Conversions and Dimensional Analysis

SI Base Units

Length (L)	meter (m)
Mass	kilogram (kg)
Time	second (s)
Electric current (I)	ampere (A)
Temperature	Kelvin (K)

Constants

name	symbol	value	units	base units*
Speed of light	c	3.000E8	m/s	m/s
Planck's constant	h	6.626E-34	J * s	(kg * m^2)/s
Avogadro's #	N_A or L	6.022E23	mol^{-1}	mol^{-1}
Gas constant	R	8.314	J/(k * mol)	(kg * m^2)/(s^2 * K * mol)

*base unit: defined by SI units

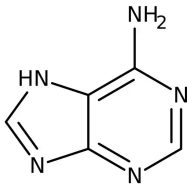
quantity	name	symbol	equivalents	SI base unit equivalents
Electric charge (quantity of electricity)	coulomb	C	$s \bullet A$ $F \bullet V$	$s \bullet A$
Electrical capacitance	farad	F	C/V s/Ω	(s^4 * A^2)/(kg * m^2)
Electrical conductance	siemens	S	$1/\Omega$ A/V	(s^3 * A^2)/(kg * m^2)
Electrical resistance	ohm	Ω	$1/S$ V/A	(kg * m^2)/(s^3 * A^2)
Energy, work, heat	joule	J	$N \bullet m$ $C \bullet V$ $W \bullet s$	(kg * m^2)/s^2
Force, weight	newton	N	$kg \bullet m/s^2$	(kg * m)/s^2
Frequency	hertz	Hz	$1/s$	s^{-2}
Magnetic field strength	tesla	T	$V \bullet s/m^2$ Wb/m^2 $N/(A \bullet m)$	kg/(s^2 * A)
Power	watt	W	J/s $V \bullet A$	(kg * m^2)
Pressure	pascal	Pa	N/m^2	kg/(m * s^2)
Temperature relative to 273.15 K	degree	°C	K	K
Voltage, Δ electric potential, EMF	volt	V	W/A J/C	(kg * m^2)/(s^3 * A)

Chemical Structure Characteristics

Nucleotides

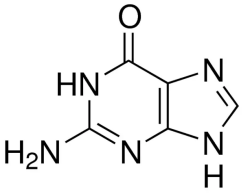
Purines

Adenine



NH_2 always alone above molecule

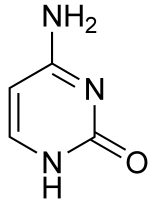
Guanine



=O (excited)
NH_2 down, left

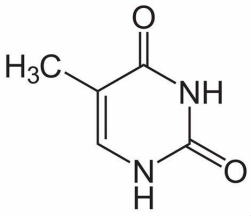
Pyrimidines

Cytosine



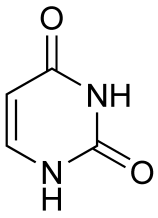
Drooping =O
NH_2 at top

Thymine



Two =O
Methyl (CH_3) opposite =O

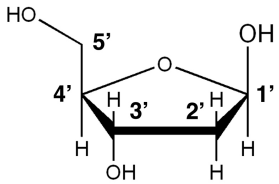
Uracil



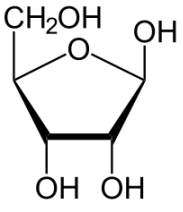
Same as thymine without methyl
Used instead of T in RNA

DNA/RNA Carbohydrates

Deoxyribose



Ribose



Protein types

Enzymes

Catalyze biochemical reactions by lowering activation energy

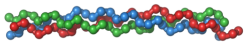
Amylase ***Lipase*** ***ATP synthase***



Structural

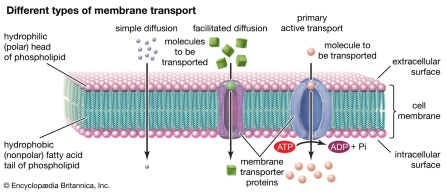
Provide support and shape to cells/tissue

Collagen ***Keratin***




Transport

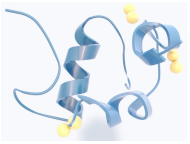
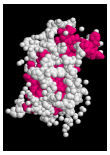
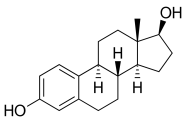
Facilitate movement across membranes or within the bloodstream



Hormones

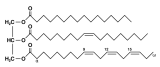
Regulatory signaling molecules, typically secreted by endocrine glands

Insulin ***Growth H.*** ***Estrogen***

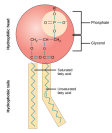
Lipid types

Triglycerides



Energy storage in adipose tissue with 3 fatty acids esterified to a glycerol backbone

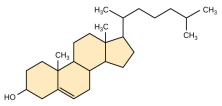
Phospholipids



Major component of cell membranes with a glycerol backbone, 2 fatty acid chains, and a phosphate group (hydrophobic and hydrophilic)

Steroids

Characterized by a four-ring structure



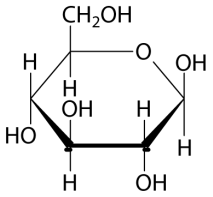
Waxes

Long-chain fatty acids esterified to long-chain alcohols

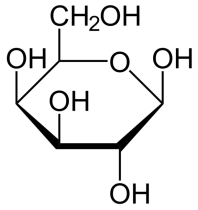
Carbohydrates

Monosaccharides

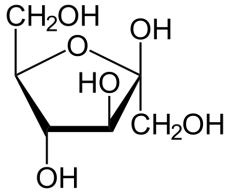
Glucose



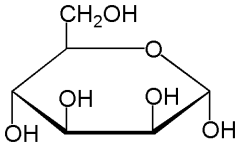
Galactose



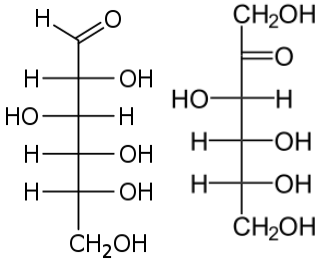
Fructose



Mannose

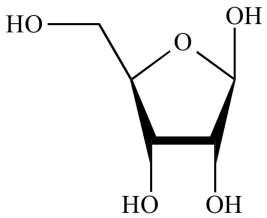


Hexose

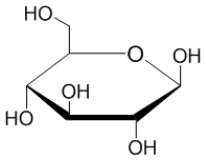


D-glucose *D-fructose*

Pentose



Pyranose



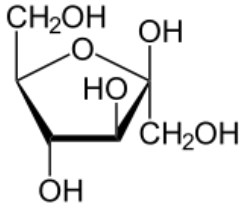
Reactions:
Oxidation/reduction
Esterification
Phosphorylation
Glycoside formation

Open-chain or cyclic
Six carbon

Open-chain or cyclic
Five carbon

Five carbon, one oxygen

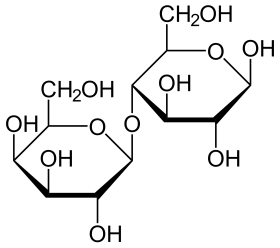
Furanose



Four carbons, one oxygen

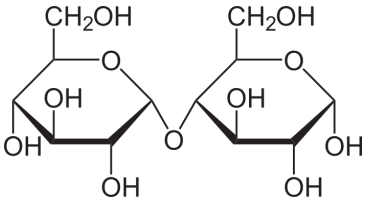
Disaccharides *(glycoside formation)*

Lactose



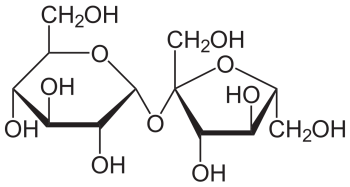
Glucose + galactose
β-glycosidic bond

Maltose



Glucose + glucose
α-glycosidic bond

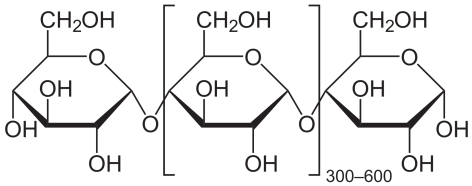
Sucrose



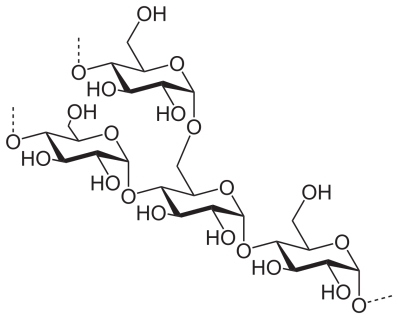
Glucose + fructose
α-glycosidic bond

Starches

Amylose

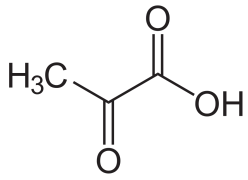


Amylopectin



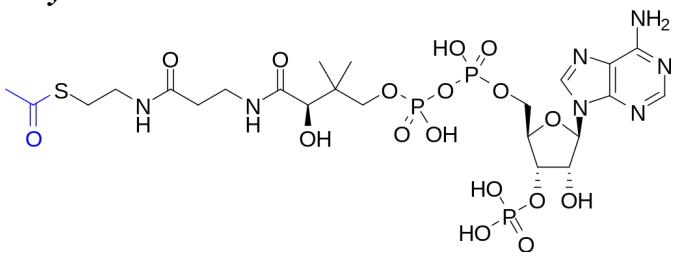
Citric Acid Cycle (molecules)

Pyruvate



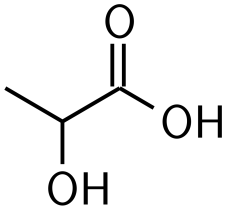
Conjugate base of pyruvic acid
Oxidized by pyruvate dehydrogenase to Acetyl-CoA

Acetyl-CoA



Glycolysis (molecules)

Lactate

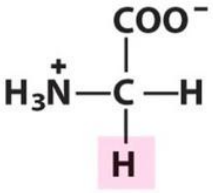


Conjugate base of lactic acid
Produced from pyruvate in glycolysis

Amino Acids

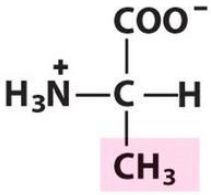
Non-polar, Hydrophobic, Neutral

Glycine



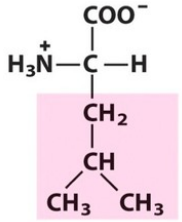
(Gly / G)
Low pK_a (amine)
Only non-chiral

Alanine



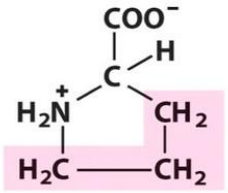
(Ala / A)
Chiral
Generic AA

Valine



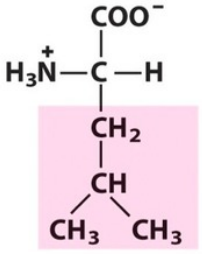
(Val / V)
Metabolism

Proline



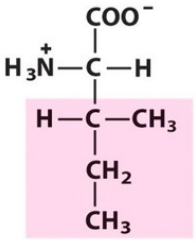
(Pro / P)
Kinked, stable, non-aromatic

Leucine



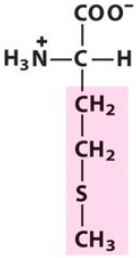
(Leu / L)

Isoleucine



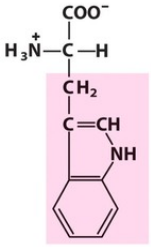
(Ile / I)
Two chiral centers

Methionine



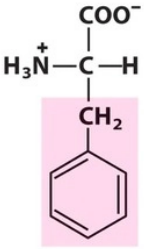
(Met / M)
Sulfur bonded, no hydrogen bonding

Tryptophan



(Trp / W)
Hydrogen bonding, Indole group
Ser, mel, vit B_3

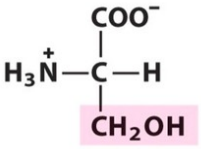
Phenylalanine



(Phe / F)
Aromatic

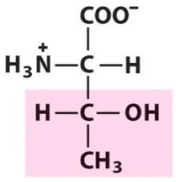
Polar, Neutral

Serine



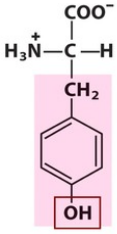
(Ser / S)
Dehydration rxns, alcohol
Phosphorylation

Threonine



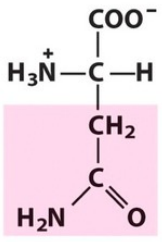
(Thr / T)
Alcohol, dual chirality
Hydrogen bonding

Tyrosine



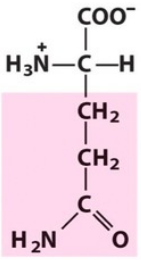
(Tyr / Y)
Polar, nonpolar R
Hydrogen bonding

Asparagine



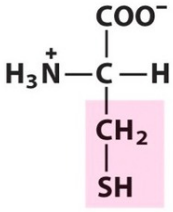
(Asn / N)

Glutamine



(Gln / Q)

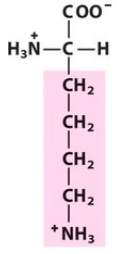
Cysteine



(Cys / C)
Nucleophilic
Disulfide bridges

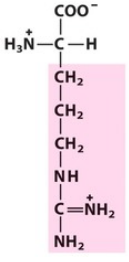
⊕ *Charge, Basic, Hydrophilic*

Lysine



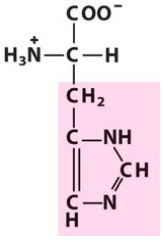
(Lys / K)

Arginine



(Arg / R)

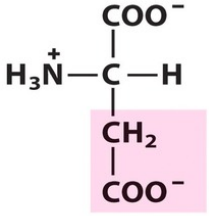
Histidine



(His / H)
pK_a=6
uncharged at pH 7

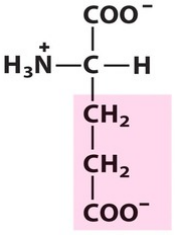
⊖ *Charge, Acidic*

Aspartic acid



(Asp / D)

Glutamic acid



(Glu / E)

Periodic Table Trends (BEAR)

B: Basicity*, ability of molecules to accept protons*

- ➢ *Increases up and left*

E: Electronegativity, electron affinity, ionization energy

- ➢ *Increases up and right*

Electronegativity*, ability of an atom to attract electrons to itself at a covalent bond*

Electron affinity*, energy associated with the addition of an electron to an atom*

Ionization energy*, amount of energy required to remove an electron from an atom*

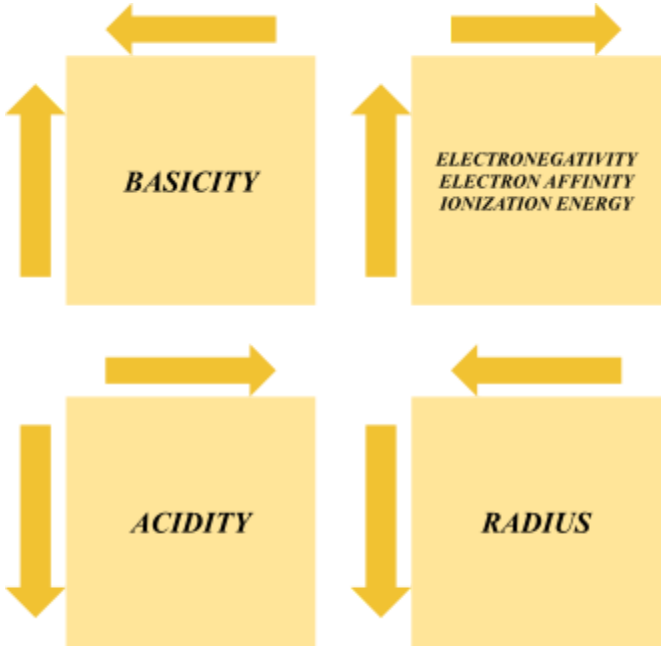
A: Acidity*, ability of a molecule to donate protons*

- ➢ *Increases down and right*

R: Radius*, size of an atom's electron cloud*

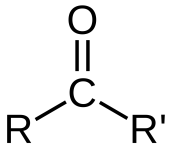
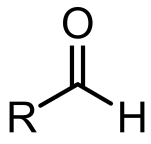
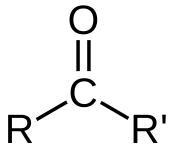
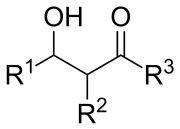
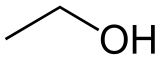
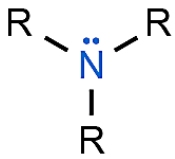
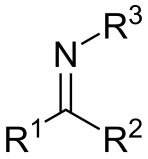
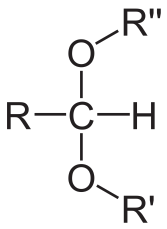
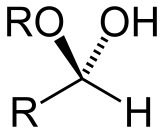
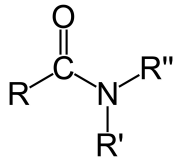
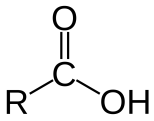
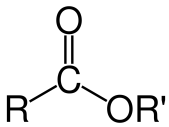
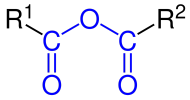
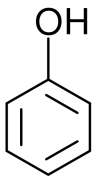
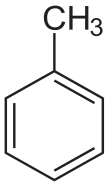
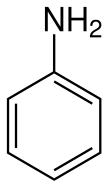
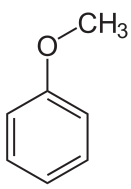
- ➢ *Increases down and left*

Group (vertical)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period (horizontal)			*Alkaline earth metals*						*Transition metals*				*Metals*		*Non metals*		*Halogens*	*Noble gases*
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo
Alkali metals																		
Lanthanides	*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27		
Actinides	**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.291		



Organic Chemistry

Major Functional Groups

Carbonyl 	***Aldehyde*** 	***Ketone*** 
Aldol 	***Alcohol*** 	
Amine 	***Imine*** 	
Acetal 	***Hemiacetal*** 	***Amide*** 
Carboxylic acid 	***Ester*** 	***Anhydride*** 
Phenol 	***Toluene*** 	***Aniline*** 
Anisol 		

Nomenclature

group	***prefix***	***suffix***
Carboxylic acids	*carboxy-*	*-oic acid*
Anhydrides	*alkanoyloxycarbonyl-*	*anhydride*
Esters	*alkoxycarbonyl-*	*-oate*
Amides	*carbamoyl-*	*-amide*
Aldehydes	*oxo-*	*-al*
Ketones	*oxo- or keto-*	*-one*
Alcohols	*hydroxy-*	*-ol*

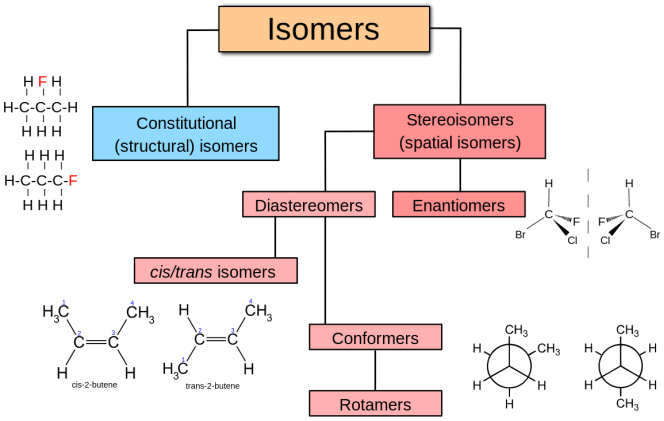
Bonding

bond order	***single***	***double***	***triple***
bond type	σ	σ, π	σ, π, 2π
hybridization	sp^3	sp^2	sp
angles	109.5^o	120^o	180^o
example	$C-C$ *alkane*	$C=C$ *alkene*	$C\equiv C$ *alkyne*

Polarity

Electronegativity	*Difference determines the polarity of the bond formed* ***Partial positive charge*** *(δ+): Electron density shifted away from atom with lower EN* ***Partial negative charge*** *(δ-): Electron density shifted towards atom with higher EN*
Covalent bonds	***Polar****: e^- not shared equally* $0.5 < \Delta EN < 1.7$ ***Nonpolar****: e^- shared equally* $\Delta EN < 0.5$
Solubility	*"Like dissolves like"*

Isomers



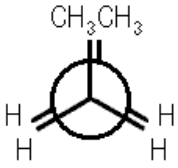
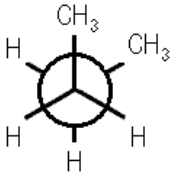
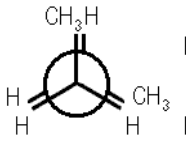
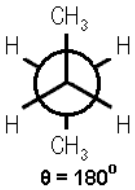
The more favored product will be more stable due to less strain and conjugation

Configurational Isomers

a. ***Enantiomer**: Non-superimposable mirror images, with opposite stereochemistry at every chiral center*
   - ➔ *Exhibit same chemical and physical properties, except rotation of plane-polarized light and reactions in chiral environments*

b. ***Diastereomer**: Non-mirror images, with differences at select chiral centers*
   - ➔ *Different chemical and physical properties*

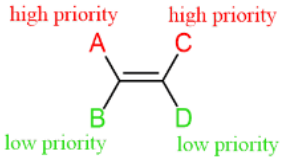
Newman Projections

Totally eclipsed  $\theta = 0^o$	***Gauche***  $\theta = 60^o$ $\theta = 300^o$
Eclipsed  $\theta = 120^o$ $\theta = 240^o$	***Anti***  $\theta = 180^o$

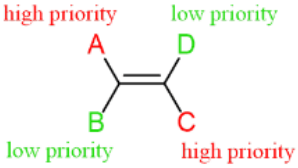
Absolute configurations

Alkenes

- ➢ *(Z): If highest priority substituents are on the same side of the double bond*



- ➢ *(E): On opposite sides*



Stereocenters

Lowest priority at front 

- ➢ *Clockwise (S)*
- ➢ *Counter-clockwise (R)*

Lowest priority at back 

- ➢ *Clockwise (R)*
- ➢ *Counter-clockwise (S)*

***Cis-trans**: Groups differ in position about an immovable bond*

Basic Concepts

Nucleophile: *"Nucleus-loving", wants* ⊕

Electrophile: *"Electron-loving", wants* ⊖

Leaving group: *Portion of the reactant that leaves the molecule as a result of reacting with another reagent*

- ➢ *Best LGs are those able to stabilize the extra electrons given to it*
- ➢ *Most common: Weak bases, large groups with resonance or electron-withdrawing atoms*

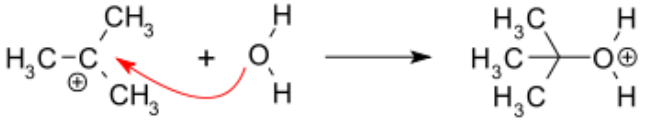
pK_a and S_N reactions

- ➢ *pK_a < environment, pH = deprotonation*
- ➢ *pK_a > environment, pH = protonation*

S_N1 Reactions: *Substitution reaction with a unimolecular rate-determining step (first-order substrate, zero-order nucleophile)*

1. ***Leaving group leaves, carbocation is left***

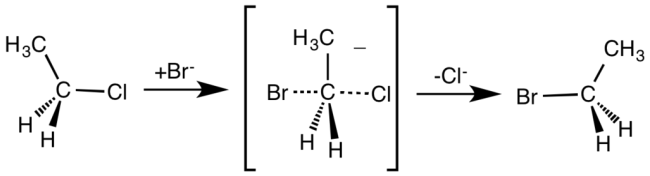
2. ***Nucleophile attacks carbocation***



Notes: *Produces a racemic mixture, strong nucleophile is not needed, favored under increased steric hindrance (e.g., 3° carbon) and polar, protic solutions*

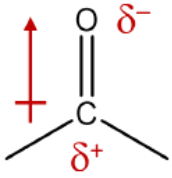
S_N2 Reactions

1. ***Nucleophile attacks as the leaving group leaves***



Notes: *Flip the stereochemistry, optically active inverted products, favored with strong nucleophile and polar, aprotic solvents, not favored under steric hindrance*

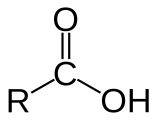
Carbonyl groups in S_N reactions



- ➢ *Electron-withdrawing oxygen leaves the carbon with a partial + charge, making it vulnerable to nucleophilic attack*

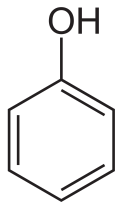
5, 10, 15, 20: 4 organic acid functional groups

Carboxylic acid



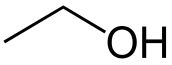
$pK_a \approx 5$

Phenol



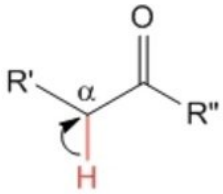
$pK_a \approx 10$

Alcohol



$pK_a \approx 15$

α-hydrogen



$pK_a \approx 20$

- ➢ *The lower the pK_a, the more acidic*

Alcohols

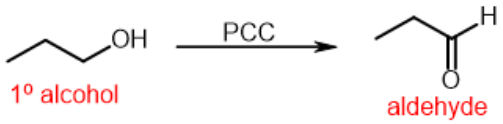
Properties*: Higher boiling point due to hydrogen bonding, weakly acidic hydroxyl hydrogen, polar (soluble in H_2O)*

Synthesis*: Aldehyde/ketone with $NaBH_4$ or $LiAlH_4$ (reduction), ester/carboxylic acid with $LiAlH_4$, S_N1 and S_N2 reactions*

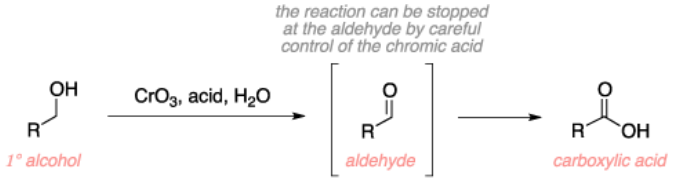
Redox Reactions

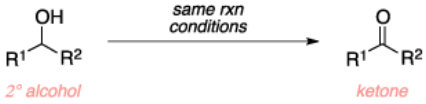
Oxidation

a. *PCC turns 1º alcohol into an aldehyde, or 2º into ketone*



b. *Jone's reagent (CrO_3), $KMnO_4$, or an alkali dichromate turns 2º alcohol into ketone, or 1º alcohol into carboxylic acid*

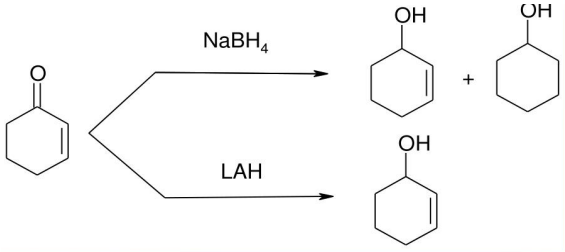




c. *3º alcohols are generally not oxidized further*

Reduction

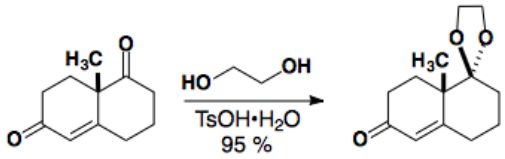
a. *$LiAlH_4$ or $NaBH_4$ (both reducing agents) converts a ketone into an alcohol*



Mesylates and Tosylates

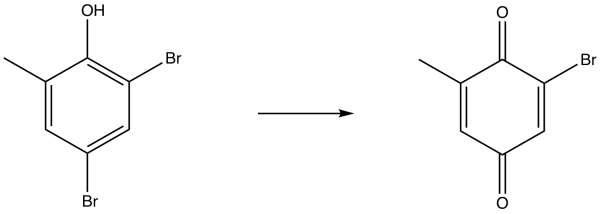
a. *Conversion of alcohol into mesylates ($-SO_3CH_3$) or tosylates ($-SO_3C_6H_4CH_3$), making them better LG for S_N reactions*

b. *Carbonyl + dialcohol results in an unreactive acetal, which can protect carbonyls and is removed by an aqueous acid*



Quinones + Hydroxyquinones

a. *Treating a phenol with an oxidizing agent results in a quinone*



b. *Quinones can get further oxidized into a hydroquinone (e.g., ubiquinone, or CoQ)*

Aldehydes and Ketones

Properties*: Relatively high boiling point due to dipole moment (not as high as alcohol)*

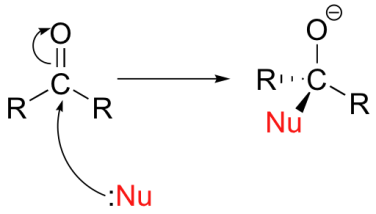
- ➢ ***Note****: Aldehydes are slightly more acidic than ketones due to less steric hindrance*

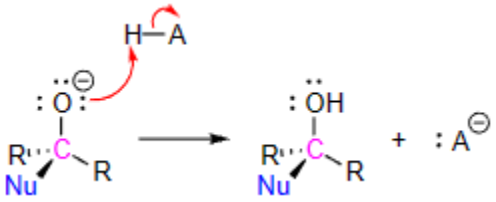
Synthesis*: Oxidation with PCC to aldehyde (1°) or ketone (2°), ozonolysis of alkenes*

Reactions

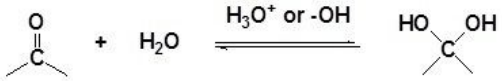
a. Nucleophilic addition

1. *Nucleophile attacks carbonyl carbon*
2. *Resulting alkoxide is protonated by addition of an acid to form alcohol*



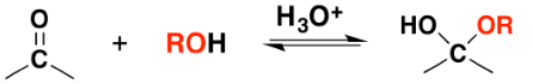


b. ***Hydration****: Aldehyde or ketone form a geminal diol in the presence of water*



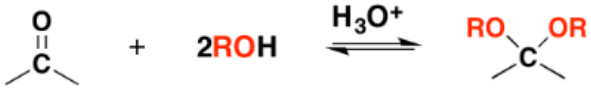
Aldehyde or Ketone — *Gem*-diol

c. ***Hemiacetal/hemiketal****: Addition of nucleophilic alcohol (ROH) by S_N1 mechanism to aldehyde/ketone to form hemiacetal/hemiketal*



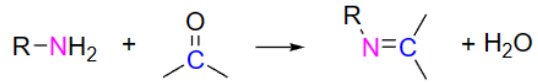
aldehyde or ketone — hemi-acetal

d. ***Acetal/ketal****: Another ROH equivalent is added to hemiacetal/hemiketal*

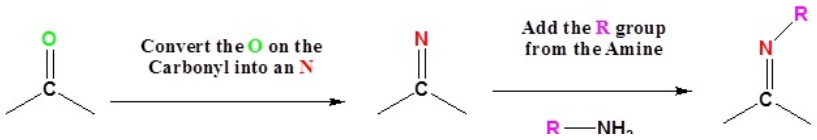


aldehyde or ketone — acetal

e. ***Condensation****: Addition of N-groups to form imines with the loss of water*

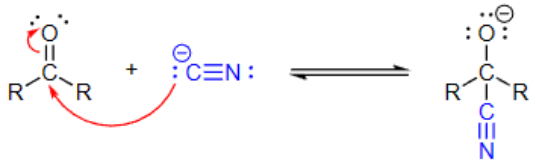


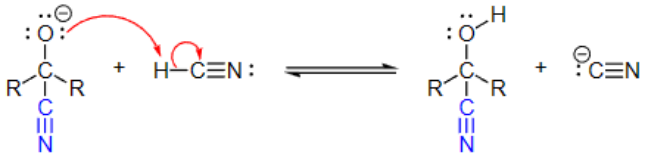
1° Amine — Aldehyde or Ketone — Imine



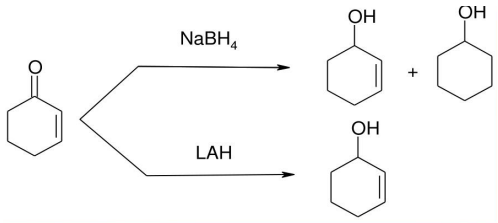
Enamine*: Tautomer of imine*

f. ***Cyanohydrin formation****: Addition of HCN yielding a stable cyanohydrin*





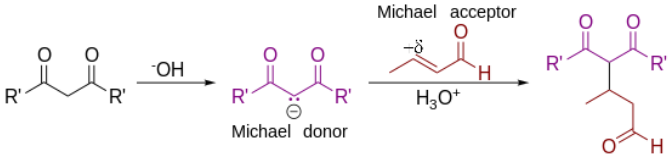
g. ***Alcohol formation****: Reduction with $LiAlH_4$ or $NaBH_4$*



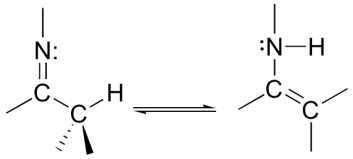
h. ***Tautomerization****: Interconversion of ketone/aldehyde with enol*

keto form of acetone — **enol** form of acetone

i. ***Michael addition****: Addition of an enolate of a ketone/aldehyde to an α, β-unsaturated carbonyl compound at the β carbon*

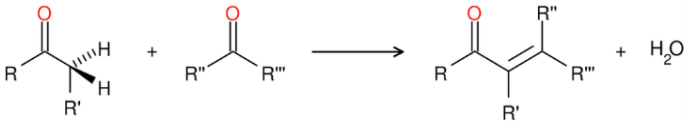


ii. ***Enamines***: *Tautomerism between imine and enamine*



imine enamine

i. ***Aldol condensation***: *Formation of an aldol in a basic environment, with dehydration*



➢ ***Retro-aldol reaction***: *Reverse aldol condensation with the addition of a base and heat*

Carboxylic Acids

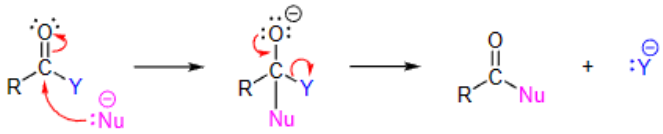
Properties*: Acidic due to resonance stabilization, polar, highly oxidized, high boiling point due to <u>two</u> H-bonds*

- ➢ *More stable conjugate base results in a more acidic of an acid*

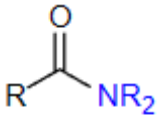
Synthesis*: Oxidation of 1° alcohol or aldehyde by a strong oxidizer ($KMnO_4$, KCr_4O_7, CrO_3), hydrolysis of nitriles*

Reactions

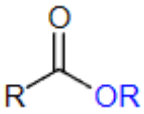
a. ***Nucleophilic acyl substitution****: Nucleophilic attack, LG leaves, carbonyl reformed*



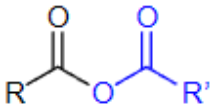
i. Amine or ammonia nucleophile, amide formed



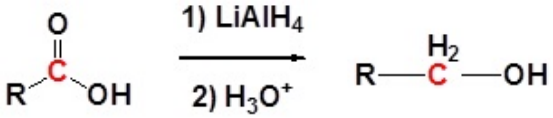
ii. Alcohol nucleophile, ester formed (acidic conditions required)



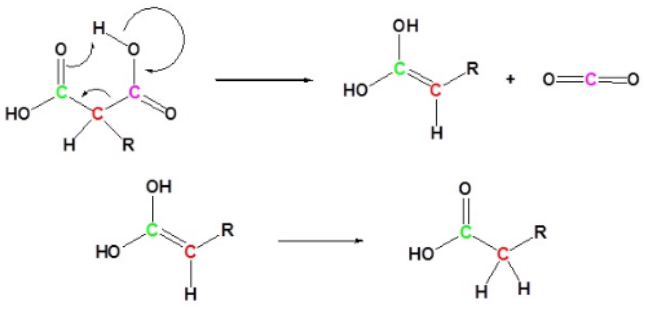
iii. Carboxylic acid nucleophile, anhydride formed



b. ***Reduction****: To 1° alcohol with $LiAlH_4$*



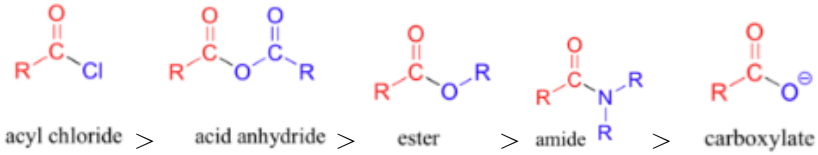
c. ***Decarboxylation****: Complete loss of a carboxyl group as CO_2, and replacement with a hydrogen, resulting in an enol*



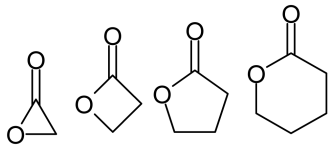
d. ***Saponification****: Long-chain carboxylic acid with a Na or KOH forming a salt (i.e., soap)*

- ➢ *Have long, nonpolar tail and a polar head*
- ➢ *Longer tails are more hydrophobic, amounting to a better soap*

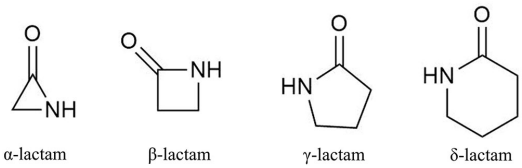
Reactivity of derivatives



Cyclic Esters *(lactones)*



Cyclic Amides *(lactam)*



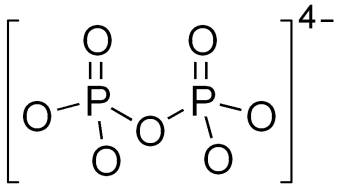
Nitrogen-phosphorous Compounds

N-containing Compounds: Amino Acids *(zitterionic)*

a. ***Strecker synthesis****: Combines aldehyde (R-group), ammonium chloride, and potassium cyanide*
b. ***Gabriel synthesis****: Combines potassium phthalimide and diethyl bromomalonate*

P-containing compounds: ATP, DNA

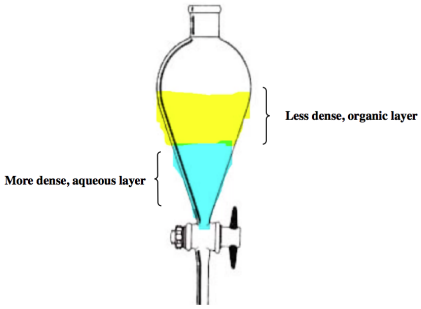
a. ***Phosphoric acid****: Phosphate group or inorganic phosphate (Pi)*
    - ➢ *At physiological pH, Pi is made up of hydrogen phosphate (HPO_4^{2-}) and dihydrogen phosphate ($H_2PO_4^-$)*
b. ***Pyrophosphate*** *(PPi), or ($P_2O_7^{4-}$): released when forming phosphodiester bonds in DNA*
    - ➢ *Unstable in aqueous solution, and is hydrolyzed to form two molecules of Pi*



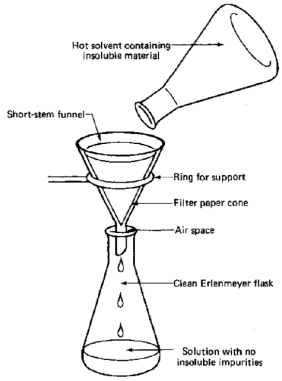
c. ***Organic phosphates****: Nucleotides with phosphate groups (e.g., ATP, GTP, in DNA)*

Purification Methods

a. ***Extraction***: *Separation of compounds based on solubility ("like dissolves like")*

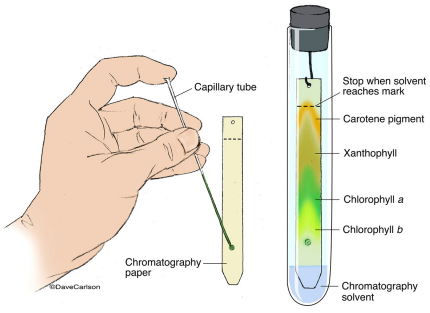


b. ***Filtration***: *Separation of solid from liquid with a filter (sped up with vacuum filtration)*



c. ***Chromatography***: *Uses a stationary phase and a mobile phase to separate compounds by polarity and size*

- ➢ *Mobile phase elutes more quickly when it has the same polarity as the eluent*
- ➢ *Larger compounds elute slower*



A. Applying spot of chlorophyll pigment B. Final chromatogram

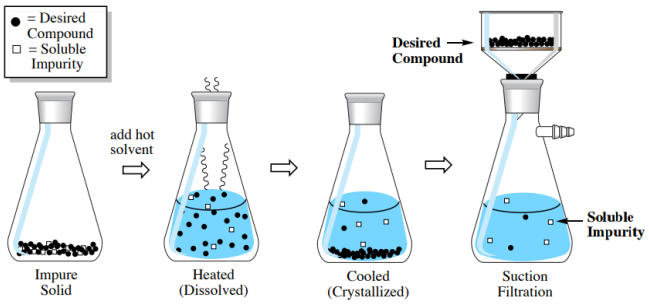
d. ***Distillation***: *Separation of liquids based on boiling point, which is heavily dependent on intermolecular forces*

i. ***Simple***: *boiling point < 150°C, 25°C apart*

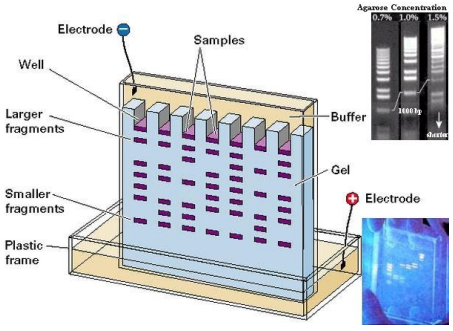
ii. ***Vacuum***: *Bp >150°C*

iii. ***Fractional***: *Bp < 25°C apart*

e. ***Recrystallization***: *Separation of solids based on their differences in solubility at varying temperatures*

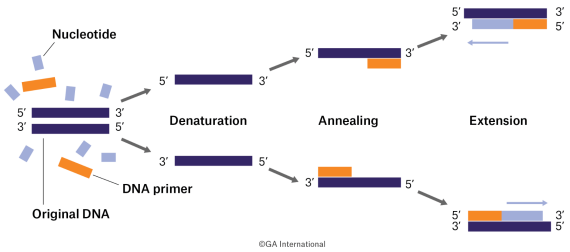


f. ***Electrophoresis***: *Separation of macromolecules based on size and/or charge*

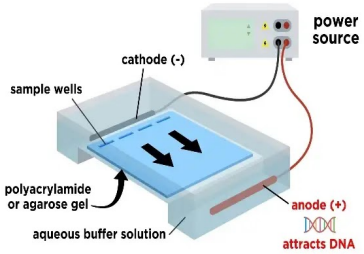


Experimental methods

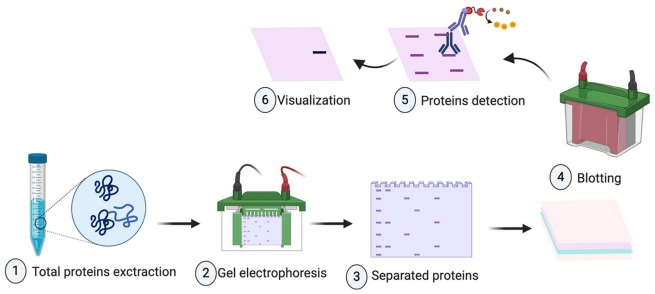
a. ***Polymerase chain reaction*** *(PCR): Used to amplify a specific DNA sequence*
Technique*: Cycles of DNA denaturation, primer annealing, and DNA extension using a DNA polymerase*
Applications*: Gene cloning, sequencing, genetic testing*



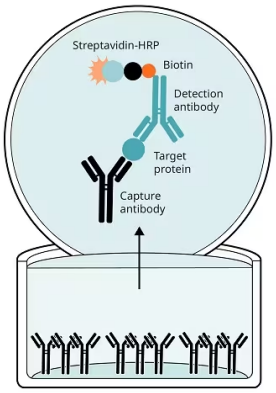
b. ***Gel electrophoresis****: Separates DNA, RNA, or proteins based on size and charge*
Technique*: Molecules are loaded onto a gel matrix and subject to an electric field, causing them to migrate [smaller moves faster]*
Applications*: DNA fragment analysis, sequencing, protein analysis*



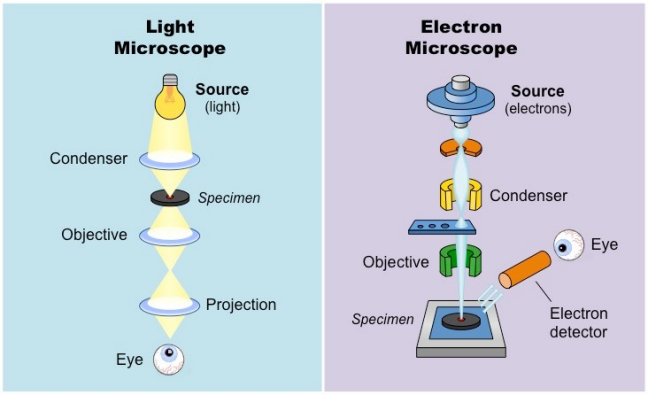
c. ***Western blotting****: Detects and analyzes specific proteins in a sample*
Techniques*: Separation by gel electrophoresis, transfer onto a membrane, then probed with antibodies that bind to specific target proteins*



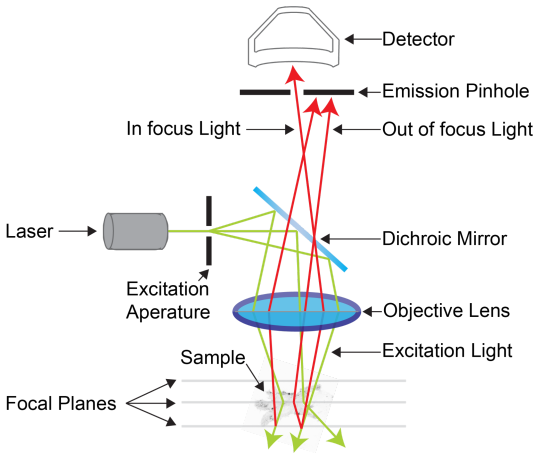
d. ***Enzyme-linked immunosorbent assay*** *(ELISA): Detects and quantifies the presence of specific proteins or antibodies in a sample*
Technique*: Immobilizes target proteins or antibody onto a surface, then adds specific antibody or antigen*
➢ *Bound antibodies are detected using an enzymatic reaction that produces a measurable signal*



e. ***Microscopy****: Visualizes biological structures at different scales*
i. ***Light****: Using visible light*
ii. ***Electron****: Using an electron beam*



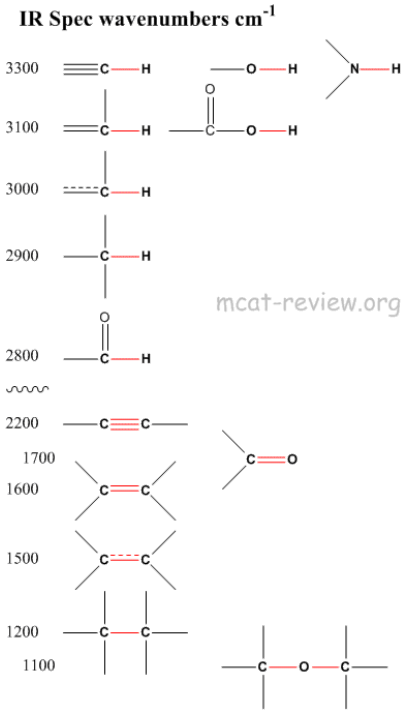
iii. ***Confocal****: Using laser scanning and fluorescence to generate 3D images*



***Spectroscopy**: Interpreting electromagnetic spectra*

a. ***IR**: Gives information about functional groups and progress of reaction*

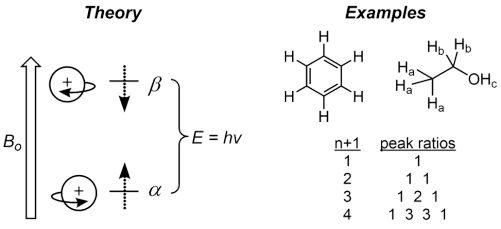
Peaks	
$O - H$	*Broad, ~3300cm^{-1}*
$N - H$	*Sharp, ~3300cm^{-1}*
$C = O$	*Sharp, ~1750cm^{-1}*



b. ***UV**: Gives information about conjugated systems, such as shifts in absorbance spectrum created by compounds containing double bonds or heteroatoms with lone pairs*
   - ➢ *Increase in conjugation indicated by increase in wavelength*
   - ➢ *Absorbance of red results in appearance of green*
   - ➢ *Useful for determining complexes of transition metals*

c. ***NMR**: Gives information about the chemical composition of a molecule*

i. Benchmark numbers indicate shifts for specific chemical bonds
   - ➢ *Hydrogens on sp^3 carbons: 0-3 ppm*
   - ➢ *Hydrogens on sp^2 carbons: 4.6-6.0 ppm*
   - ➢ *Hydrogens on sp carbons: 2-3 ppm*
   - ➢ *Aldehyde hydrogens: 9-10 ppm*
   - ➢ *Carboxylic acid hydrogens: 10.5-12 ppm*
   - ➢ *Aromatic hydrogens: 6-8.5 ppm*

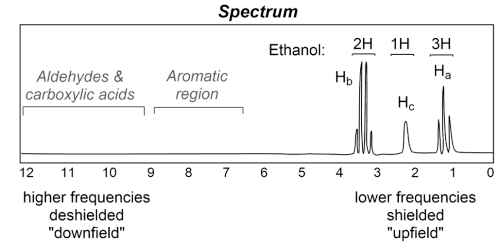


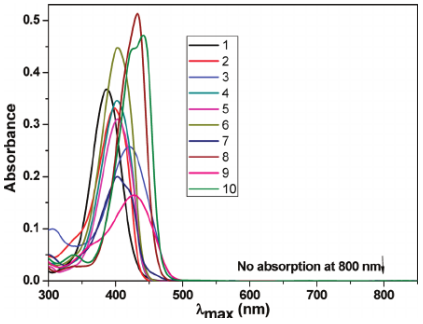
ii. When analyzing NMR spectroscopy, look for

1. ***Number of protons**: Indicated by number of peaks*
2. ***Position of peaks**: More downfield (left), more deshielded and electron-withdrawing groups*
   - ➢ *Downfield (to the left), deshielding*
   - ➢ *Upfield (to the right), shielding*
3. ***Integration of peaks**: Larger integration (height) means more protons (corresponds to area under curve)*
4. ***Splitting**: Hydrogens on adjacent carbons will split into n+1 subpeaks, with n are the number of hydrogens on the adjacent carbon*

   E.g., if n=1, then 1+1=2 (doublet)

   if n=2, then 2+1=3 (triplet)



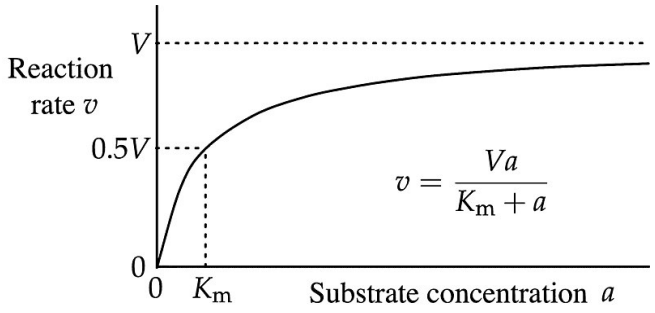


***Enzyme Kinetics**: In which the rate of forward and/or reverse reactions is changed by altering the mechanisms of the reaction*

Kinds of Enzymes

Oxidoreductase	*Perform redox reactions that involve the transfer of electrons*
Transferase	*Move a functional group from one molecule to another*
Kinase	*Add a phosphate group*
Phosphatase	*Remove a phosphate group*
Hydrolase	*Catalyze cleavage with the addition of H_2O*
Lyase	*Catalyze cleavage without the addition of H_2O or electrons*
Isomerase	*Catalyze the interconversion of isomers, including constitutional and stereoisomers*
Ligase	*Join two large biomolecules, often of the same type*
Lipase	*Catalyze the hydrolysis of fats*
Phosphorylase	*Introduces a phosphate group into an organic molecules*

Michaelis-Menten Kinetics



***V_{max}**: Maximum rate of the reaction*

***K_m**: Substrate concentration at which the enzyme runs at half of its V_{max}*

***Saturation kinetics**: The rate of reaction increases with an increase in substrate concentration, until a maximum value is reached (saturation)*

***Cooperativity**: When an enzyme has multiple active sites*

a. ***Positive cooperative**: Increases affinity for subsequent substrate molecules*
b. ***Negative cooperative**: Decreases affinity*
c. ***Non-cooperative**: Substrate does not affect affinity for subsequent substrates*

Regulation of Enzymes

***Feedback inhibition**: Enzyme inhibition by high levels of product from later in the same pathway*

***Reversible inhibition**: Ability to replace inhibitor with a compound of greater affinity, or complete removal*

a. ***Competitive**: Inhibitor similar to substrate, and binds at the active site, blocking it*
   - ➢ *K_m increases; add more substrate*
b. ***Non-competitive**: Inhibitor binds with equal affinity to the enzyme and enzyme-substrate complex (V_{max} decreases)*
c. ***Uncompetitive**: Inhibitor binds only with the enzyme-substrate complex (V_{max} and K_m decrease)*
d. ***Mixed inhibition**: Inhibitor binds with unequal affinity to the enzyme and enzyme-complex*
   - ➢ *V_{max} decreases; K_m depends on affinity for either enzyme or enzyme-complex*

***Irreversible inhibition**: Active site becomes unavailable for a prolonged duration, or permanently*

a. ***Suicide inhibitor**: Substrate analogue that binds to the active site via a covalent bond*

***Allosteric effector**: Binds at allosteric site, inducing a change in enzyme conformation, so that substrate can no longer bind to it*

a. ***Positive**: Increases activity*
b. ***Negative**: Decreases activity*

***Homotropic effector**: Allosteric regulator that is also the substrate*

***Heterotropic effector**: Allosteric regulator that is different from the substrate*

Metabolic Pathways

***<u>Glycolysis</u>**: An aerobic [or anaerobic] metabolic pathway that breaks down glucose into two three-carbon compounds, generating energy in the form of ATP*

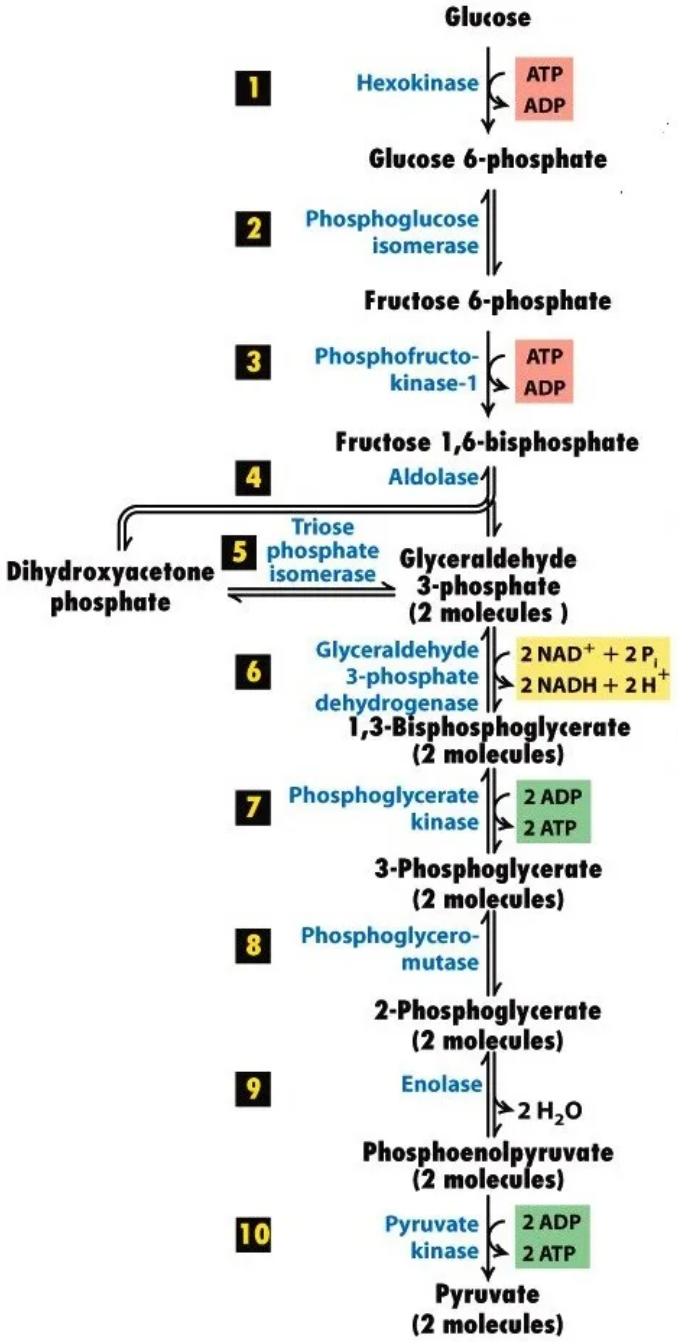
***Two steps**:*

1. ***Energy investment**: Cleavage of glucose into two three-carbon sugars (i.e., DHAP, G3P) of pyruvate*
2. ***Energy payoff**: Complete conversion to pyruvate, and production of ATP and NADH*

Overview

Location	*Cytoplasm*
Intermediates	***<u>In order</u>**: Glucose, G6P, F6P, F-1,6-BP, DHAP, G3P, 1,3-BPG, 3-PG, 2-PG, PEP, pyruvate* ➢ *DHAP, G3P are isomers and thus can be interconverted*
Key enzymes, steps, roles, functions	***<u>Irreversible</u>** (requiring ATP, 1-5)* ***Hexo/glucokinase** [1]: Phosphorylation of glucose → glucose 6-phosphate* ➢ *Prevents gluc. from diffusing out* ***Phosphofructokinase**(PFK)-1 [3]: Phosphorylation of fructose 6-phosphate → fructose 6-bisphosphate* ➢ *Rate-limiting, regulated* ***<u>Reversible</u>** (energy-releasing, 6-10)* ***G3P dehydrogenase** [6] (two-step):* 1. *Oxidation of G3P* 2. *Reduction of NAD^+ to NADH [= 1 NADH]* *Phosphorylation of glyceraldehyde 3-phosphate → 1,3-bisphosphoglycerate* ➢ *Generates 2 NADH per glucose* ***Phosphoglycerate kinase** [7]: Removal of a phosphate group from 3-bisphosphoglycerate to ADP [= 1 ATP]* ➢ *Generates 2 ATP per glucose* ***Pyruvate kinase** [10, last]: Conversion of PEP to pyruvate (removal of phosphate) [= 1 ATP]* ➢ *Generates 2 pyruvate per glucose* ***<u>Yield</u>**: 1 glucose = 2 ATP, 2 NADH; 2 pyruvate [may enter CAC after oxidation, or undergo fermentation]*
Regeneration of NAD^+	1. ***Aerobic respiration**: NADH transfers electrons to the ETC* 2. ***Lactic acid fermentation**: In the absence of oxygen, pyruvate may be directly reduced by NADH to form lactate, regenerating NAD^+*

Main regulatory sites	***HK**: Inhibited by G6P (neg. feedback)* ***PFK-1**: Allosterically regulated by F-2,6-BP (activator), ATP and citrate (neg. regulators)* ***Pyruvate kinase**: Allosterically regulated by F-1,6-BP (activator), ATP and alanine (neg. regulator)*
Allosteric inhibitors	*ATP, citrate, acetyl-CoA (inhibits PK)*
Allosteric activators	*F-2,6-BP (PFK-1), AMP (PFK-1), F-1,6-BP (PK)*



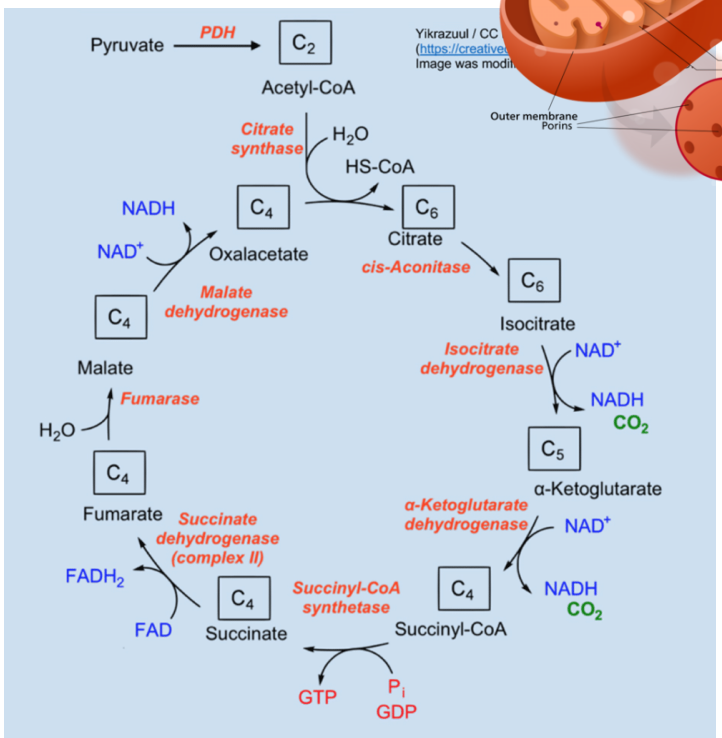
Fermentation: *An anaerobic process that converts organic compounds (e.g., carbohydrates) into simpler compounds (e.g., alcohol, lactic acid), releasing energy in the absence of oxygen*

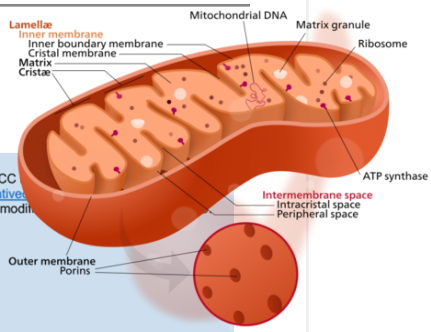
- ➢ *ETC does not function without oxygen, therefore fermentation relies on substrate-level phosphorylation to generate ATP*

Overview

Lactic acid fermentation	***Location***: *Bacteria, muscle cells*
Key enzyme, role, function, yield	***Lactate dehydrogenase*** *(LDH): Central enzyme that reduces pyruvate to lactate (e^- from NADH)* *Isomers of LDH:* *a.* ***LDH-1***: *In the heart* *b.* ***LDH-5***: *In skeletal muscle* ***Yield***: *1 glucose = 2 lactic acid, 2 NADH, 2 ATP*

[CAC]





Krebs (Citric Acid) Cycle (CAC): *Involves the oxidation of acetyl-CoA to generate ATP, NADH, $FADH_2$*

Acetyl-CoA: *Produced from pyruvate molecules generated by glycolysis and transported to the mitochondrial membrane*

- ➢ *Each pyruvate undergoes oxidative decarboxylation by pyruvate dehydrogenase complex (PDC), releasing CO_2, making acetyl-CoA*

Overview

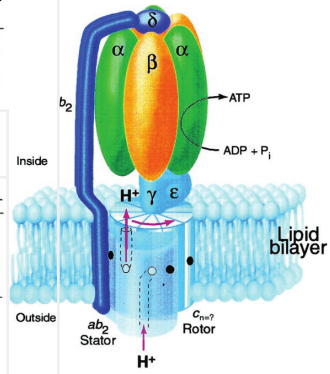
Location	*Mitochondrial matrix*
Intermediates	***In order***: *Acetyl-CoA, citrate, isocitrate, α-ketoglutarate, succinyl-CoA, succinate, fumarate, malate, oxaloacetate (regenerated)*
Key enzymes, steps, roles, functions	***Pyruvate dehydrogenase complex***: *Converts pyruvate to acetyl-CoA* --- ***Citrate synthase***: *Forms citrate from acetyl-CoA and oxaloacetate* ***Aconitase***: *Isomerizes citrate → isocitrate* ***Isocitrate dehydrogenase***: *Oxidative decarboxylation of isocitrate → α -ketoglutarate* ➢ *1 NADH and CO_2 generated* ***α-ketoglutarate dehydrogenase complex***: *Oxidative decarboxylation of α -ketoglutarate → succinyl-CoA, CO_2, and NADH* ➢ *1 NADH and CO_2 generated* ***Succinyl-CoA synthetase***: *Converts succinyl-CoA → succinate* ➢ *1 GTP generated [can be converted to ATP]* ***Succinate dehydrogenase*** *(Complex II): In the ETC, participates in the oxidation of succinate → fumarate* ➢ *1 $FADH_2$ generated* ***Fumarase***: *Hydrates fumarate → malate* ***Malate dehydrogenase***: *Oxidation of malate → oxaloacetate* ➢ *1 NADH generated* ***Yield***: *1 acetyl-CoA = 1 ATP [← GTP], 3 NADH, 1 $FADH_2$, 4 CO_2, 1 oxaloacetate (put back into cycle)* ➢ *Krebs cycle operates twice per glucose due production of 2 pyruvate from glycolysis*

***Electron Transport Chain* (ETC)**: *Uses oxidative phosphorylation to facilitate the transfer of electrons to molecular oxygen, generating an H^+ gradient to drive ATP synthesis [in aerobic respiration]*

Overview

Location	*Inner mitochondrial membrane*
Complexes** (four major complexes), **roles, yield	***Complex I** (NADH dehydrogenase): Largest, accepts e^- from NADH, transferring to coenzyme Q* ➢ *Pumps H^+ across inner membrane from matrix to intermembrane spa.* ***Complex II** (succinate dehydrogenase): Also in CAC, accept e^- from $FADH_2$ transferring to coenzyme Q* ***Complex III** (cytochrome bc1): Accepts e^- from coenzyme Q transferring to cytochrome c* ➢ *Pumps H^+* ***Complex IV** (cytochrome c oxidase): Final complex, receiving e^- from cytochrome c and transferring to O_2, facilitating its reduction to H_2O* ➢ *Pumps H^+* ***Yield**: 1 NADH = 2.5-3 ATP* *2 $FADH_2$ = 1.5-2 ATP*
Electron carriers, capacity	***NADH**: Coenzyme generated during glycolysis and CAC* ➢ ***Capacity**: 2 e^- + H^+* ***$FADH_2$**: Coenzyme generated during CAC* ➢ ***Capacity**: 2 e^- + 2 H^+* ***Coenzyme Q** (ubiquinone): Lipid-soluble molecule embedded in the inner mitochondrial membrane, accepting e^- from NADH and $FADH_2$* ➢ ***Capacity**: 1 or 2 e^-* ***Cytochrome c**: Protein in the intermembrane space; binds to cytochrome c oxidase and carries e^- between III and IV* ➢ ***Capacity**: 1 e^-* ***Iron-sulfur** (Fe-S) proteins: Involved in e^- transfer between I and II* ➢ ***Capacity**: Fe and S, 1 e^-*

ATP Synthase



***Two main components**:*

1. ***F_1 subunit**: α and β subunits form the catalytic sites for ATP synthesis*
2. ***F_o subunit**: Forms a channel for H^+ movement*

***ATP synthesis**: ATP synthase acts as a molecular rotary motor, utilizing the flow of protons to drive the synthesis of ATP*

➢ *H^+ flow through F_o induces rotation of the F_1 central stalk, which then causes the conformational changes necessary to produce ATP in the F_1 subunit*

Significance of O_2 as the final acceptor

***High electronegativity**: Because of oxygen's strong affinity for e^-, it has high redox potential, thus allowing for complete oxidation of glucose*

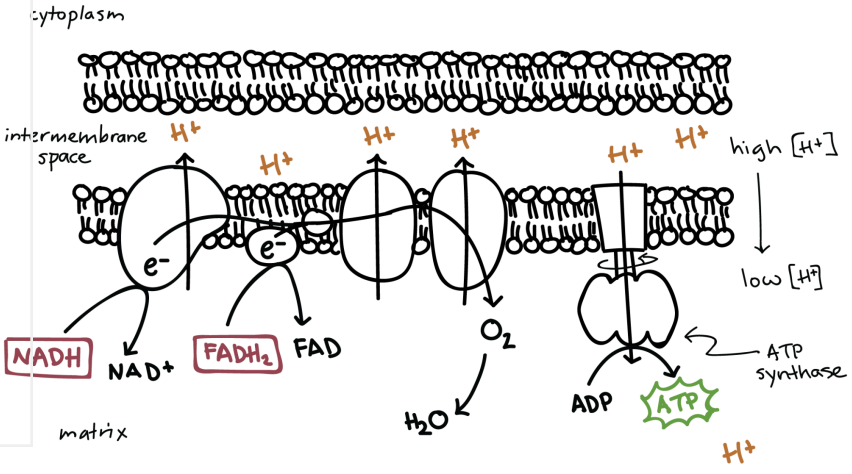
***Prevents excess reduction**: NADH and $FADH_2$ would become highly reduced if oxygen was not present*

Oxygen is reduced by accepting electrons, ultimately forming water as the end product

Chemiosmosis in the ETC

***Chemiosmosis**: The movement of ions across a semipermeable membrane-bound structure, down their electron gradient*

In the ETC, this involves coupling of electron transport and proton movement across the inner mitochondrial membrane



***Gluconeogenesis**: The synthesis of new glucose molecules from non-carbohydrate sources (i.e., lactate, amino acids, glycerol)*

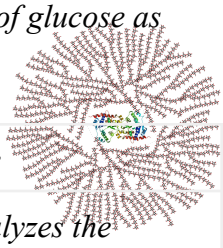
Overview

Differences from glycolysis	***Purpose**: Synthesizes new glucose, does not break it down (glycolysis)* ***Substrates**: Uses various substrates other than glucose* ***Location**: Liver (main), kidneys, small intestine* ***Regulation**: Regulated by glucagon, cortisol, and insulin* ***Energy balance**: Entirely energy consuming process*
Key enzymes, steps, roles, functions	***Pyruvate carboxylase** (mitochondria): Converts pyruvate → oxaloacetate; requires biotin as a cofactor* ***Phosphoenolpyruvate carboxykinase** (PEPCK) (cytoplasm, mitochondria): Converts oxaloacetate to PEP* ***FBPase**: Converts F-1,6-BP to F-6-P* ***G6Pase**: G6P to glucose (final)*
Intermediates that cannot be used	***Acetyl-CoA**: Instead goes into CAC or used for synthesis of fatty acids or ketone bodies* ***Acetoacetate**: Ketone body produced during the breakdown of fatty acids; can be converted back to acetyl-CoA* ***Palmitate**: Saturated fatty acid, which can be broken down into acetyl-CoA*

Roles of glucagon and insulin

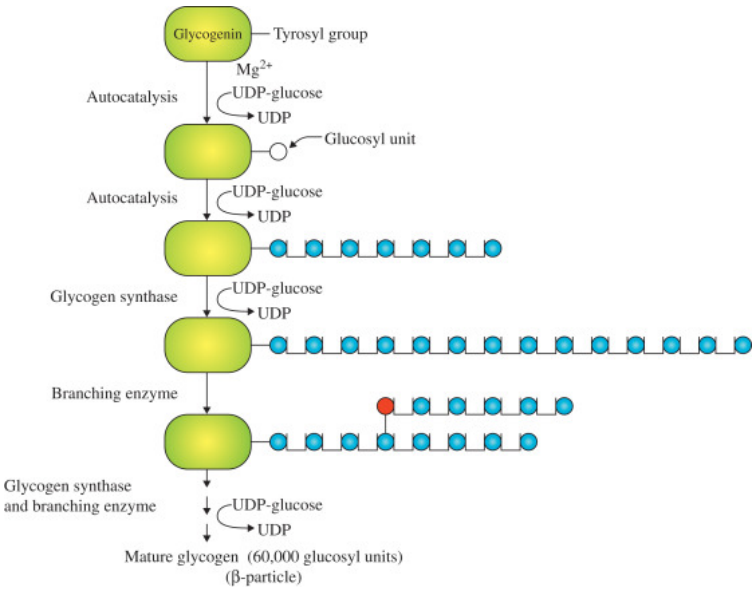
Glucagon	*Opposite to insulin, increasing blood sugar* ➢ *Promotes glycogenolysis, stimulates gluconeogenesis, facilitates lipolysis* *Location: α-cells in pancreatic islets*
Insulin	*Hormone that helps regulate blood sugar levels by facilitating uptake, use, and storage of glucose* ➢ *Translocation of GLUT4 to the cell membrane* ➢ *Enhances glycogenesis, inhibits glycogenolysis, promoting lipogenesis* *Location: β-cells in pancreatic islets*

***Glycogenesis**: The conversion and storage of glucose as glycogen*



Overview

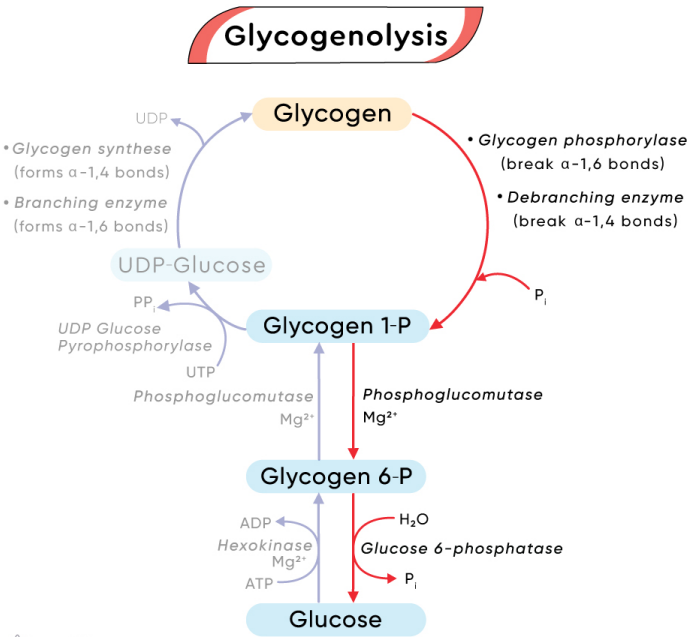
Location	*Liver and skeletal muscle*
Key enzyme, steps, roles, functions, steps	***Glycogen synthase**: Catalyzes the transfer of glucose from UDP-glucose to an existing glycogen chain* ➢ *α-1,4-glycosidic bond* --- ***Activation**: Before glycogenesis, glucose must be converted into G6P (by hexo/glucokinase), then G6P → G1P (by phosphoglucomutase)* ***Glycogen primer**: Short chain of glucose residues attached to glycogenin (protein) formed by glycogenin auto-glycosylation, used in the beginning of glycogen synth.* ***Elongation**: After primer formation, glycogen synthase adds glucose residues* ***Branching**: Glycogen branching enzyme (amylo-α-1,4→1,6-transglycosylase) introduces branches into chain by cleaving portions of the glycogen chain and transferring to form a new branch with α-1,6-glycosidic bond*
Relevant bonds	*α-1,4-glycosidic: Formed in elongation, when glycogen synthase transfers glucose from UDP-glucose to the non-reducing end of the chain* *α-1,6-glycosidic: Formed in branching, when glycogen branching enzyme cleaves a portion of the glycogen chain, and transfers it to a new location*



Glycogenolysis: *The enzymatic breakdown of glycogen into individual glucose molecules*

Overview

Location	*Liver (maintains blood glucose levels) and skeletal muscle (local source of energy)*
Key enzymes, steps, roles, functions	*Glycogen phosphorylase: Catalyzes removal of glucose residues from glycogen by breaking α-1,4-glycosidic bonds at the non-reducing ends* ➢ *Releases as G1P* *Phosphoglucomutase: Converts G1P → G6P [which can enter glycolysis]*
Regulation	*Glucagon: Stimulates glycogenolysis in the liver to increase blood glucose levels* *PKA: Hormone signal that regulates glycogen phosphorylase*



Fatty Acid Synthesis: *The synthesis of fatty acid in the form of triglycerides, which can be used for cell functions*

Overview

Location	*Cytoplasm (liver, adipose tissue)*
Substrates	***Acetyl-CoA****: Derived from various sources, including glucose metabolism, amino acid breakdown, fatty acid oxidation* ***Malonyl-CoA***
Key enzymes, steps, roles, functions	***Acetyl-CoA carboxylase****: Converts acetyl-CoA → malonyl-CoA* ***Fatty acid synthase*** *(FAS): Catalyzes a series of reactions (i.e., condensation, reduction, dehydration) to extend the fatty acid chain by two carbons per cycle* --- ***Activation****: After release from FAS, the fatty acid is activated by attached CoA to form fatty acyl-CoA*
Regulation	***Insulin****: Activates acetyl-CoA carboxylase* ***Glucagon****: Inhibit fatty acid synthesis*

β-***oxidation of Fatty Acids***: *Breakdown of fatty acids*

Overview

Location	*Mitochondrial matrix*
Substrates	*Long-chain fatty acids (12 or more carbon)*
Key enzymes, steps, roles, functions, steps	***Acyl-CoA synthase*** *(or fatty acyl-CoA ligase): Activation of fatty acid by addition of a CoA → fatty acyl-CoA* ***Acyl-CoA dehydrogenase****: Oxidation of fatty acyl-CoA forming a trans-double bond between α and β carbons* ***Enoyl-CoA hydratase****: Add H_2O across the trans-double bond → β -hydroxyacyl-CoA* β-***ketothiolase****: Cleaves β -hydroxyacyl-CoA → acetyl-CoA and acyl-CoA [step is repeated until entire fatty acid is converted to acetyl-CoA]* ➢ *Acetyl-CoA can enter Krebs cycle to generate ATP*
Regulation	***Glucagon, adrenaline****: Stimulates* ***Insulin****: Inhibits*

***Pentose Phosphate Pathway* (PPP)**: *[hexose monophosphate shunt] Generates NADPH, R5P, and facilitates the interconversion of sugars*

Two distinct phases:

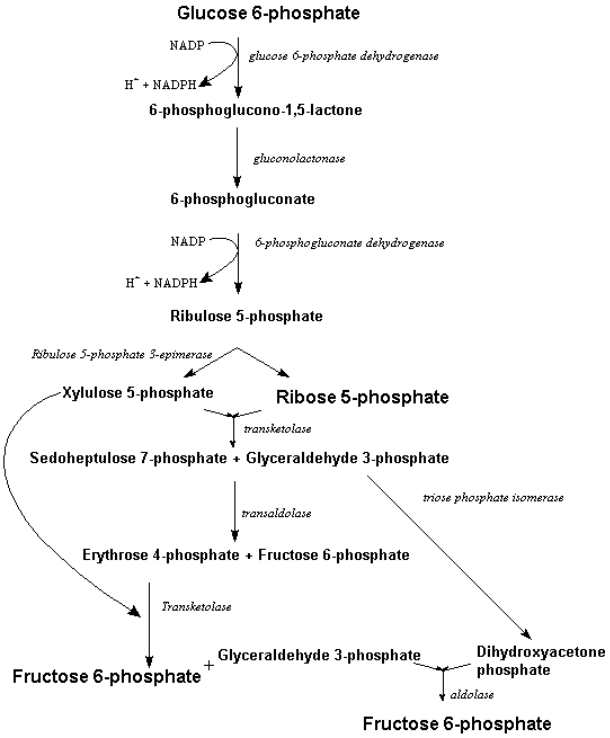
1. ***Oxidative***: *Generates NADPH by oxidizing G6P*
2. ***Non-oxidative***: *Involves the interconversion of sugars and generation of R5P; may be independent of the oxidative phase*

NADPH: *Cofactor involved in anabolic reactions (e.g., fatty acid synthesis, nucleotide synthesis), redox balance, and defending against oxidative stress*

Ribose-5-phosphate: *5-carbon sugar that is an essential component for the synthesis of nucleotides (e.g., DNA, RNA)*

Overview

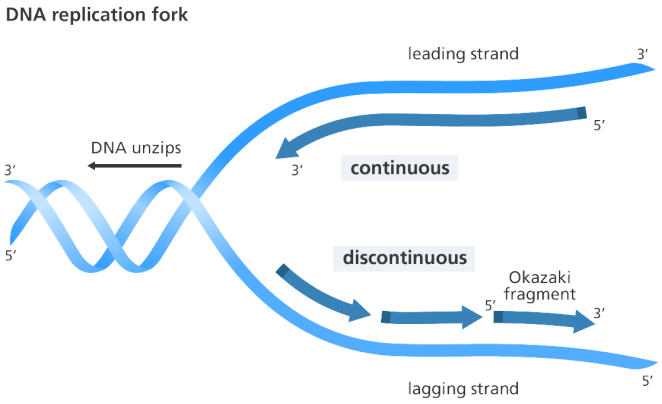
Location	*Cytoplasm*
Key enzymes, steps, roles, functions	***Oxidative*** *G6P dehydrogenase (G6PD): Oxidizes G6P → NADPH* ➢ *Generates R5P* ***Non-oxidative***: ***Transketolase***: *Transfers a 2-carbon unit between sugar molecules* ***Transaldolase***: *Transfers a 3-carbon unit between intermediates* ➢ *These enzymes allow for the synthesis of R5P or the generation of glycolytic intermediates [that can enter into glycolysis]*
Regulation	***G6P***: *Availability, demand, and cellular redox state regulates this process* ***NADP+:*** *Activates G6P dehydrogenase* ***NADPH***: *Inhibits G6P dehydrogenase*

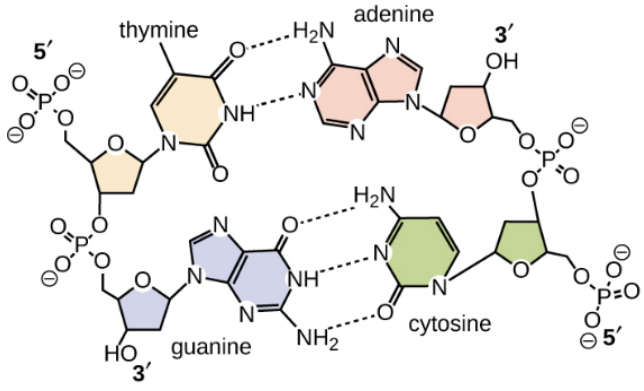


DNA Synthesis *(replication): A semiconservative process by which newly synthesized DNA consists of one original strand (template) and one newly synthesized complementary strand*

Overview

Location	*Nucleus*
Key enzymes, steps, roles, functions	*DNA helicase: Unwinds and separates the DNA double helix* *DNA polymerase: Catalyzes the addition of nucleotides to the growing DNA strand using the template as a guide* ➢ *Primase: Synthesizes a short RNA primer that provides a starting point for DNA polymerase* *DNA ligase: Joins Okazaki fragments and seals any remaining nicks*
Regulation	*Includes checkpoints, enzymes, protein complexes*





T — A: Two hydrogen bonds; G — C: Three hydrogen bonds

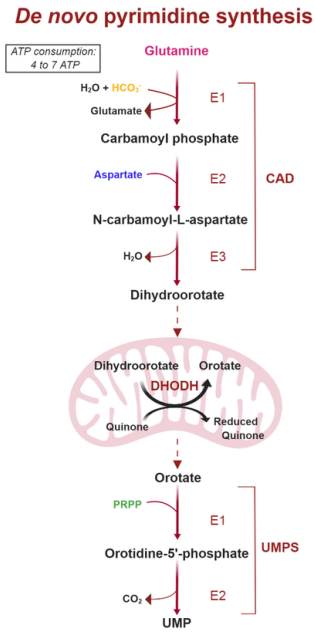
Nucleotide Biosynthesis*: Nucleotide synthesis*

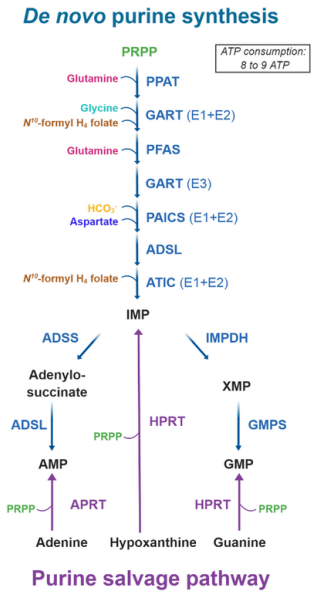
Two methods of synthesis*:*

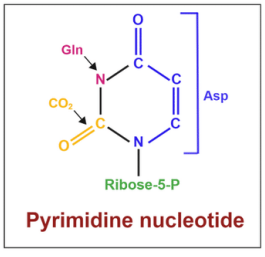
1. ***De Novo synthesis****: From simple precursors*
2. ***Salvage pathway****: Recycling and conversion of nucleobases obtained from dietary sources or breakdown of nucleic acids*

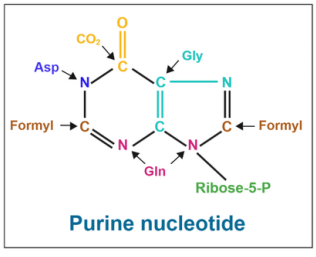
Overview

Purines	***Location****: Cytoplasm* ***Precursors****: Amino acids (glycine, glutamine, aspartate),* CO_2*, THF* ***Key enzyme****: PRPP amidotransferase, which progressively builds the purine ring structure* ***Regulation****: Feedback inhibition by purines and other available precursors*
Pyrimidines	***Location****: Cytoplasm, mitochondria* ***Precursors****: Aspartate, glutamine,* CO_2*, ATP* ***Key enzyme****: Carbamoyl phosphate synthetase II* ***Overall mechanism****: Building of the pyrimidine structure beginning with carbamoyl phosphate formation and ending with the addition of R5P* ***Regulation****: Feedback inhibition by end-products*



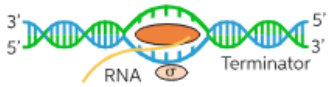
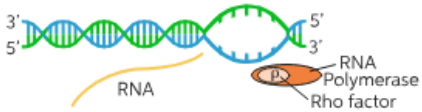






***DNA Transcription**: Synthesis of RNA using DNA as a template*

Overview

Location	*Nucleus (eukaryotic), cytoplasm (prokaryotic)*
Steps	1. ***Initiation*** ***RNA polymerase**: Binds to the promoter region [which signals the start point and determines the DNA template being used]* ➢ *A small section of DNA is unwound to expose the template*  2. ***Elongation**: RNA polymerase adds complementary RNA nucleotides (base pairing: A-U, G-C), and DNA reforms behind it* ➢ *RNA polymerase moves 3'→5'* ➢ *Synthesis occurs 5'→3'*  3. ***Termination**: Occurs when termination sequence is reached, causing RNA polymerase to detach and release* 
Post-transcription modifications	*Addition of a 5' cap, addition of poly-A tail at 3' end, removal of introns through RNA splicing*

Types of RNA:

a. ***Messenger RNA** (mRNA): Carries the genetic information from DNA to ribosomes for protein synthesis*
b. ***Ribosomal RNA** (rRNA): Combines with proteins to form ribosomes*
c. ***Transfer RNA** (tRNA): Transfers amino acids to the ribosomes during protein synthesis*

***DNA Translation**: Process of protein synthesis that involves decoding the information stored in mRNA and assembly of amino acids into a polypeptide chain*

Location	*Ribosomes*
Steps	1. *Initiation: Binding of mRNA to ribosome and tRNA at start codon* *Start codon: AUG (methionine)* 2. *Elongation: Reading of the mRNA codon sequence, with amino acids being brought by a specific tRNA* ➢ *Ribosome catalyzes the formation of peptide bonds between adjacent AA* 3. *Termination: Occurs when stop codon is reached on the mRNA sequence* *Stop codon: UAA, UAG, UGA* *Release factors: Bind to stop codon, causing release of the completed polypeptide chain*
Post-translational modifications	*Folding, cleavage of signal peptides, addition of functional groups, binding of cofactors*