

**+2 CHEMISTRY  
STUDY MATERIAL**

## **Unit – 8 Ionic Equilibrium**

### **It includes**

- **Book Back Answers**
- **Knowledge Based Questions**
- **Book Inside Questions**

**FOR  
MORE STUDY MATERIAL  
QUESTION PAPERS  
BULK ORDERS  
ACADEMIC SUPPORT**

**CONTACT  
SAIVEERA ACADEMY  
8098850809**

**UNIT 8 - Ionic Equilibrium****Book Back****Answer the following questions****1. What are lewis acids and bases? Give two example for each.**

A lewis acid is a **positive ion (or) an electron deficient molecule**

**Example :** Molecules that contain a polar double bond :  $\text{SO}_2$

All metal ions (or) atoms  $\text{Fe}^{2+}$

A lewis base is a **anion (or) neutral molecule with at least one lone pair of electrons.**

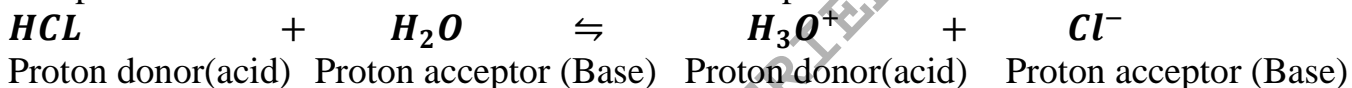
**Example :** Molecules that contain carbon – carbon multiple bond ,

All metal oxides  $\text{CaO}$ ,

**2. Discuss the Lowery – Bronsted concept of acids and bases.**

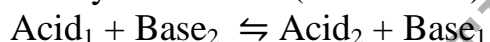
- According to their concept, an acid is defined as a substance that has a tendency to donate a proton to another substance and base is a substance that has a tendency to accept a proton from other substance.
- In other words, an acid is a proton donor and a base is a proton acceptor.
- When hydrogen chloride is dissolved in water, it donates a proton to the later. Thus,  $\text{HCl}$  behaves as an acid and  $\text{H}_2\text{O}$  is base.

The proton transfer from the acid to base can be represented as



- $\text{H}_3\text{O}^+$  donates a proton to  $\text{Cl}^-$  to form  $\text{HCl}$  i.e., the products also behave as acid and base.

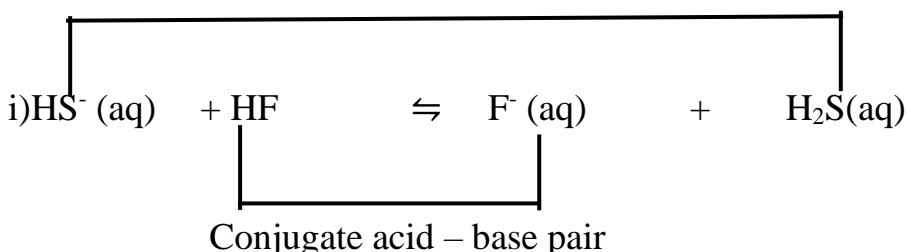
Lowry – Bronsted (acid – base) reaction is represented as



- The species that remains after the donation of a proton is a base ( $\text{Base}_1$ ) and is called the conjugate base of the Bronsted acid ( $\text{Acid}_1$ ) .
- In other words, chemical species that differ only by a proton are called conjugate acid – base pairs.

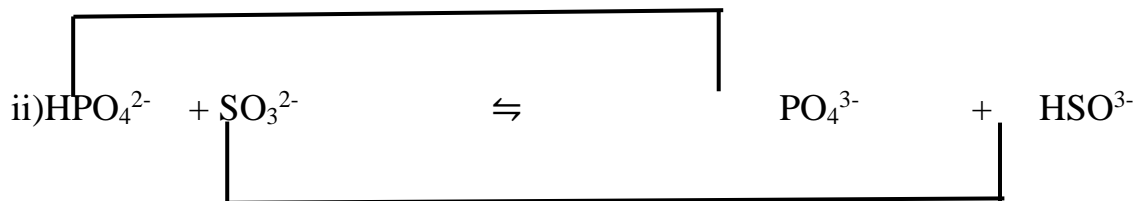
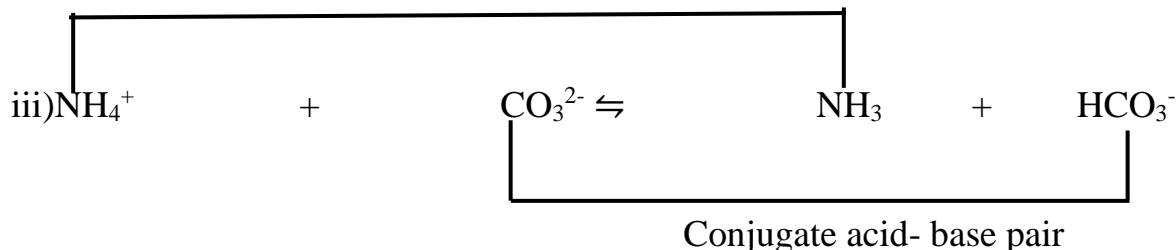
**3. Identify the conjugate acid base pair for the following reaction in aqueous solution**

Conjugate acid- base pair



**FOR MORE STUDY MATERIALS , QUESTION PAPERS AND ACADEMIC SUPPORT  
CONTACT – 8098850809**

Conjugate acid- base pair

Conjugate acid- base pair  
Conjugate acid- base pair

Conjugate acid- base pair

**4. Account for the acidic nature of HClO<sub>4</sub>. In terms of Bronsted – Lowry theory, identify its conjugate base.**

- With increase in oxidation number of particular halogen atom, the acidic character of corresponding oxoacids increases.
- The oxidation number of chlorine is 7 which weakens the strength of O-H bond (lesser attraction for proton) and increases acidity. Due to this HClO<sub>4</sub> is more acidic.
- According to Bronsted – Lowry theory, a strong acid has weak conjugate base and a weak acid has a strong conjugate base.
- According to Bronsted – Lowry theory, removal of proton from an acid is its conjugate base.
- ClO<sub>4</sub><sup>-</sup> is conjugate base of HClO<sub>4</sub>.

**5. When aqueous ammonia is added to CuSO<sub>4</sub> solution, the solution turns deep blue due to the formation of tetramminecopper (II) complex,  $[\text{Cu}(\text{H}_2\text{O})_4]_{aq}^{2+} + 4\text{NH}_3(aq) \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]_{aq}^{2+}$  among H<sub>2</sub>O and NH<sub>3</sub> Which is stronger Lewis base. NH<sub>3</sub> is stronger base than H<sub>2</sub>O**

**6. The concentration of hydroxide ion in a water sample is found to be  $2.5 \times 10^{-6}$  M. Identify the nature of the solution.**

$$[\text{OH}^-] = 2.5 \times 10^{-6}$$

$$\begin{aligned} \text{pOH} &= -\log[\text{OH}^-] \\ &= -\log(2.5 \times 10^{-6}) \\ &= -(-6 \log 10) - \log(2.5) \\ &= 6 - 0.3979 \\ &= 5.6021 \end{aligned}$$

$$\text{pH} + \text{pOH} = 14$$

**FOR MORE STUDY MATERIALS , QUESTION PAPERS AND ACADEMIC SUPPORT  
CONTACT – 8098850809**

$$\begin{aligned} \text{pH} &= 14 - 5.6021 \\ &= 8.3979 \end{aligned}$$

7. A lab assistant prepared a solution by adding a calculated quantity of HCl gas 25°C to get a solution with  $[\text{H}_3\text{O}^+] = 4 \times 10^{-5}\text{M}$ . Is the solution neutral (or) acidic (or) basic.

$$[\text{H}_3\text{O}^+] = 4 \times 10^{-5}$$

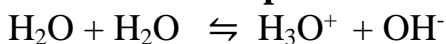
$$\begin{aligned} \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(4 \times 10^{-5}) \\ &= -(-5\log 10) - \log(4) \\ &= 5 - 0.6020 \\ &= 4.398 \end{aligned}$$

The solution is **acidic**.

### 9. Define solubility product

It is defined as product of molar concentration of constituent ions, each raised to the power of its stoichiometric co-efficient in a balanced equilibrium equation.

### 10. Define ionic product of water. Give its value at room temperature.



$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

The concentration of pure liquid water is one

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

The ionic product of water represented as  $K_w$  is defined as product of concentration of  $[\text{H}_3\text{O}^+]$  &  $[\text{OH}^-]$  in water at a particular temperature.

$K_w$  value of water in room temperature is  $1.00 \times 10^{-14} \text{ mol}^2\text{dm}^{-6}$

### 11. Explain common ion effect with an example

- Acetic acid is a weak acid. It is not completely dissociated in aqueous solution and hence the following equilibrium exists.  
 $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$
- The added salt, sodium acetate ( $\text{CH}_3\text{COONa}$ ), completely dissociates to produce  $\text{Na}^+$ ,  $\text{CH}_3\text{COO}^-$   
 $\text{CH}_3\text{COONa} \rightarrow \text{CH}_3\text{COO}^- + \text{Na}^+$
- Hence the overall concentration of  $\text{CH}_3\text{COO}^-$  and the acid dissociation equilibrium is disturbed.
- To maintain the equilibrium, by Le chatelier's principle the excess  $\text{CH}_3\text{COO}^-$  ions combines with  $\text{H}^+$  ions to produce much more unionized  $\text{CH}_3\text{COOH}$  i.e., the equilibrium will shift towards the left.
- Therefore dissociation of  $\text{CH}_3\text{COOH}$  is suppressed.
- Thus, the dissociation of a weak acid ( $\text{CH}_3\text{COOH}$ ) is suppressed in the presence of a salt ( $\text{CH}_3\text{COONa}$ ) containing an ion common to the weak electrolyte.

**FOR MORE STUDY MATERIALS , QUESTION PAPERS AND ACADEMIC SUPPORT**

**CONTACT – 8098850809**

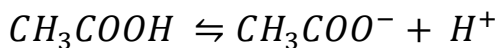
➤ It is called the common ion effect.

### 12. Derive an expression for Ostwald's dilution law

- Ostwald's dilution law relates the dissociation constant of the weak acid ( $K_a$ ) with its degree of dissociation ( $\alpha$ ) and the concentration ( $C$ ).
- Degree of dissociation ( $\alpha$ ) is the fraction of the total number of moles of a substance that dissociates at equilibrium.

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{total number of moles}}$$

The dissociation of acetic acid can be represented as



$$K_a = \frac{[CH_3COO^-][H^+]}{CH_3COOH}$$

	$CH_3COOH$	$[H^+]$	$CH_3COO^-$
Initial number of moles	1	-	-
Degree of dissociation of $CH_3COOH$	$\alpha$	-	-
Number of moles at equilibrium	$1 - \alpha$	$\alpha$	$\alpha$
Equilibrium Concentration	$C(1 - \alpha)$	$C\alpha$	$C\alpha$

$$K_a = \frac{C\alpha \times C\alpha}{C(1 - \alpha)} = \frac{\alpha^2 C}{C(1 - \alpha)}$$

Value of  $\alpha$  is small and hence in the denominator  $(1 - \alpha) \cong 1$ .

$$K_a = \alpha^2 C$$

$$\alpha = \sqrt{\frac{K_a}{C}}$$

When dilution increases, the degree of dissociation of weak electrolyte also increases. This statement is known as Ostwald's dilution Law

### 13. Define pH

pH of a solution is defined as the negative logarithm of base 10 of the molar concentration of the hydronium ions present in the solution.

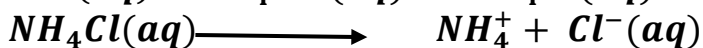
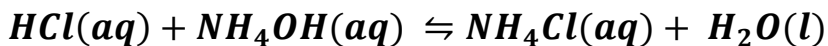
$$pH = -\log_{10} [H_3O^+]$$

### 18. Derive an expression for the hydrolysis constant and degree of hydrolysis of salt of strong acid and weak base

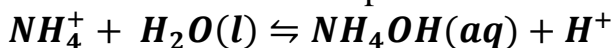
#### Hydrolysis constant ( $K_h$ )

**FOR MORE STUDY MATERIALS , QUESTION PAPERS AND ACADEMIC SUPPORT  
CONTACT – 8098850809**

When a strong acid(HCl) reacts with a weak base(NH<sub>4</sub>OH) will produce a salt NH<sub>4</sub>Cl, and water



NH<sub>4</sub><sup>+</sup> is a strong conjugate acid of the weak base NH<sub>4</sub>OH and it has a tendency to react with OH<sup>-</sup> from water to produce unionised NH<sub>4</sub>OH



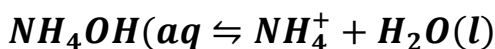
$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+][H_2O]}$$

Since [H<sub>2</sub>O] is found to be constant and the hydrolysis constant expression reduced to

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} \dots\dots\dots(1)$$

$$K_w = [OH^-][H^+] \dots\dots\dots(2)$$

For the dissociation of the weak base NH<sub>4</sub>OH



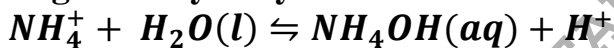
$$K_b = \frac{[NH_4^+][H_2O]}{[NH_4OH]} \dots\dots\dots(3)$$

$$\frac{K_w}{K_b} = \frac{[NH_4OH][H^+]}{[NH_4^+]} = K_h$$

There is no such tendency shown by Cl<sup>-</sup> and therefore [H<sup>+</sup>] > [OH]<sup>-</sup> the solution is acidic and the pH is less than 7.

$$K_h K_b = K_w$$

**Degree of hydrolysis**



	NH <sub>4</sub> <sup>+</sup>	[H <sup>+</sup> ]	NH <sub>4</sub> OH
<b>Initial number of moles</b>	1	-	-
<b>Degree of Hydrolysis of NH<sub>4</sub><sup>+</sup></b>	h	-	-
<b>Number of moles at equilibrium</b>	1- h	h	h
<b>Equilibrium Concentration</b>	C(1- h)	C h	Ch

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]}$$

$$= \frac{Ch \times Ch}{C(1-h)} = \frac{h^2C}{C(1-h)}$$

$$K_h = h^2C$$

**FOR MORE STUDY MATERIALS , QUESTION PAPERS AND ACADEMIC SUPPORT  
CONTACT – 8098850809**

$$h = \sqrt{\frac{K_h}{C}}$$

$$h = \sqrt{\frac{K_w}{K_b \times C}}$$

pH

$$[H^+] = \sqrt{K_h \cdot C}$$

$$= \sqrt{\frac{K_w}{K_b} \cdot C} \dots \dots \dots (4)$$

$$\text{pH} = -\log_{10} [H^+]$$

Sub  $[H^+]$  in above equation

$$\text{pH} = -\log \left( \sqrt{\frac{K_w}{K_b} \cdot C} \right)$$

$$= -\log \left( \frac{K_w}{K_b} \cdot C \right)^{1/2}$$

$$= -\frac{1}{2} \log K_w - \frac{1}{2} \log C + \frac{1}{2} \log K_b$$

$$= 7 - \frac{1}{2} (\log C + pK_b)$$

**Book inside****Short answers****1.Explain Arrhenius Concept of acids and bases****Acid**

According to him, an acid is a substance that dissociates to give hydrogen ions in water

**Base**

According to him ,a base is a substance that dissociates to give hydroxyl ions in water.

**2.What are the Limitations of Arrhenius concept**

- i. Arrhenius theory does not explain the behaviour of acids and bases in non aqueous solvents such as acetone, Tetrahydrofuran etc...
- ii. This theory does not account for the basicity of the substances like ammonia (NH<sub>3</sub>) which do not possess hydroxyl group.

**3.Why ionic product of water increases with increases in temperature?**

- The dissociation of water is an endothermic reaction.
- With the increase in temperature, the concentration of H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> also increases, and hence the ionic product also increases.

**FOR MORE STUDY MATERIALS , QUESTION PAPERS AND ACADEMIC SUPPORT  
CONTACT – 8098850809**

**4. Derive a Relation between pH and pOH**

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+] \dots\dots\dots(1)$$

$$\text{pOH} = -\log_{10} [\text{OH}^-] \dots\dots\dots(2)$$

Adding (1) & (2)

$$\begin{aligned} \text{pH} + \text{pOH} &= -\log_{10} [\text{H}_3\text{O}^+] - \log_{10} [\text{OH}^-] \\ &= -(\log_{10} [\text{H}_3\text{O}^+] + \log_{10} [\text{OH}^-]) \\ &= -\log_{10}([\text{H}_3\text{O}^+] \times [\text{OH}^-]) \end{aligned}$$

$$\begin{aligned} \text{Since } K_w &= [\text{H}_3\text{O}^+][\text{OH}^-] \\ &= -\log_{10} K_w \end{aligned}$$

$$\begin{aligned} \text{At } 25^\circ\text{C } K_w &= 10^{-14} \\ &= -\log_{10}(10^{-14}) \end{aligned}$$

$$\text{pH} + \text{pOH} = 14$$

**5. What is buffer solution? Write down its types**

Buffer is a solution which consists of a mixture of a weak acid and its conjugate base (or) a weak base and its conjugate acid. This buffer solution resists drastic changes in its pH upon addition of a small quantities of acids (or) bases, and this ability is called buffer action

**Types**

**1. Acidic buffer solution :** a solution containing a weak acid and its salt.

Example : solution containing acetic acid and sodium acetate

**2. Basic buffer solution :** a solution containing a weak base and its salt.

Example : Solution containing  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$

**6. Define buffer index**

- It is the quantitative measure of the buffer capacity.
- It is defined as the number of gram equivalents of acid or base added to 1 litre of the buffer solution to change its pH by unity.

$$\beta = \frac{dB}{d(\text{pH})}$$

**dB** = number of gram equivalents of acid / base added to one litre of buffer solution.

**d(pH)** = The change in the pH after the addition of acid / base.

**7. What is Salt Hydrolysis?**

- Salts completely dissociate in aqueous solutions to give their constituent ions.
- The ions so produced are hydrated in water. In certain cases, the cation, anion or both react with water and the reaction is called salt hydrolysis.

**FOR MORE STUDY MATERIALS , QUESTION PAPERS AND ACADEMIC SUPPORT**

**CONTACT – 8098850809**



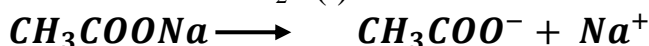
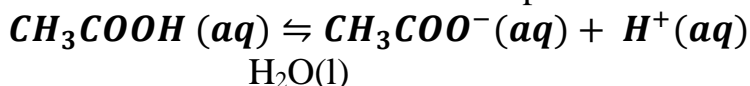
Long answers**1.Explain buffer action with example**

To resist changes in its pH on the addition of an acid (or) a base, the buffer solution should contain both acidic as well as basic components so as to neutralize the effect of added acid (or)

base and at the same time, these components should not consume each other.

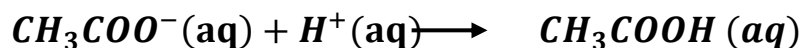
Solution containing acetic acid and sodium acetate was taken

The dissociation of the buffer components occurs as below

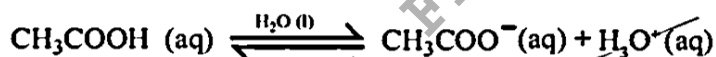
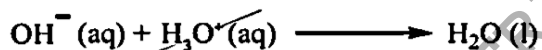


If an acid is added to this mixture, it will be consumed by the conjugate base  $\text{CH}_3\text{COO}^-$  to form the undissociated weak acid i.e., the increase in the concentration of  $\text{H}^+$  does not reduce

the pH significantly.



If a base is added, it will be neutralized by  $\text{H}_3\text{O}^+$ , and the acetic acid is dissociated to maintain the equilibrium. Hence the pH is not significantly altered.

**2.Derive Henderson – Hasselbalch equation**

- It is used to find the pH of the buffer solution
- concentration of hydronium ion in an acidic buffer solution depends on the ratio of the concentration of the weak acid to the concentration of its conjugate base present in the solution i.e.,

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{acid}]_{\text{eq}}}{[\text{base}]_{\text{eq}}}$$

- The weak acid is dissociated only to a small extent. Moreover, due to common ion effect, the dissociation is further suppressed and hence the equilibrium concentration of the acid is nearly equal to the initial concentration of the unionised acid.
- Similarly, the concentration of the conjugate base is nearly equal to the initial concentration of the added salt.

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{acid}]}{[\text{salt}]}$$

- [acid] and [salt] represent the initial concentration of the acid and salt used to prepare the buffer solution

**FOR MORE STUDY MATERIALS , QUESTION PAPERS AND ACADEMIC SUPPORT**

**CONTACT – 8098850809**

Taking negative logarithm on both sides of the equation

$$-\log[H_3O^+] = -\log K_a - \log \frac{[acid]}{[salt]} \dots \dots \dots (1)$$

$$pH = -\log_{10} [H_3O^+]$$

$$pK_a = -\log_{10} [K_a]$$

Sub above equation in (1)

$$pH = pK_a - \log \frac{[acid]}{[salt]}$$

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

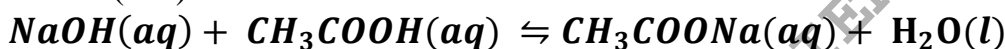
Similarly for a basic buffer

$$pOH = pK_b + \log \frac{[salt]}{[base]}$$

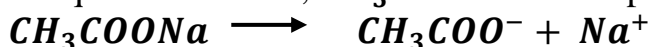
### 3. Derive an expression for the hydrolysis constant and degree of hydrolysis of salt of strong base and weak acid

#### Hydrolysis constant

When sodium hydroxide (strong base) and acetic acid (weak base) to give sodium acetate (salt) and water.



In aqueous solution,  $CH_3COONa$  is completely dissociated as



$CH_3COO^-$  is a conjugate base of the weak acid  $CH_3COOH$  and it has a tendency to react with  $H^+$  from water to produce unionised acid

There is no such tendency for  $Na^+$  to react with  $OH^-$



$[OH^-] > [H^+]$ , the solution is basic due to hydrolysis and the pH is greater than 7.

Hydrolysis constant

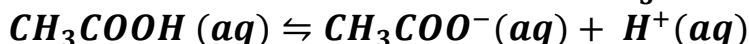
$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-][H_2O]}$$

Since  $[H_2O]$  is found to be constant and the hydrolysis constant expression reduced to

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \dots \dots \dots (1)$$

$$K_w = [OH^-][H^+] \dots \dots \dots (2)$$

For the dissociation of the weak acid  $CH_3COOH$



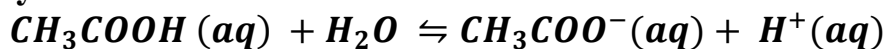
$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \dots \dots \dots (3)$$

**FOR MORE STUDY MATERIALS , QUESTION PAPERS AND ACADEMIC SUPPORT  
CONTACT – 8098850809**

$$\frac{K_w}{K_a} = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = K_h$$

$$K_h K_a = K_w$$

Degree of hydrolysis



	$CH_3COOH$	$H^+$	$CH_3COO^-$
Initial number of moles	1	-	-
Degree of Hydrolysis of $CH_3COOH$	h	-	-
Number of moles at equilibrium	1-h	h	h
Equilibrium Concentration	C(1-h)	Ch	Ch

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$= \frac{Ch \times Ch}{C(1-h)} = \frac{h^2 C}{C(1-h)}$$

$$K_h = h^2 C$$

$$h = \sqrt{\frac{K_h}{C}}$$

$$h = \sqrt{\frac{K_w}{K_a \times C}}$$

**pH**

$$[OH^-] = \sqrt{K_h \cdot C}$$

$$= \sqrt{\frac{K_w}{K_a} \cdot C} \dots \dots \dots (1)$$

$$pH + pOH = 14$$

$$Ph = 14 - pOH$$

Sub  $[OH^-]$  in above equation

$$pH = 14 + \log \left( \sqrt{\frac{K_w}{K_a} \cdot C} \right)$$

$$= 14 + \log \left( \frac{K_w}{K_a} \cdot C \right)^{1/2}$$

**FOR MORE STUDY MATERIALS , QUESTION PAPERS AND ACADEMIC SUPPORT****CONTACT – 8098850809**

$$= 14 + \frac{1}{2} \log K_w + \frac{1}{2} \log C - \frac{1}{2} \log K_a$$

$$= 7 + \frac{1}{2} (\log C + pK_a)$$

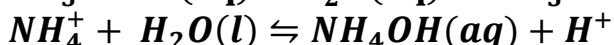
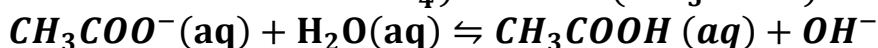
**4. Derive an expression for the hydrolysis constant and degree of hydrolysis of salt of weak base and weak acid**

**Hydrolysis constant**

Hydrolysis of ammonium acetate as follows



In this case both cation ( $NH_4^+$ ) and anion ( $CH_3COO^-$ ) have a tendency to react with water



$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} \dots\dots(1)$$

$$K_b = \frac{[NH_4^+][H_2O(l)]}{[NH_4OH]} \dots\dots(2)$$

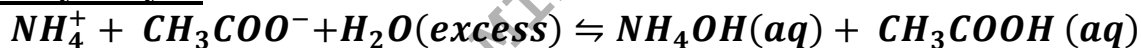
$$K_w = [OH^-][H^+] \dots\dots(3)$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \dots\dots(4)$$

Using relation (2), (3), (4) in (1)

$$K_h = \frac{K_w}{K_a \cdot K_b} \dots\dots(5)$$

**Degree of hydrolysis**



	$NH_4^+$	$CH_3COO^-$	$NH_4OH(aq)$	$CH_3COOH(aq)$
Initial number of moles	1	1	0	0
Degree of Hydrolysis of salt	h	h	-	-
Number of moles at equilibrium	1-h	1-h	h	h
Equilibrium Concentration	C(1-h)	C(1-h)	Ch	Ch

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]}$$

$$= \frac{Ch \times Ch}{C(1-h) \times C(1-h)}$$

**FOR MORE STUDY MATERIALS , QUESTION PAPERS AND ACADEMIC SUPPORT  
CONTACT – 8098850809**

$$= \frac{h^2}{(1-h)^2}$$

1-h is small, then  $1-h \approx 1$  and

$$K_h = \frac{h^2}{1}$$

$$h = \sqrt{K_h} \dots \dots \dots (6)$$

Sub  $K_h$  value in (6)

$$h = \sqrt{\frac{K_w}{K_a \cdot K_b}}$$

**pH**

$$\text{pH} = -\log [H^+]$$

$$[H^+] = K_a \sqrt{K_h}$$

$$\text{pH} = -\log \left( \frac{K_a \cdot K_w}{K_b} \right)^{1/2}$$

$$= -\frac{1}{2} (\log K_a + \log K_w - \log K_b)$$

$$= 7 + \frac{1}{2} (\text{p}K_a - \text{p}K_w)$$

The nature of the solution depends on strength of acid or base

If  $K_a > K_b$  - solution is acidic and  $\text{pH} < 7$

If  $K_a < K_b$  - solution is basic and  $\text{pH} > 7$

If  $K_a = K_b$  - solution is neutral and  $\text{pH} = 7$

MKS TAMIL FRIENDS

**FOR MORE STUDY MATERIALS , QUESTION PAPERS AND ACADEMIC SUPPORT**

**CONTACT – 8098850809**