CHAPTER **6**

IONIC EQUILIBRIUM

6.1 INTRODUCTION

Arrhenius theory: According to this theory, 'Acids are the substances which give H^+ on dissolution in water while bases are the substances which give OH^- on dissolution in water.'

Examples:

- (i) $HCl(g) + Water \Rightarrow H^+(aq) + Cl^-(aq)$
- (ii) $CH_3COOH + Water \Rightarrow H^+_{(aq)} + CH_3COO^-_{(aq)}$
- (iii) $\operatorname{Ca(OH)}_{2} + \operatorname{Water} \rightleftharpoons \operatorname{Ca}^{2+}_{(aq)} + 2OH_{(aq)}^{2+}$

The high dielectric constant of water lowers the force of attractions between the oppositely charged ions and thus causes the dissociations of the electrolyte. The greater the number of H^+ or OH^- ions given by an acid or a base in water, the greater will be the strength of the acid or the base.

6.1.1 Limitation of Arrhenius Theory

- (a) It fails to explain the behaviour of acids and bases in non-aqueous solvents.
- (b) It fails to explain the neutralization reactions giving rise to salt formation in absence of a solvent.
 - E.g., (i) $CO_{2(g)} + CaO_{(s)} \rightarrow CaCO_{3(s)}$ (ii) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(g)$ or (s)
- (c) It fails to explain the acidic character of certain salts, e.g., AlCl₃, BF₃, etc. and basic character of NH₃, PH₃, etc.

6.1.2 Proton Transfer Theory (Bronsted and Lowry Concept)

According to this theory, 'An acid is a substance which has a tendency to donate a proton to other substances, and a base is a substance which has a tendency to accept a proton from any other substances.'

E.g., Acid $\rightleftharpoons H^+$ + Base

(a) Characteristic of Proton Transfer Theory:

(i) The proton donated by an acid is incapable of independent existence and is always solvated.

 $CH_3COOH + H_2O \Rightarrow CH_3COO^- + H_3O^+$

 (ii) A cation may behave as an acid and an anion may behave as a base in water, however, some of them behave as amphoteric.

E.g., $Ag^+ + 2H_2O \rightleftharpoons AgOH + H_3O^+$.

 $CO_3^{2-} + H_2O \rightleftharpoons OH^- + HCO_3^-$

A substance which can act both as an acid as well as a base in different reactions is called amphoteric.

An acid-base pair which differs by a proton is called conjugate acid-base pair.

 $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$

where HCO₃⁻ is amphoteric

6.1.3 Conjugate Acids and Bases

Pairs of the substances which can be formed from one another by the gain or loss of a proton are known as conjugate acid-base pair.

Acid $\xrightarrow{-H^+}$	Conjugate Base	Base $\xrightarrow{H^+}$	Conjugate Base
HCl	Cl⁻	NH ₃	NH_4^+
H_2SO_4	HSO ₄ ⁻	$C_{2}H_{5}^{-}$	C_2H_6
NH ₃	NH ₂ ⁻	H ₂ O	H ₃ O ⁺

The stronger an acid, the weaker must be its conjugate base and vice versa.

e.g.,
$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$
;
_{Acid}
 $Ch_3COOH + H_2O \rightarrow H_3O^+ + CH_3COO^-$ order of acidic strength is
_{Acid}
_{Acid}

 $HCl > CH_3COOH$ and order of basic strength of conjugate bases are $CH_3COO^- > Cl^-$.

All Arrhenious acids are Bronsted acids while all Arrhenious bases is not Bronsted bases, e.g., NaOH, is an Arrhenious base as it furnishes OH⁻ but is not a Bronsted base as it is not capable of accepting a proton as such.

Leveling Effect: In a solvent like H_2O , all strong acid are almost completely dissociated and therefore their acidic strength cannot be compared. This phenomenon is termed as leveling effect.

6.1.4 Lewis concept of Acids and Bases

According to this theory, 'An acid is a species that is capable of accepting a pair of electrons to form a dative covalent bond and a base is a species that is capable of donating a pair of electrons to form a dative covalent bond'.

Example:

(a) $BF_3 + NH_3 \rightarrow F_3B NH_3$



- (b) $BF_3 + F_{Base}^- \rightarrow BF_4^-$
- (c) $\operatorname{Cu}_{\operatorname{Acid}}^{2+} + 4\operatorname{CN}_{\operatorname{Base}}^{+} \rightarrow [\operatorname{Cu}(\operatorname{CN})_{4}]^{2-}$

(a) Classification of Lewis Acid:

- (i) Molecules in which central atom has an incomplete octet, e.g., BF₃, AlCl₃, etc.
- (ii) Molecules which have a central atom with empty d-orbitals, e.g., SiX₄, GeX₄, PX₃, TiCl₄, etc.
- (iii) Molecules having multiple covalent bond between atoms of dissimilar electronegativity,
 e.g., CO₂, SO₂, SO₃, etc.

$$O = C = O + OH^{-} \longrightarrow HCO_{3}^{-}$$

(b) Characteristics of Lewis Bases:

(i) Neutral species having at least one lone pair of electrons.

e.g.,
$$NH_3$$
, $R - NH_2$, $R - O - H$, $R - NH - R$, R_3N ; $R - S - R$, $R - O - R$, etc.

(ii) Negatively charged species, e.g., CN⁻, OH⁻, Cl⁻, SO₄⁻²⁻, CO₃⁻²⁻, etc.

6.1.5 Classification of Acids

- (a) Hydroacids: Some example of hydroacids are HCN, H₂S, H₂Se, H₂Te, HCl, HBr, HF, Hl,N₃H, etc. For hydroacids as we move down in the group the acidic strength increases as well as when we move from left to right in a period acid strength increases.
 - e.g., (i) HF < HCl < HBr < Hl; (in group)
 - (ii) $NH_3 < H_2O < HF$; (in period)
- (b) Acid anhydride and oxyacids: Oxides of non-metals having same oxidation number of a non-metal in their respective oxyacids and themselves are known as acid anhydrides. The acid anhydrides on dissolution in water give their respective oxyacids.

e.g., $SO_3 + H_2O \rightarrow H_2SO_4$ (+6)(anhydride) (oxyacid)

e.g., $H_4P_2O_3$ is not an acid because there is no replacable hydrogen.

- For obtaining acid anhydride from any oxyacid, subtract H₂O in such a way that no hydrogen remains.
- If an acid anhydride can form more than one oxyacids (containing all the central atom in each case in same oxidation state) then we must consider ortho, meta and pyronotation.

6.1.5.1 Acidic strength of oxyacids

(a) Higher the oxidation number of common central atom in oxy acids, more will be the acidic character if basicity is same.

e.g., $\operatorname{HClO}_4 > \operatorname{HClO}_3 > \operatorname{HCLO}_2 > \operatorname{HClO}_{(+3)} > \operatorname{HClO}_{(+1)}$

(b) If central atom is different but basicity is same then as the electronegativity of central atom increases acidic strength of oxyacid also increases HClO₄ > HBrO₄ > HIO₄.

Notes:

□ Ions of acids containing-ic suffix are written as-ate, while those containing-ous suffix can be written as-ite





6.2 ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION

According to this theory, 'An electrolyte on dissolution in water furnishes two type of ions, positive (cation) and negative (anion). A chemical equilibrium exists between undissociated electrolyte and dissociated ions.' If α is the degree of dissociation of an electrolyte AB, then

	AB	⇒	A^+	+	B
Before dissociation	1		0		0
after dissociation	$1-\alpha$		α		α
where degree of dissocation	$(\alpha) = M$	oles dos	sociated		
where degree of dissocation	$(u) = \frac{1}{\text{Total n}}$	noles pre	esent initia	lly	

The degree of dissociation of a strong electrolyte is assumed to be unity at infinite dilution, i.e., $\alpha = 1$.

6.2.1 Strong and Weak Electrolytes

- (a) Strong Electrolytes: Electrolytes which ionize almost completely when dissolved in water are called strong electrolytes, e.g., (all salts except CdBr₂, HgCl₂), mineral acids like HCl, H₂SO₄, HNO₃, etc and bases like NaOH, KOH, etc.
- (b) Weak Electrolytes: Substances which dissociate only to a small extent in aqueous solution are weak electrolytes, e.g., all organic acids (except suphonic acids), inorganic acids like HCN, H₃BO₃ etc. and bases like NH₃, amines, etc.

6.2.2 Factors Influencing Degree of Dissociation

The variation of ' α ' of an electrolyte is governed by:

- (a) **Nature of solute:** All ionic compounds, i.e., strong electrolytes have $\alpha \approx 1$ at normal dilution. Most of the polar covalent compounds, i.e., weak electrolytes have $\alpha \ll 1$.
- (b) Nature of solvent: Solvents having high dielectric constants are themselves feebly ionized but an electrolyte in such a solvent show higher degree of dissociation than in a solvent of low dielectric constant (say methanol).
- (c) Dilution: The extent of dissociation of an electrolyte increases with dilution of solution.
- (d) **Temperature:** The extent of dissociation of an electrolyte increases with an increase in temperature.
- (e) **Common ion effect:** Addition of another solute having ion common to that of weak electrolyte shows a decrease in degree of dissociation of a weak electrolyte. This is known as common ion effect.

6.2.3 Ostwald Dilution Law

The application of law of mass action to weak electrolytes is known as Ostwald dilution law. Considering a weak electrolyte HA in equilibrium

HA	4	H^+	+	A-
t = 0	с	0		0
$t = t_{eq}$	c (1-α)	cα		cα

According to law of chemical equilibrium, $K_a = \frac{[H^+][A^-]}{[HA]} = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$, where K_{α} is dissociation

constant of an acid.

Since for a weak electrolyte, $\alpha \ll 1$

$$\Rightarrow K_{a} = c\alpha^{2} \text{ or } \alpha = \sqrt{\frac{K_{a}}{c}} \qquad K_{b} = \text{dissociation constant of a base}$$
$$K_{b} = \frac{c\alpha^{2}}{1-\alpha} \text{ and } K_{b} = c\alpha^{2} \text{ and } \alpha = \sqrt{\frac{K_{b}}{c}}$$

Notes:

- Ostwald dilution law is not applicable for strong electrolytes.
- The smaller the value of K_{α} , the weaker the acid.
- (a) Relative strength of weak acids and weak bases: Relative strength of two weak acids is a measure of $[H_3O^+] = [H^+]$ when concentrations of two acids are same, i.e., $c_1 = c_2$.

 $\Rightarrow \frac{\text{Relative strength of acid 1}}{\text{Relative strength of acid 2}} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$

Relative strength of two weak bases is a measure of [OH-]

$$\Rightarrow \frac{\text{Relative strength of base 1}}{\text{Relative strength of base 2}} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

Ionic Equilibrium

- (b) **Dissociation of polyprotic acids:** Substance which are capable of furnishing more than one proton to water are known as polyprotic or polybasic acids.
 - e.g., Considering a triprotic acid, i.e., phosphoric acid $(\mathrm{H_{3}PO_{4}})$

$$H_{3}PO_{4} + H_{2}O \rightleftharpoons H_{3}O^{+} + H_{2}PO_{4}^{-}; K_{a_{1}} = \frac{[H_{2}PO_{4}^{-}][H^{+}][H_{2}O_{4}]}{[H_{3}PO_{4}][H_{2}O]}$$
$$H_{2}PO_{4}^{-} + H_{2}O \rightleftharpoons H_{3}O^{+} + HPO_{4}^{2-}; K_{a_{2}} = \frac{[HPO_{4}^{2-}][H^{+}]}{[H_{2}PO_{4}^{-}]}$$
$$HPO_{4}^{2-} + H_{2}O \rightleftharpoons H_{3}O^{+} + PO_{4}^{3-}; K_{a_{2}} = \frac{[PO_{4}^{3-}][H^{+}]}{[HPO_{4}^{2-}]}$$

The value of the three ionization constants follow a decreasing trend $K_{a_1} > K_{a_2} > K_{a_3}$.

The reason for the decrease in the dissociation constant of successive stages is that in the first stage of dissociation, the proton comes from a neutral molecule while in the second stage of dissociation, the proton is detached from a negatively charged ion and in the third dissociation, it is detached from a doubly charged negative ion.

(c) Acidity and pK_a: The dissociation constant of an acid (K_a) is usually expressed in terms of pK_a, i.e., negative logarithm of K_a.

 $\mathbf{pK}_{a} = -\log \mathbf{K}_{a}$: similarly ($\mathbf{pK}_{b} = -\log \mathbf{K}_{b}$). For bases

The strength of a base is inversely related to pK_b values of the base, i.e., the larger is the value of pK_b the weaker is the base.

Notes:

- Acidic strength \$\pi\$ K_a \$\pi\$ \$\frac{1}{pK_a}\$
 Basic strength \$\pi\$ K_b \$\pi\$ \$\frac{1}{pK_b}\$
- (d) Ionic Product of Water: Since water is amphiprotic it gives H₃O⁺ and OH⁻ as a result of self ionization (auto protolysis).

H ₂ O	+	H ₂ O	#	H ₃ O ⁺ +	OH-
Acid 1		Base 1		Acid 2	Base 2

Applying the law of mass action, law of dissociation constant

$$K_{c} = \frac{[H_{3}O^{+}][OH^{-}]}{[H_{2}O]^{2}} = \frac{[H^{+}][OH^{-}]}{[H_{2}O]}$$

Since dissociation takes place to a very small extent, hence the concentration of undissociated water molecules [H,O] may be regarded as constant.

 $K_w = [H^+] [OH] = 1 \times 10^{-14} \text{ at } 25^{\circ}\text{C}$

The numerical value of K_w increases with increase in temperature.

Since in pure water, the concentration of H⁺ and OH⁻ ions must be equal to one another, hence, Hence $[H^+] = [OH^-] = 1 \times 10^{-7} \text{ mol dm}^{-3}$.

(i) If $[H^+] > \sqrt{K_{W^2}}$ the solution is acidic. if $[H^+] = \sqrt{K_{W^2}}$ the solution is neutral. if $[H^+] < \sqrt{K_w}$ the solution is basic.

Molarity and degree of dissociation of water

e.g., An aqueous solution in which $[H^+]$ is less than 1×10^{-7} mol/litre is said to be alkaline.

- \therefore [H⁺] = c α = 10⁻⁷ and concentration or molarity of water = 55.6
 - $\therefore \alpha \frac{10^{-7}}{55.6} = 1.8 \times 10^{-9}$ or % dissociation = 1.8 x 10⁻⁷.
- (e) Relation between K_w , K_a and K_b :

For a conjugate acid, base pair HA and A⁻ in aqueous solution.

HA \Rightarrow H⁺ + A⁻; K

 $A^- + H_2O \Rightarrow HA + OH^-; K_h$

On adding these two equations, we get

 $H_2O \rightleftharpoons H^+ + OH^-; K_w = K_a \times K_b.$

This relationship shows that product of dissociation constant of an acid and the dissociation constant of its conjugate base is the ionic product of water.

i.e., $K_w = K_a \times K_b$ $\Rightarrow pK_w = pK_a + pK_b = 14 \text{ at } 25^{\circ}\text{C}.$

6.3 THE pH VALUE AND pH SCALE

The concept of pH was introduced by Soren Sorensen. According to him, 'the pH of a solution is the negative logarithm (to the base 10) of the concentration of H^+ ions which it contains.'

Thus, $pH = -log_{10}[H^+] = -log_{10}[H_3O^+]$

$$\Rightarrow$$
 [H⁺] = [H₃O⁺] = 10^{-pf}

 \Rightarrow pH + pOH = pK_w = 14 at 25°C.

6.3.1 pH of Strong Acids or Strong Bases

When a strong acid is added to water, as in an aqueous solution of, HCl, in addition to the self-ionization of water,

 $H_2O + H_2O \Rightarrow H_3O^+ + OH^$ ionization of acid also occurs.

 $HCl + H_2O \rightarrow H_2O^+ + Cl^-$

The self-ionization of water occurs to a slight extent while ionization of HCl goes essentially to completion. As a result, we conclude that.

(a) In calculating $[H_3O^+]$ in an aqueous solution of a strong acid, the strong acid is the only significant source of H_3O^+ , unless the solution is extremely dilute (e.g., less than 10^{-6} M).

Total $[H_3O^+] = 10^{-7} + 10^{-8} M \Longrightarrow pH < 7$

(b) In calculating [OH⁻] in an aqueous solution of a strong base, the strong base is the only significant source of OH⁻ unless the solution is extremely dilute. (e.g., less than 10⁻⁶ M). Total [OH⁻] = 10⁻⁷ + 10⁻⁸ = 11 x 10⁻⁸M ⇒ pOH < 7</p>

Notes:

- Total [H_3O^*] or [OH] in two strong acids / base $\left[H_3O^*\right] = \frac{\Sigma NV}{\Sigma V}; \left[OH^-\right] = \frac{\Sigma NV}{\Sigma V}$
- The resultant solution of a mixture of a strong acid (Normality N_{1} , volume V_{1}) and a strong base (Normality N_{2} , volume V_{2})
- (i) is neutral if $N_1 V_1 = N_2 V_2$
- (ii) is basic if $N_2 V_2 > N_1 V_1$ and resultant $[OH^-] = \frac{N_2 V_2 N_1 V_1}{V_1 + V_2}$
- (iii) is acidic if $N_1 V_1 > N_2 V_2$ and resultant $[H_3 O^+] = \frac{N_1 V_1 N_2 V_2}{V_1 + V_2}$

6.3.2 pH of weak acids and weak bases

(a) Considering a weak monobasic acid

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

$$t = 0 \qquad c \qquad 0 \qquad 0$$

$$t = t_{eq} \qquad c(1-\alpha) \qquad c\alpha \quad c\alpha$$

- :. $pH = \frac{1}{2}[pK_a \log c];$ $pH = 14 pOH = 14 \frac{1}{2}[pK_b \log c]$
- (b) Total $[H_3O^+]$ in a mixture of two weak acids can be given as $[H_3O^+] = \sqrt{K_{a_1}c_1 + K_{a_2}c_2}$
 - Total [OH⁻] in a mixture of weak bases can be written as $[OH^-]_T = \sqrt{K_{b_1}C_1 + K_{b_2}C_2}$

6.3.3 Common Ion Effect

If a salt of a weak acid is added to a solution of the acid itself, the dissociation of the acid is diminished. So, 'The suppression of the dissociation of a weak acid or a weak base on the addition of its own ions is called common ion effect.'

E.g., dissociation of acetic acid CH₃COOH
$$\Rightarrow$$
 CH₃COO⁻ + H⁺ \Rightarrow K_a = $\frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

The equilibrium constant K_a has a definite value at a given temperature. If another electrolyte containing CH_3COO^- or H^+ ions can be added to the given solution, it will increase the [CH₃COO] and [H⁺] ions, and in order to K_a remain a constant, the [CH₃COOH] must increase, so that equilibrium will shift to the left side.

6.4 BUFFER SOLUTIONS

Buffers are the solution which resists the change in their pH on addition of a small amount of a strong acid or a strong base.

In order for a solution to act as a buffer it must have two compounds, one of which is able to neutralize acids, and the other bases. Common buffer solution are mixtures containing a



- (i) weak acid and its conjugate base (one of its salts), i.e., acidic buffer
- (ii) weak base and its conjugate acid (one of its salts), i.e., basic buffer

(iii) salt buffer

6.4.1 Buffer of a Weak acid and its Salt with a Strong Base

It is possible to prepare a buffer solution by the addition of a weak acid and a salt of the acid. We shall explain the buffer action by the following example, $CH_3COOH + CH_3COONa$

Applying law of mass action to the dissociation equilibrium of CH₃COOH

$$CH_{3}COOH \Rightarrow CH_{3}COO^{-} + H^{+}$$

$$K_{a} = \frac{[CH_{3}COO^{-}][H^{+}]}{[CH_{3}COOH]}$$

$$\Rightarrow [H^+] = \frac{K_a[CH_3COO^-]}{[CH_3COO^-]}; \text{ where } [CH_3COO^-] = [Salt] = \text{Initial concentration of the salt}$$

 $[CH_{3}COOH] = [acid] = Initial concentration of acid; taking log of both sides and multiplying by -ve sign we get.$

$$\Rightarrow pH = pK_a + log \frac{[Salt]}{[Acid]}$$

This equation is known as Hendersen' equation.

6.4.2 Buffer of a Weak base and its Salt with a Strong Acid

It consists of a weak base and its salt with strong acid, e.g., $NH_4OH + NH_4Cl$, and applying law of mass action to the dissociation equilibrium of NH_4OH .

 $NH_4OH \Rightarrow NH_4^+ + OH^-$

$$\Rightarrow K_{b} = \frac{[NH_{4}^{+}][OH^{-}]}{[NH_{4}OH]};$$

Hence,
$$[OH^{-}] = \frac{K_b [NH_4OH]}{[NH_4^{+}]}$$
; where $[NH_4^{+}] = [salt] = Initial concentration of the salt$

 $[NH_4OH] = [base] = Initial concentration of base$

$$\Rightarrow pOH = pK_b + log \frac{[Salt]}{[Base]}.$$

(a) **Buffer Capacity:** The capacity of a solution to resist alteration in its pH is known as its buffer capacity.

Buffer capacity of a solution is defined as the change in the concentration of a buffer acid (or base) required for changing its pH value by one unit keeping total concentration of acid + salt or base + salt constant.

Considering an acidic buffer solution with concentration of acid and the concentration of salts $pH = pKa + log_{10}S/a$. To this buffer solution, if small amount of a strong base Δb is added then the

new pH becomes $pH_2 = pK_a + log\left(\frac{S + \Delta b}{a - \Delta b}\right)$, change in pH of the solution.

$$\Delta pH = pH_2 - pH_1 = \log \frac{S + \Delta b}{a - \Delta b} - \log \frac{S}{a}$$

$$= \log_{10} \left(\frac{(S + \Delta b)a}{(a - \Delta b)S} \right) = \log_{10} \left(\frac{1 + \Delta b/S}{(a1 - \Delta b/a)} \right) = \frac{1}{2.303} \ln \left(\frac{1 + \Delta b/S}{1 - \Delta b/a} \right)$$

$$\therefore \quad \frac{\Delta b}{S} <<1 \text{ and } --<<$$

$$\Rightarrow \quad \Delta pH = \frac{1}{2.303} \left(\frac{\Delta b}{S} + \frac{\Delta b}{a} \right) \Rightarrow \quad \Delta pH = \frac{\Delta b}{2.303} \left(\frac{a + S}{a \times S} \right) \Rightarrow \quad \frac{\Delta b}{\Delta pH} = 2.303 \times \left(\frac{a \times S}{a + S} \right)$$

- (b) Buffer Range: The range of pH over which a buffer is most effective is termed as the buffer range.
 - (i) An acidic buffer will be effective with the pH range $(pK_a 1)$ to $(pK_a + 1)$, i.e., $(pK_a \pm 1)$.
 - (ii) A basic buffer will be effective over the pH range ($pK_w pK_b \pm 1$).

Note:

=

To make a buffer solution of a given pH, first it is necessary to choose a weak acid or weak base whose pK_a or pK_b value is as close as possible to the required pH.

6.4.2.1 Salient features of buffer solutions

- (i) It has definite pH, i.e., it has reserve acidity or alkalinity.
- (ii) Its pH does not change on standing for long.
- (iii) Its pH does not change on dilution.
- (iv) Its pH is slightly changed by the addition of small amount of acid or base.
- (v) More efficient buffers are those which have pH between 3 and 11.
- (vi) No strong acid or base should remain till the end after their addition in a buffer solution.

6.4.2.2 Uses of buffer solution

- (a) Qualitative analysis of a mixture, e.g., removal of phosphate.
- (b) Industrial process such as manufacture of paper, dyes, inks, paints, drug, etc.
- (c) Digestion of food.
- (d) Preservation of foods and fruits.
- (e) Agriculture and dairy products preservations.

Blood as a Buffer Solution: The normal pH value of blood plasma is 7.4. Severe illness or death can result from sustained variations of a few tenths of a pH unit. Dissolved ratio of HCO_3^- to H_2CO_3 is helpful in controlling pH of blood.

6.5 VOLUMETRIC TITRATIONS

6.5.1 Indicators

An indicator is a substance which is used to determine the end point of a reaction or a substance which indicates the completion of a reaction.

The nature of an indicator depends upon the nature of a titrant used. There are many types of indicators known.

- (i) Acid-base indicaors, e.g., phenolphthalein, methyl orange, etc.
- (ii) Redox indicators, e.g., $KMnO_4$, $K_2Cr_2O_7$, etc.
- (iii) Adsorption indicators, e.g., Starch paper with I₂.

Acid-Base Indicators: An acid-base indicator is a substance which possesses one colour in acid solution and different colour in alkaline medium or the substances whose colour changes with change in pH.

6.5.2 Theory of Indicators

Ostwald Theory: According to this theory

- (i) Indicators are either weak acids or weak bases.
- (ii) Their unionized molecules posses different colour from those of the ions which they give in the solution.
- (iii) An acidic indicator yields a coloured anion while a basic indicator gives coloured cation in solution.
- (iv) Since they are weak electrolytes, they are not sufficiently ionized in solution. But in presence of strong acid or base, their degree of ionization is considerably high and they produce a large number of coloured ions.
- (v) An indicator changes colour when the concentration of [H⁺] in solution is equal to dissocaition constant of the indicator, i.e., indicator is 50 per cent dissociated.

$$pH = pKIn + \log_{10} \frac{[In^{-}]}{[HIn]}$$

For a person to observe both colour of a solution, minimum change in pH must be equal to 2 units.

Range of Indicators: It is the range of pH in or which indicator does not work.

Lower and higher values of pH between which exact colour of indicator cannot be seen are known as range of indicator. Range of indicator is from $pK_{ln} - 1$ to $pK_{ln} + 1$.

6.6 SALT HYDROLYSIS

The phenomenon of the interaction of anions and cations of the salt with H^+ and OH^- ions furnished by water yielding acidic or alkaline (or sometimes even neutral) solutions is known as salt hydrolysis.

Salt are strong electrolytes, here when dissolved in water, they dissociate almost completely into cations and anions.

In salt hydrolysis, cation or anion or both of a salt react with water to produce acidity or alkalinity. The process of hydrolysis is actually the reverse of neutralization.

Salt + Water \Rightarrow Acid + Base

Note:

- Only that component of a salt can participate in hydrolysis which is derived from a weak electrolyte.
- □ The nature of a solution depends upon the component of a salt which is derived from a strong electrolyte.
- Depending on the nature of an acid or a base there can be four types of salts.

6.6.1 Salt of a Strong Acid and a Weak Base

The cation of a salt which comes from a weak base take part in hydrolysis.

e.g., $NH_4^+ + H_2O \Rightarrow NH_4OH + H^+$ Initially c 0 0 Finally c(1-h) ch ch \Rightarrow pH = 7 - 1/2 pK_b - 1/2 log c.

6.6.2 Salt of a Weak Acid and a Strong Base

The anion of a salt which comes from a weak acid takes part in hydrolysis, e.g., CH₃COONa

 $\begin{array}{ll} \mathrm{CH}_{3}\mathrm{COO}^{-} + \mathrm{H}_{2}\mathrm{O} \rightleftharpoons \mathrm{CH}_{3}\mathrm{COOH} + \mathrm{OH}^{-}\\ \mathrm{Initially} & \mathrm{c} & 0 & 0\\ \mathrm{Finally} & \mathrm{c}(1\mathrm{-h}) & \mathrm{ch} & \mathrm{ch}\\ \Rightarrow & \mathrm{pH} = \mathrm{pK}_{w} - \mathrm{pOH} = 7 + 1/2 \ \mathrm{pK}_{a} + 1/2 \ \mathrm{log} \ \mathrm{c} \end{array}$

6.6.3 Salt of a Weak Acid and Weak Base

Both the anion and cation of a salt take part in hydrolysis

e.g., $CH_3COO^- + H_2O \Rightarrow CH_3COOH + OH^ NH_4^+ + H_2O \Rightarrow NH_4OH + H^+$ Combined these two, we get $CH_3COO^- + NH_4^+ + H_2O \Rightarrow CH_3COOH + NH_4OH$ Initially c c 0 0 Finally c(1-h) c(1-h) ch ch $\Rightarrow pH = 7 + 1/2pK_a - 1/2 pK_b$

6.6.4 Salt of a strong acid and a strong base

Salt of a strong acid and a strong base do not undergo hydrolysis because both the ions are not reactive.

Note:

Degree of hydrolysis always increases with increase in temperature because at elevated temperature, increase in K_w is greater as compared to K_a and K_a .

6.7 SOLUBILITY AND SOLUBILITY PRODUCT

6.7.1 Solubility Product

The solubility product of a sparingly soluble salt forming a saturated solution in water is given by the product of the concentrations of the ions raised to a power equal to the number of times of ions occur in the equation representing the dissocaition of the electrolyte. Considering a sparingly soluble salt, $A_m B_n \Rightarrow mA^{n+} + nB^{m-}$ $K_{sp} = [A^{n+}]^m [B^{m-}]^n$ If molar solubility of this salt is S moles/litre, then $K_{sp} = (ms)^m (ns)^n$ $K_{sp} = (m^m n^n) s^{n+m}$.

6.7.2 Applications of Solubility Product Principle

- (a) **Predicting Precipitation Reaction:** A substance gets precipitated when the ionic product, i.e., the product of concentration of its ions present in a solution exceeds the solubility product of the substance. When
 - (i) Ionic product (IP) > K_{sp} ; Precipitation takes till IP equals K_{sp} .
 - (ii) Ionic product (IP) $< K_{sp}$; A precipitate will not be formed and the solution will be unsaturated.
 - (iii) Ionic product (IP) = K_{m}^{T} ; A precipitate will not form and the solution is saturated in that salt.
- (b) **Preferential Precipitation of an Insoluble Salt:** It can be explained on the basis of their respective solubility product. 'As a rule, the compound with the lower solubility product get precipitated in preference'.

Since K_{sp} of Agl < K_{sp} of AgCl

- : Agl gets precipitated in preference to AgCl.
- (c) Salting out of Soap: The saturated solution of soap (RCOONa), the sodium salt of higher fatty acids show precipitation of soap on addition of NaCl. This is because of the fact that an increase in Na⁺ concentration helps in crossing over ionic product to their K_{sp} value.

 $C_{17}H_{35}COONa(s) \approx C_{17}H_{35}COO^{-}(aq) + Na^{+}(aq)$ $K_{sn} = [C_{17}H_{35}COO^{-}] [Na^{+}].$

When NaCl is added, [Na⁺] increases due to which ionic product also increasess which results in precipitation of soap:

(d) Cationic analysis: Cation analysis is based on the principle of K_{sp} and common ion effect. The decrease in the ionization (solubility) of a weak electrolyte in the presence of a common ion from a strong electrolyte is called common ion effect, e.g., ionization of H₂S (weak acid) decreases in presence of HCl (H⁺ is the common ion).

Group I: Cations (Ag⁺, Hg₂⁺, Pb²⁺) are precipitated as chlorides since their K_{sp} values are low.

Group II: Cations (Pb^{2+} , Cu^{2+} , Cd^{2+} , Hg^{2+} , Bi^{3+} , Sb^{3+}) are precipitated as their sulphides since their IP values are decreased due to low [s^{2-}] because of common ion effect.

Group III: Cations (Al³⁺, Fe³⁺, Cr³⁺) are precipitated as their hydroxides, since their IP values are decreased by the addition of NH_4Cl to NH_4OH .

Group IV: Cations $(Zn^{2+}, Mn^{2+}, Ni^{2+})$ are precipitated as their sulphides, since their IP values are decreased due to increased [S²⁻] because of common ion effect.

- (i) CH₃COONa, NaCN, Na₂CO₃, Na₃PO₄, etc.
- (ii) NH_4Cl , $CuSO_4$, $Al(NO_3)_3$, NH_4NO_3 , etc.
- (iii) CH_3COONH_4 , $Mg(CN)_2$, $CaCO_3$, $(NH_4)_3PO_4$, etc.