24
O_2	0.40
SO_2	0.58

Data: KL.

Table 79.1 Transport properties of gases at 1 atm

	κ/(mW K^{-1} m^{-1})	η/μP	
	273 K	273 K	293 K
Air	24.1	173	182
Ar	16.3	210	223
C_2H_4	16.4	97	103
CH_4	30.2	103	110
Cl_2	7.9	123	132
CO_2	14.5	136	147
H_2	168.2	84	88
He	144.2	187	196
Kr	8.7	234	250
N_2	24.0	166	176
Ne	46.5	298	313
O_2	24.5	195	204
Xe	5.2	212	228

Data: KL.

Table 80.1 Viscosities of liquids at 298 K, η/(10^{-3} kg m^{-1} s^{-1})

Benzene	0.601
Carbon tetrachloride	0.880
Ethanol	1.06
Mercury	1.55
Methanol	0.553
Pentane	0.224
Sulfuric acid	27
Water†	0.891

† The viscosity of water over its entire liquid range is represented with less than 1 per cent error by the expression $\log(\eta_{20}/\eta)=A/B$,
$A=1.370\,23(t-20)+8.36\times10^{-4}(t-20)^2$ $B=109+t$ $t=\theta/°\mathrm{C}$
Convert kg m^{-1} s^{-1} to centipoise (cP) by multiplying by 10^3 (so $\eta\approx1$ cP for water).
Data: AIP, KL.

Table 80.2 Ionic mobilities in water at 298 K, u/(10^{-8} m^2 s^{-1} V^{-1})

Cations		Anions	
Ag^+	6.24	Br^-	8.09
Ca^{2+}	6.17	$CH_3CO_2^-$	4.24
Cu^{2+}	5.56	Cl^-	7.91
H^+	36.23	CO_3^{2-}	7.46
K^+	7.62	F^-	5.70
Li^+	4.01	$[Fe(CN)_6]^{3-}$	10.5
Na^+	5.19	$[Fe(CN)_6]^{4-}$	11.4
NH_4^+	7.63	I^-	7.96
$[N(CH_3)_4]^+$	4.65	NO_3^-	7.40
Rb^+	7.92	OH^-	20.64
Zn^{2+}	5.47	SO_4^{2-}	8.29

Data: Principally Table 80.1 and $u=\lambda/zF$.

Table 81.1 Diffusion coefficients at 298 K, $D/(10^{-9}\ \text{m}^2\ \text{s}^{-1})$

Molecules in liquids				**Ions in water**			
I_2 in hexane	4.05	H_2 in CCl_4(l)	9.75	K^+	1.96	Br^-	2.08
in benzene	2.13	N_2 in CCl_4(l)	3.42	H^+	9.31	Cl^-	2.03
CCl_4 in heptane	3.17	O_2 in CCl_4(l)	3.82	Li^+	1.03	F^-	1.46
Glycine in water	1.055	Ar in CCl_4(l)	3.63	Na^+	1.33	I^-	2.05
Dextrose in water	0.673	CH_4 in CCl_4(l)	2.89			OH^-	5.03
Sucrose in water	0.5216	H_2O in water	2.26				
		CH_3OH in water	1.58				
		C_2H_5OH in water	1.24				

Data: AIP.

Table 83.1 Kinetic data for first-order reactions

	Phase	θ/°C	k_r/s^{-1}	$t_{1/2}$
$2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$	g	25	3.38×10^{-5}	5.70 h
	HNO_3(l)	25	1.47×10^{-6}	131 h
	Br_2(l)	25	4.27×10^{-5}	4.51 h
$C_2H_6 \rightarrow 2\ CH_3$	g	700	5.36×10^{-4}	21.6 min
Cyclopropane → propene	g	500	6.71×10^{-4}	17.2 min
$CH_3N_2CH_3 \rightarrow C_2H_6 + N_2$	g	327	3.4×10^{-4}	34 min
Sucrose → glucose + fructose	aq(H^+)	25	6.0×10^{-5}	3.2 h

g: High pressure gas-phase limit.
Data: Principally K.J. Laidler, *Chemical kinetics*. Harper & Row, New York (1987); M.J. Pilling and P.W. Seakins, *Reaction kinetics*. Oxford University Press, Oxford (1995); J. Nicholas, *Chemical kinetics*. Harper & Row, New York (1976). See also JL.

Table 83.2 Kinetic data for second-order reactions

	Phase	θ/°C	$k_r/(\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$
$2\ NOBr \rightarrow 2\ NO + Br_2$	g	10	0.80
$2\ NO_2 \rightarrow 2\ NO + O_2$	g	300	0.54
$H_2 + I_2 \rightarrow 2\ HI$	g	400	2.42×10^{-2}
$D_2 + HCl \rightarrow DH + DCl$	g	600	0.141
$2\ I \rightarrow I_2$	g	23	7×10^{9}
	hexane	50	1.8×10^{10}
$CH_3Cl + CH_3O^-$	methanol	20	2.29×10^{-6}
$CH_3Br + CH_3O^-$	methanol	20	9.23×10^{-6}
$H^+ + OH^- \rightarrow H_2O$	water	25	1.35×10^{11}
	ice	−10	8.6×10^{12}

Data: Principally K.J. Laidler, *Chemical kinetics*. Harper & Row, New York (1987); M.J. Pilling and P.W. Seakins, *Reaction kinetics*. Oxford University Press, Oxford (1995); J. Nicholas, *Chemical kinetics*. Harper & Row, New York (1976).

Table 85.1 Arrhenius parameters

First-order reactions	**$A/\mathrm{s^{-1}}$**	**$E_a/(\mathrm{kJ\ mol^{-1}})$**
Cyclopropane → propene	1.58×10^{15}	272
$CH_3NC \rightarrow CH_3CN$	3.98×10^{13}	160
cis-CHD=CHD → *trans*-CHD=CHD	3.16×10^{12}	256
Cyclobutane → 2 C_2H_4	3.98×10^{13}	261
$C_2H_5I \rightarrow C_2H_4 + HI$	2.51×10^{17}	209
$C_2H_6 \rightarrow 2\ CH_3$	2.51×10^{7}	384
$2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$	4.94×10^{13}	103.4
$N_2O \rightarrow N_2 + O$	7.94×10^{11}	250
$C_2H_5 \rightarrow C_2H_4 + H$	1.0×10^{13}	167

Second-order, gas-phase	**$A/(\mathrm{dm^3\ mol^{-1}\ s^{-1}})$**	**$E_a/(\mathrm{kJ\ mol^{-1}})$**
$O + N_2 \rightarrow NO + N$	1×10^{11}	315
$OH + H_2 \rightarrow H_2O + H$	8×10^{10}	42
$Cl + H_2 \rightarrow HCl + H$	8×10^{10}	23
$2\ CH_3 \rightarrow C_2H_6$	2×10^{10}	*ca.*0
$NO + Cl_2 \rightarrow NOCl + Cl$	4.0×10^{9}	85
$SO + O_2 \rightarrow SO_2 + O$	3×10^{8}	27
$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$	2×10^{8}	44
$C_6H_5 + H_2 \rightarrow C_6H_6 + H$	1×10^{8}	*ca.*25

Second-order, solution	**$A/(\mathrm{dm^3\ mol^{-1}\ s^{-1}})$**	**$E_a/(\mathrm{kJ\ mol^{-1}})$**
$C_2H_5ONa + CH_3I$ in ethanol	2.42×10^{11}	81.6
$C_2H_5Br + OH^-$ in water	4.30×10^{11}	89.5
$C_2H_5I + C_2H_5O^-$ in ethanol	1.49×10^{11}	86.6
$C_2H_5Br + OH^-$ in ethanol	4.30×10^{11}	89.5
$CO_2 + OH^-$ in water	1.5×10^{10}	38
$CH_3I + S_2O_3^{2-}$ in water	2.19×10^{12}	78.7
Sucrose + H_2O in acidic water	1.50×10^{15}	107.9
$(CH_3)_3CCl$ solvolysis		
in water	7.1×10^{16}	100
in methanol	2.3×10^{13}	107
in ethanol	3.0×10^{13}	112
in acetic acid	4.3×10^{13}	111
in chloroform	1.4×10^{4}	45
$C_6H_5NH_2 + C_6H_5COCH_2Br$ in benzene	91	34

Data: Principally J. Nicholas, *Chemical kinetics*. Harper & Row, New York (1976) and A.A. Frost and R.G. Pearson, *Kinetics and mechanism*. Wiley, New York (1961).

Table 87.1 Arrhenius parameters for gas-phase reactions

	$A/(\mathrm{dm^3\ mol^{-1}\ s^{-1}})$			
	Experiment	Theory	$E_a/(\mathrm{kJ\ mol^{-1}})$	P
$2\ NOCl \rightarrow 2\ NO + Cl_2$	9.4×10^{9}	5.9×10^{10}	102.0	0.16
$2\ NO_2 \rightarrow 2\ NO + O_2$	2.0×10^{9}	4.0×10^{10}	111.0	5.0×10^{-2}
$2\ ClO \rightarrow Cl_2 + O_2$	6.3×10^{7}	2.5×10^{10}	0.0	2.5×10^{-3}
$H_2 + C_2H_4 \rightarrow C_2H_6$	1.24×10^{6}	7.4×10^{11}	180	1.7×10^{-6}
$K + Br_2 \rightarrow KBr + Br$	1.0×10^{12}	2.1×10^{11}	0.0	4.8

Data: Principally M.J. Pilling and P.W. Seakins, *Reaction kinetics*. Oxford University Press, Oxford (1995).

Table 88.1 Arrhenius parameters for reactions in solution. See Table 85.1.

Table 95.1 Maximum observed standard enthalpies of physisorption, $\Delta_{ad}H^{\ominus}/(\mathrm{kJ\ mol^{-1}})$ at 298 K

C_2H_2	−38	H_2	−84
C_2H_4	−34	H_2O	−59
CH_4	−21	N_2	−21
Cl_2	−36	NH_3	−38
CO	−25	O_2	−21
CO_2	−25		

Data: D.O. Haywood and B.M.W. Trapnell, *Chemisorption*. Butterworth (1964).

Table 95.2 Standard enthalpies of chemisorption, $\Delta_{ad}H^{\ominus}/(\mathrm{kJ\ mol^{-1}})$ at 298 K

Adsorbate	Adsorbent (substrate)											
	Ti	Ta	Nb	W	Cr	Mo	Mn	Fe	Co	Ni	Rh	Pt
H_2		−188			−188	−167	−71	−134			−117	
N_2		−586						−293				
O_2						−720					−494	−293
CO	−640							−192	−176			
CO_2	−682	−703	−552	−456	−339	−372	−222	−225	−146	−184		
NH_3				−301				−188		−155		
C_2H_4		−577		−427	−427			−285		−243	−209	

Data: D.O. Haywood and B.M.W. Trapnell, *Chemisorption*. Butterworth (1964).

PART 5 Character tables

The groups C_1, C_s, C_i

C_1, 1	E	$h=1$
A	1	

$C_s = C_h$, m	E	σ_h	$h=2$	
A′	1	1	x, y, R_z	x^2, y^2, z^2, xy
A″	1	−1	z, R_x, R_y	yz, zx

$C_i = S_2$, $\bar{1}$	E	i	$h=2$	
A$_g$	1	1	R_x, R_y, R_z	$x^2, y^2, z^2, xy, yz, zx,$
A$_u$	1	−1	x, y, z	

The groups C_{nv}

C_{2v}, 2mm	E	C_2	σ_v	σ'_v	$h=4$	
A$_1$	1	1	1	1	z, z^2, x^2, y^2	
A$_2$	1	1	−1	−1	xy	R_z
B$_1$	1	−1	1	−1	x, zx	R_y
B$_2$	1	−1	−1	1	y, yz	R_x

C_{3v}, 3m	E	$2C_3$	$3\sigma_v$	$h=6$	
A$_1$	1	1	1	z, z^2, x^2+y^2	
A$_2$	1	1	−1		R_z
E	2	−1	0	$(x, y), (xy, x^2-y^2)\ (yz, zx)$	(R_x, R_y)

C_{4v}, 4mm	E	C_2	$2C_4$	$2\sigma_v$	$2\sigma_d$	$h=8$	
A$_1$	1	1	1	1	1	z, z^2, x^2+y^2	
A$_2$	1	1	1	−1	−1		R_z
B$_1$	1	1	−1	1	−1	x^2-y^2	
B$_2$	1	1	−1	−1	1	xy	
E	2	−2	0	0	0	$(x, y), (yz, zx)$	(R_x, R_y)

C_{5v}	E	$2C_5$	$2C_5^2$	$5\sigma_v$	$h=10$, $\alpha=72°$	
A$_1$	1	1	1	1	z, z^2, x^2+y^2	
A$_2$	1	1	1	−1		R_z
E$_1$	2	$2\cos\alpha$	$2\cos 2\alpha$	0	$(x, y), (yz, zx)$	(R_x, R_y)
E$_2$	2	$2\cos 2\alpha$	$2\cos\alpha$	0	(xy, x^2-y^2)	

C_{6v}, 6mm	E	C_2	$2C_3$	$2C_6$	$3\sigma_d$	$3\sigma_v$	$h=12$	
A$_1$	1	1	1	1	1	1	z, z^2, x^2+y^2	
A$_2$	1	1	1	1	−1	−1		R_z
B$_1$	1	−1	1	−1	−1	1		
B$_2$	1	−1	1	−1	1	−1		
E$_1$	2	−2	−1	1	0	0	$(x, y), (yz, zx)$	(R_x, R_y)
E$_2$	2	2	−1	−1	0	0	(xy, x^2-y^2)	

$C_{\infty v}$	E	$2C_\phi$†	$\infty\sigma_v$	$h=\infty$	
A$_1(\Sigma^+)$	1	1	1	z, z^2, x^2+y^2	
A$_2(\Sigma^-)$	1	1	−1		R_z
E$_1(\Pi)$	2	$2\cos\phi$	0	$(x, y), (yz, zx)$	(R_x, R_y)
E$_2(\Delta)$	2	$2\cos 2\phi$	0	(xy, x^2-y^2)	
⋮	⋮	⋮	⋮		

† There is only one member of this class if $\phi=\pi$.

The groups D_n

D_2, 222	E	C_2^z	C_2^y	C_2^x	$h=4$	
A$_1$	1	1	1	1	x^2, y^2, z^2	
B$_1$	1	1	−1	−1	z, xy	R_z
B$_2$	1	−1	1	−1	y, zx	R_y
B$_3$	1	−1	−1	1	x, yz	R_x

D_3, 32	E	$2C_3$	$3C'_2$	$h=6$	
A$_1$	1	1	1	z^2, x^2+y^2	
A$_2$	1	1	−1	z	R_z
E	2	−1	0	$(x, y), (yz, zx), (xy, x^2-y^2)$	(R_x, R_y)

D_4, 422	E	C_2	$2C_4$	$2C'_2$	$2C''_2$	$h=8$	
A$_1$	1	1	1	1	1	z^2, x^2+y^2	
A$_2$	1	1	1	−1	−1	z	R_z
B$_1$	1	1	−1	1	−1	x^2-y^2	
B$_2$	1	1	−1	−1	1	xy	
E	2	−2	0	0	0	$(x, y), (yz, zx)$	(R_x, R_y)

The groups D_{nh}

D_{3h}, $\bar{6}2m$	E	σ_h	$2C_3$	$2S_3$	$3C_2'$	$3\sigma_v$	$h=12$	
A_1'	1	1	1	1	1	1	z^2, x^2+y^2	
A_2'	1	1	1	1	−1	−1		R_z
A_1''	1	−1	1	−1	1	−1		
A_2''	1	−1	1	−1	−1	1	z	
E'	2	2	−1	−1	0	0	(x, y), (xy, x^2-y^2)	
E''	2	−2	−1	1	0	0	(yz, zx)	(R_x, R_y)

D_{4h}, $4/mmm$	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	$h=16$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	x^2+y^2, z^2	
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1		R_z
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1	x^2-y^2	
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1	xy	
E_g	2	0	−2	0	0	2	0	−2	0	0	(yz, zx)	(R_x, R_y)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

D_{5h}	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_5^3$	$5\sigma_v$	$h=20$	$\alpha=72°$
A_1'	1	1	1	1	1	1	1	1	x^2+y^2, z^2	
A_2'	1	1	1	−1	1	1	1	−1		R_z
E_1'	2	$2\cos\alpha$	$2\cos 2\alpha$	0	2	$2\cos\alpha$	$2\cos 2\alpha$	0	(x, y)	
E_2'	2	$2\cos 2\alpha$	$2\cos\alpha$	0	2	$2\cos 2\alpha$	$2\cos\alpha$	0	(x^2-y^2, xy)	
A_1''	1	1	1	1	−1	−1	−1	−1		
A_2''	1	1	1	−1	−1	−1	−1	1	z	
E_1''	2	$2\cos\alpha$	$2\cos 2\alpha$	0	−2	$-2\cos\alpha$	$-2\cos 2\alpha$	0	(yz, zx)	(R_x, R_y)
E_2''	2	$2\cos 2\alpha$	$2\cos\alpha$	0	−2	$-2\cos 2\alpha$	$-2\cos\alpha$	0		

$D_{\infty h}$	E	$2C_\phi$	…	$\infty\sigma_v$	i	$2S_\infty$	…	$\infty C_2'$	$h=\infty$	
A_{1g} (Σ_g^+)	1	1	…	1	1	1	…	1	z^2, x^2+y^2	
A_{1u} (Σ_u^+)	1	1	…	1	−1	−1	…	−1	z	
A_{2g} (Σ_g^-)	1	1	…	−1	1	1	…	−1		R_z
A_{2u} (Σ_u^-)	1	1	…	−1	−1	−1	…	1		
E_{1g} (Π_g)	2	$2\cos\phi$	…	0	2	$-2\cos\phi$	…	0	(yz, zx)	(R_x, R_y)
E_{1u} (Π_u)	2	$2\cos\phi$	…	0	−2	$2\cos\phi$	…	0	(x, y)	
E_{2g} (Δ_g)	2	$2\cos 2\phi$	…	0	2	$2\cos 2\phi$	…	0	(xy, x^2-y^2)	
E_{2u} (Δ_u)	2	$2\cos 2\phi$	…	0	−2	$-2\cos 2\phi$	…	0		
⋮	⋮	⋮	…	⋮	⋮	⋮	…	⋮		

The cubic groups

T_d, $\bar{4}3m$	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$	$h=24$
A_1	1	1	1	1	1	$x^2+y^2+z^2$
A_2	1	1	1	−1	−1	
E	2	−1	2	0	0	$(3z^2-r^2, x^2-y^2)$
T_1	3	0	−1	−1	1	(R_x, R_y, R_z)
T_2	3	0	−1	1	−1	(x, y, z), (xy, yz, zx)

O_h, $m3m$	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	$h=48$
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1	
E_g	2	−1	0	0	2	2	0	−1	2	0	$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1	(xy, yz, zx)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1	
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1	
E_u	2	−1	0	0	2	−2	0	1	−2	0	
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1	

The icosahedral group

I	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	$h=60$
A	1	1	1	1	1	$x^2+y^2+z^2$
T_1	3	$\frac{1}{2}(1+\sqrt{5})$	$\frac{1}{2}(1-\sqrt{5})$	0	−1	(x, y, z) (R_x, R_y, R_z)
T_2	3	$\frac{1}{2}(1-\sqrt{5})$	$\frac{1}{2}(1+\sqrt{5})$	0	−1	
G	4	−1	−1	1	0	
H	5	0	0	−1	1	$(2z^2-x^2-y^2, x^2-y^2, xy, yz, zx)$

Further information: P.W. Atkins, M.S. Child, and C.S.G. Phillips, *Tables for group theory*. Oxford University Press, Oxford (1970). In this source, which is available on the web (see p. *x* for more details), other character tables such as D_2, D_4, D_{2d}, D_{3d}, and D_{5d} can be found.

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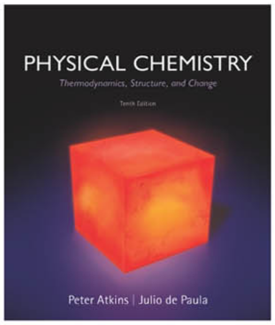

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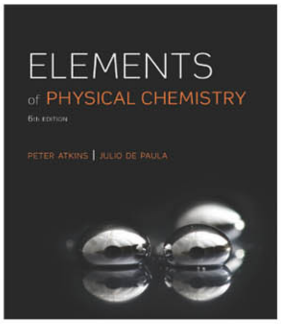

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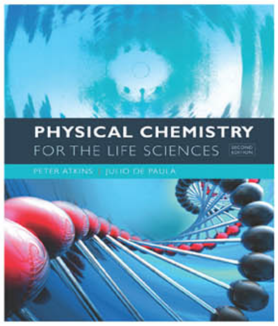

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