Notes
Topic – IONIC EQUILIBRIA

- **Ionic equilibria**:-
  The equilibrium between ions and unionized molecules in the solutions is called as **ionic Equilibria.**

$$\text{Unionized molecule} \rightleftharpoons \text{Ions}$$

Ionic equilibria

Substance/Electrolyte

Strong Electrolyte

The electrolytes which ionizes completely in aqueous solution are called as strong electrolytes.

Ex: - Strong Acid, Strong Base

Weak Electrolyte

The electrolytes which do not ionizes or dissociates completely in aqueous solution are called as weak electrolytes.

Ex: - Weak Acid, weak Base

❖ Degree of dissociation (α):-

The ratio of number of moles dissociated to the total number of moles is called as <u>degree of dissociation (α)</u>.

$$\alpha = \frac{\textit{number of moles dissociated}}{\textit{Total number of moles of electrolyte}}$$

❖ Percentage Dissociation (% α)

$$\boxed{\alpha\% = \alpha x 100}$$

❖ For solving, numerical, generally we use 'α' for calculations, and not % α

❖ Various theory for Acids and Bases

- Arrhenius Theory
- Bronsted Lowry Theory
- Lewis theory

❖ Arrhenius theory :-

Acid- Substance which gives H^+ ions in aqueous solution.

Ex:- $HCL \xrightarrow{\text{Water}} H^+ + Cl^-$

Base- Substance which gives OH^- ions in aqueous solution.

Ex:-$NaOH \xrightarrow{\text{water}} Na^+ + OH^-$

❖ Bronsted- Lowry theory:-

Acid- Substance which donate H^+ ion to other substance.

Base – Substance which accept H^+ ion from other substance.

$$\underset{\substack{\textbf{Acid}\\ \text{donates}\\ H^+\ \text{Ion}}}{HCl} + \underset{\substack{\textbf{Base}\\ \text{accepts}\\ H^+\ \text{ion}}}{NH_3} \rightleftharpoons \underset{\substack{\uparrow\\ \text{conjugate}\\ \text{Base}}}{Cl^-} + \underset{\substack{\uparrow\\ \text{conjugate}\\ \text{Acid}}}{NH_4^{(+)}}$$

Ex- $HCl + NH_3 \rightleftharpoons Cl^- + NH_4^{(+)}$

<u>Conjugate Base :-</u> The base which is produced, when acid donates H^+ ion is called as Conjugated base.

<u>Conjugate Acid</u>

The acid which is produced, when base accept H^+ ion is called as Conjugated Acid.

$$\boxed{\textbf{Acid}} \xrightarrow{-H^+} \boxed{\text{Conjugated Base}}$$

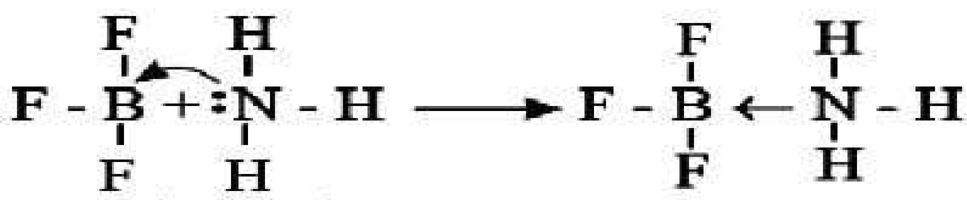
$$\boxed{\textbf{Base}} \xrightarrow{+H^+} \boxed{\text{Conjugated Acid}}$$

- <u>Lewis theory</u>

  Acid: - The species which accept shared electron pair.

  Base: - The species which donate shared electron pair.

  ex:



(acid) (base)

- <u>Amphoteric Nature</u>
  The nature in which, the substance shows both acidic as well as basic behavior is called as amphoteric nature.

- <u>Dissociation of strong acid and strong base and weak acid and base weak Base</u>
  Strong Acid or Strong Base $\longrightarrow$
  (Represented By single Arrow)

Weak Acid or Weak Base $\rightleftharpoons$
(Represented By double Arrow)

- Examples

Strong Acid	Strong Base	Weak Acid	Weak Base
$HCl, HNO_3, H_2SO_4, HBr, HI$	$NaOH, KOH$	$HF, HCOOH, CH_3COOH, H_2S$	$Fe(OH)_3, Cu(OH)_2$

- $\text{Constant} = \frac{[\text{Product}]}{[\text{Reactant}]}$

- $\underline{A + B} \longrightarrow \underline{C + D}$ $\longrightarrow$ Normal Reactions
- $\underline{A + B} \rightleftharpoons \underline{C + D}$ $\longrightarrow$ Dissociation Reactions

Reactants Products

Dissociation of

Weak Acid

$HA \rightleftharpoons H^+ + A^-$

$K_a = \frac{(H+)(A-)}{(HA)}$

K_a = Dissociation constant of acid

Weak Base

$BOH \rightleftharpoons B^+ + OH^-$

$K_b = \frac{(B+)(OH-)}{(BOH)}$

K_b = Dissociation Constant of Base

Ostwald's dilution Law

For weak Acid

	$HA \rightleftharpoons$	H^+ +	A^-
Initial amount	1	0	0
Amount of equilib^m	1-α	α	α
Conc	$\frac{1-\alpha}{v}$	$\frac{\alpha}{v}$	$\frac{\alpha}{v}$

$K_a = \frac{[H+][A-]}{[HA]}$

$$= \frac{(\frac{\alpha}{V})(\frac{\alpha}{V})}{(\frac{1-\alpha}{V})}$$

$= \frac{\alpha 2}{(1-\alpha)v}$ for dilute solution

$= \frac{\alpha}{v(1)}$ [1-α≅] and also

$\boxed{K_a = \alpha^2 c}$ $\frac{1}{v} = c$

For weak Base

	$BOH \rightleftharpoons$	B^+	OH^-
Initial amount	1	0	0
Amount at equilib^m	1-α	α	α
Concentration	$\frac{1-\alpha}{v}$	$\frac{\alpha}{v}$	$\frac{\alpha}{v}$

$K_a = \frac{[OH-][B+]}{[BOH]}$

$= (\frac{\propto}{V})(\frac{\propto}{V}) / \frac{1-\propto}{V}$

$= \frac{\propto 2}{(1-\propto)V}$

$= \frac{\propto 2}{1xv}$ for dilute sol^n (1-∝≅ 1)

$\boxed{K_b = \propto^2 C}$ $\frac{1}{V} = c$

or

$$\boxed{\alpha = \sqrt{\frac{ka}{c}}}$$

$$\boxed{\alpha = \sqrt{kaXV}}$$

$$\boxed{\propto = \sqrt{\frac{Kb}{C}}}$$

$$\boxed{\propto = \sqrt{Kbxv}}$$

Autoionization of water

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

Equilibrium constant = Keq = $\frac{[Product]}{[Reactant]}$ = $[H_3O^+][OH^-] / [H2O]^2$

So $[H_3O^+]\ [OH^-] = keq \times [H_2O]^2$ ………….. $[H_2O]^2 = K'' = \text{constant}$

$[H_3O^+]\ [OH^+] = Keq \times K''$

$$\boxed{[H_3O^+]\ [OH^-] = K_w}$$

Or $\boxed{K_w = [H^+]\ [OH^-]}$

$$\boxed{\text{Ionic product of water} = K_w = [H^+]\ [OH^-] = 1\times10^{-14}}$$

Some important Formula

1. $P^H = -\log_{10}[H^+]$
2. $P^{OH} = -\log_{10}[OH^-]$
3. $K_w = [H^+]\ [OH^-] = [H_3O^+]\ [OH] = 1\times10^{-14}$
4. $P^H + P^{OH} = 14$ (P^H scale)

Types of solution

Acidic Solution

$P^H < 7$

$[H^+] > 10^{-10}$

Neutral or alkaline solution

$P^H = 7$

$[H^+] = [OH^-] = 10^{-7}$

Basic solution

$P^H > 7$

$[H^+] < 10^{-7}$

SA= strong acid
SB= Strong base
WA= Weak acid
WB= weak base

Types of salt

$SA + SB \longrightarrow salt + H_2O$

$HCl + NaOH \longrightarrow NaCl + H_2O$

$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + H_2O$

$HNO_3 + NaOH \longrightarrow NaNO_3 + H_2O$

$HCl + KOH \longrightarrow KCl + H_2O$

$HNO_3 + KOH \longrightarrow KNO_3 + H_2O$

$WA + SB \longrightarrow salt + H_2O$

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

$HCN + KOH \longrightarrow KCN + H_2O$

$H_2CO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O$

$SA + WB \longrightarrow Salt + H_2O$

$HCL + NH_4OH \longrightarrow NH_4Cl + H_2O$

$H_2SO_4 + Cu(OH)_2 \longrightarrow CuSO_4 + H_2O$

$HNO_3 + NH_4OH \longrightarrow NH_4NO_3 + H_2O$

$2HCl + Cu(OH)_2 \longrightarrow CuCl_2 + H_2O$

$WA + WB \longrightarrow Salt + H_2O$

$CH_3COOH + NH_4OH \longrightarrow CH_3COOH + H_2O$

$HCN + NH_4OH \longrightarrow NH_4CN + H_2O$

- Hydrolysis Concept

Hydrolysis of salt

The reactions in which or anions or both ion of salt react with ions of water is called as <u>Hydrolysis of salt.</u>

- <u>Hydrolysis of salt of</u>

Strong acid and strong base

$HCl + NaOH \rightarrow NaCl + H_2O$

Strong Acid And Weak Base

$H_2SO_4 + Cu(OH)_2 \rightarrow CuSO_4 + H_2O$

Weak acid and strong Base

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

Weak acid and weak Base

$K_a > K_b$

$HF + NH_4OH \rightarrow NH_4F + H_2O$

$K_a < K_b$

$HCN + NH_4OH \rightarrow NH_4CN + H_2O$

$K_a = K_b$

$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4$

Steps involved while doing hydrolysis of any salt

$$\text{Acid} + \text{Base} \longrightarrow \text{Salt} + H_2O$$

$$\text{Salt} \longrightarrow \text{Cation} + \text{Anion}$$

$$(C^+)\ \text{Cation} + \underset{H^+ \quad OH^-}{H_2O} \longrightarrow \underset{\text{Base}}{C(OH)} + H^+ \text{ or } H_3O^+$$

$$A^-(\text{Anion}) + \underset{H^+ \quad OH^-}{H_2O} \longrightarrow \underset{\text{Acid}}{AH} + OH^-$$

Some important tips →

(11)

1] acid → anion मिलता है + H^+

2) Base → cation मिलता है + OH^-

3) जो भी strong है, उससे बनने वाला ion का कभी भी hydrolysis मत करो।

4) जो भी weak है, उससे बनने वाला ion का ही hydrolysis कराओ।

5) ex In case of SA + SB → दोनों है strong, तो cation and anion का Hydrolysis नहीं होगा।

ex In case of SA + WB → Base है weak, तो cation का hydrolysis होगा।

ex In case of WA + SB → acid है weak, तो, anion का hydrolysis करो।

ex In case of WA + WB → दोनों के दोनों है weak, तो cation और anion दोनों का hydrolysis करो।

I) Hydrolysis of salt of strong acid and strong base

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

SA SB Salt

$$NaCl \longrightarrow Na^+ + Cl^-$$

Here cation and anion formed are from strong acid and strong base, so they do not undergoes hydrolysis so $[H_3O^+]=[OH^-]$

and nature of solution is neutral.

II) Hydrolysis of salt of strong acid and weak base

$$H_2SO_4 + Cu(OH)_2 \longrightarrow Cu(SO_4)_2 + H_2O$$

SA WB salt

$$Cu(SO_4)_2 \longrightarrow Cu^{+2} + 2\ SO_4^{2-}$$

Cu^{+2} (cation) is from $Cu(OH)_2$

$Cu(OH)_2$ is a weak base, so Cu^{+2} undergoes hydrolysis

$$Cu^{+2} + H_2O \rightleftharpoons Cu(OH)_2 + H_3O^+ \text{ or } H^+$$

As the acid is strong, so nature of solution is acidic

So $[H_3O^+]>[OH^-]$

III) Hydrolysis of salt of weak acid and strong base

$$\underset{\text{Weak acid}}{CH_3COOH} + \underset{\text{Strong Base}}{NaOH} \longrightarrow \underset{\text{Salt}}{CH_3COONa} + \underset{\text{Water}}{H_2O}$$

$$CH_3COONa \longrightarrow \underset{\text{Anion}}{CH_3COO^{(-)}} + \underset{\text{cation}}{Na^{(+)}}$$

As $CH_3COO^{(-)}$ anion comes from acid (CH_3COOH)

As CH_3COOH is a weak acid, so CH_3COO^- ion undergoes hydrolysis

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

In the solution base is strong, so the nature of solution is basic

IV) Hydrolysis of salt of weak acid and weak base

In case of weak acid and weak base, the cation and anion both undergoes hydrolysis as both acid and bases are weak

3 cases

$K_a > K_b$ | $K_b > K_a$ | $K_a = K_b$

K_a = dissociation = constant for acid

K_b = Dissociation = constant for base

Hydrolysis of weak acid and weak base

→ $K_b = K_a$

$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O$

Acid Base Salt

$CH_3COONH_4 \rightleftharpoons CH_3COO^- + NH_4^+$

Anion Cation

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H_3O^+$

CH_3COO^- and NH_4^+ ion hydrolysis to same extent, So H_3O^+ and OH^- are equally formed , So solution is neutral and so $K_b = K_a$

→ $K_b > K_a$

$HCN + NH_4OH \rightarrow NH_4CN + H_2O$

Acid Base Salt

$NH_4CN \rightleftharpoons NH_4^+ + CN^-$

Cation anion

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H_3O^+$

$CN^- + H_2O \rightleftharpoons HCN + OH^-$

CN^- hydrolysis to higher extent than NH_4^+, So more OH^- is formed , So solution is basic in nature, So $K_b > K_a$

→ $K_a > K_b$

$HF + NH_4OH \rightarrow NH_4F + H_2O$

Acid Base salt

$NH_4F \rightleftharpoons NH_4^+ + F^-$

cation anion

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H_3O^+$

$F^- + H_2O \rightleftharpoons HF + OH^-$

NH_4^+ hydrolysis F^- higher than , So more H_3O^+ is formed , So solution is acidic in nature , So $K_a > K_b$

- Buffer
  The solution which do not change its P^H, when small amount of strong acid or strong base is added to it, is called as buffer solution.

Types of Buffer solution

Acidic buffer solution

A solution which contains

$\boxed{\text{Weak acid + salt of weak acid and strong base}}$

is called as acidic buffer solution

$$p^H = p^{Ka} + \log_{10}\frac{[salt]}{[acid]}$$

$$p^{Ka} = -\log_{10}K_a$$

Basic buffer solution

A solution which contains

$\boxed{\text{Weak base + salt of weak base and strong acid}}$

is called as basic buffer solution

$$p^{OH} = p^{Kb} + \log_{10}\frac{[salt]}{[Base]}$$

$$p^{Kb} = -\log_{10}K_b$$

Properties of Buffer

p^H do not change

- By addition of strong acid or strong base
- By addition of H_2O(dilution)
- By keeping it for long time

Application of buffer

- In biochemical system
- Agriculture
- Industry
- Medicine
- Analytical chemistry

- **Solubility equlibria:-**
  The equilibria that exist between the undissolved solid and dissolved ions in solution is called as solubility equilibria.

$$\boxed{\text{Undissolved solid} \rightleftharpoons \text{dissolved ions}}$$

- **Sparingly soluble compounds**
  The compound that dissolve slightly in water, is called as sparingly soluble compound

- **Solubility product**
  The product of concentration of ions in a saturated solution is called as solubility product (Ksp).
  Ksp for AgCl = $[Ag^{+}][Cl^{-}]$

$AxBy \rightleftharpoons xA^{y+} + YB^{x-}$

Ex: $BaSO_4 \rightleftharpoons 1Ba^{+2} + 1SO_4^{2-}$.......Ksp= $[Ba^{+2}][SO_4^{2-}]$

Ex: $CaF_2 \rightleftharpoons 1Ca^{+2} + 2F^{1-}$ ...... Ksp= $[Ca^{+2}][F^{1-}]^2$

Ex: $Bi_2S_3 \rightleftharpoons 2Bi^{+3} + 3S^{2-}$..........Ksp= $[Bi^{+3}]^2[S^{2-}]^3$

- **Solubility:-**
  The ratio of amount of solute in grams per unit volume of solution is called as solubility.
  Unit of solubility = $\frac{gram}{litre}$

- **Molar solubility:-**
  The ratio of solubility in g/L per unit molar mass is called as molar solubility
  Unit of molar solubility is $\frac{mol}{litre}$

- **Imp Relation**

$$\text{Solubility } \left(\frac{g}{l}\right) \underset{\textbf{X (molecular mass)}}{\overset{\textbf{/ (molecular mass)}}{\rightleftarrows}} \text{ molar solubility } \left(\frac{mol}{l}\right)$$

$\boxed{Ksp=X^x.Y^y.S^{x+y}}$

In case of Bx Ay $\rightleftharpoons$ x B^{+y}+ y A^{x-}

So $\boxed{Ksp=[B^{+y}]^x[A^{x-}]^y \cdot S^{x+y}}$

Where S= Solubility

For example

1.For AgBr

$$Ag_1Br_1 \rightleftharpoons 1Ag^{1+} + 1Br^{1-}$$

$$\text{So } Ksp = (1)^1\,(1)^1\,S^{1+1} = \boxed{S^2 = Ksp}$$

2.For Pb I_2

$$Pb\;\; I_2 \rightleftharpoons 1Pb^{+2} + 2I^{1-}$$

$$\text{So } ksp = (1)^1(2)^2\,S^{1+2} = \boxed{4S^3 = Ksp}$$

3.For $Al(OH)_3$

$$Al(OH)_3 \rightleftharpoons 1Al^{+3} + 3(OH^{1-})$$

$$\text{So } Ksp = (1)^1\,(3)^3 .\,S^{1+3} = \boxed{27\,S^4 = Ksp}$$

<u>Condition of precipitation</u>

$IP = ksp$	$IP > Ksp$	$IP < Ksp$
↓	↓	↓
Solution is saturated	Solution is supersaturated	Solution is unsaturated
↓	↓	↓
Equilibrium exist	Precipitation occurs	Precipitation do not occurs

- <u>Common ion effect:-</u>
- Let CH_3COOH be the weak acid.
- CH_3COOH be the salt of weak acid and strong base.
- CH_3COOH dissociates very less, as it is weak acid
- CH_3COONa dissociates completely, as it is stronger salt
- As below:-

$CH_3COOH \rightleftharpoons CHCOO^{(-)} + H^{(+)} \longrightarrow$ less $CH_3COO^{(-)}$ ions are formed

$CH_3COONa \longrightarrow CH_3COO^{(-)} + Na^{(+)} \longrightarrow$ more $CH_3COO^{(-)}$ ions are formed

- So in overall, more $CH_3COO^{(-)}$ (acetate ions are formed) to the right side, as a result of which, according to the Le-chateliers principle, the reaction shifts towards the left side.
- Due to these shift of equilibrium to the left side, the dissociation of CH_3COOH is suppressed.
- The common ion in both the above reaction is $CH_3COO^{(-)}$ (acetate ion) and hence the effect generated is termed as **common ion effect.**