

CHEMICAL EQUILIBRIUM



CHEMICAL REACTION:

Symbolic representation of any chemical change in terms of reactants and products is called chemical reaction.

Types of chemical reaction :

(a) On the basis of physical state :

Homogeneous reaction	Heterogeneous reaction		
All reactants and products are in same phase.	Reactants and products are in two or more phases.		
$N_2(g) + 3H_2(g) \Longrightarrow 2NH_3(g)$	$Zn(s) + CO_2(g) \Longrightarrow ZnO(s) + CO(g)$		

(b) On the basis of direction :

	Reversible reaction	Irreversible reaction		
(i)	Chemical reaction in which products can be	Chemical reaction in which products cannot be		
	converted back into reactants.	converted back into reactants.		
	$N_2 + 3H_2 \implies 2NH_3$	$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$		
	$3\text{Fe} + 4\text{H}_2\text{O} \implies \text{Fe}_3\text{O}_4 + 4\text{H}_2$	$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$		
	$H_2 + I_2 \implies 2HI$	$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$		
(ii)	Proceed in forward as well as	Proceed only in one direction (forward direction)		
	backward direction.			

(iii)	Possible in closed container	Generally possible in open container		
(iv)	These attain equilibrium	These do not attain equilibrium.		
(v)	Reactants are never completely	Reactants are nearly completely converted into		
	converted into products	products.		
(vi)	Generally thermal dissociations are held	Generally thermal decompositions are held		
	in closed vessel.	in open vessel.		
	(1) $\operatorname{PCl}_{5(g)} \Longrightarrow \operatorname{PCl}_{3(g)} + \operatorname{Cl}_{2(g)}$	$2\text{KClO}_{3(s)} \longrightarrow 2\text{KCl}_{(s)} + 3\text{O}_{2(g)}$		
	(2) $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$			
(vii)	Neutralisation reaction except strong	Neutralisation reaction of strong acid and		
	acid and strong base.	strong base.		
	$HCl + NH_4OH \implies NH_4Cl + H_2O$	$HCl + NaOH \longrightarrow NaCl + H_2O$		

(c) On the basis of speed:

	Fast reactions	Slow reactions		
(i)	Generally these reactions are ionic reactions.	Generally these reactions are molecular reactions.		
$HCl(Acid) + NaOH(Base) \rightarrow NaCl(Salt)$		$H_2 + I_2 \rightarrow 2HI$		
	$+ H_2O$ (Water)			
(ii)	Rate determination is impossible.	Rate determination is possible.		

(d) On the basis of heat :

	Exothermic reaction	Endothermic reaction		
(i)	Heat is evolved in these type of chemical reactions	Heat is absorbed in these type of		
		chemical reactions.		
	$R \rightarrow P + x \text{ kcal}$	$R \rightarrow P - x \text{ kcal}$		
(ii)	Change in heat energy (with product) $\Delta Q = (+)$ ve	$\Delta Q = (-)$ ve		
(iii)	Change in enthalpy or internal energy $\Delta H = (-)$ ve	$\Delta H = (+) ve$		
	$\Delta H = -\Delta Q$			

Note

- (i) Whenever questioner doesn't ask about direction then we take forward direction only.
- (ii) In a reversible reaction if forward reaction is exothermic then the backward reaction will be endothermic and vice-versa.

CHEMICAL EQUILIBRIUM AND ACTIVE MASS



A. CHEMICAL EQUILIBRIUM :

The most important characteristic property of a reversible reaction is that it always attains a state of chemical equilibrium.

Consider a general reversible reaction in a closed vessel

$$A + B \xrightarrow{R_f} C + D$$

where $R_{f} =$ forward rate of reaction

 R_{h} = backward rate of reaction

Initially rate of forward reaction is maximum and rate of backward reaction is zero, but as the concentration of products increases the rate of backward reaction also starts increasing and rate of forward reaction decreases due to decrease in concentration of reactant.

At a certain stage, rate of forward reaction becomes equal to the rate of backward reaction called equilibrium state.

At equilibrium state :

Rate of forward reaction $(R_{f}) = Rate of backward reaction (R_{b})$



- * The concentrations of the reactants and products do not change with time.
- * At this stage, number of moles of substances produced per second in the forward reaction is equal to the number of moles of substances which disappear per second in the backward reaction.

Characteristics of equilibrium :

- (a) Chemical equilibrium is dynamic in nature i.e. the reaction although appears to be stopped but actually takes place in both the directions with the same speed.
- (b) Chemical equilibrium can be approached from both sides

2HI \implies H₂ + I₂ or H₂ + I₂ \implies 2HI At equilibrium, each reactant and product has a fixed concentration and this is independent of the fact whether the reaction starts from forward direction or backward direction with the reactant or with the product.

- (c) Equilibrium is not affected by the presence of catalyst. The catalyst only helps in attaining equilibrium rapidly.
- (d) The measurable properties of the system like temperature, concentration, colour, density etc. don't undergo any change with time at the chemical equilibrium conditions.
- (e) Homogeneous equilibrium is the equilibrium in which the reactants and products are in the same phase.

$$CH_{3}COOC_{2}H_{5}(\ell) + H_{2}O(\ell)$$

$$\xrightarrow{H^{+}} CH_{3}COOH(\ell) + C_{2}H_{5}OH(\ell)$$

(f) Heterogeneous equilibrium is the equilibrium in which the reactants and products are in two or more phases.

 $Zn(s) + CO_2(g) \implies ZnO(s) + CO(g)$

B. ACTIVE MASS :

The term active mass means the concentration of the reactants expressed in moles per litre (molar concentration) or the pressure of the reacting gas in atmosphere. In case of gases and solutions, the molar concentration means the number of gram molecules present per litre.

Active mass is usually expressed by enclosing the symbol of the reactant in square bracket [].

Active mass

$$= \frac{\text{Number of gram moles of the substance}}{\text{Volume in litres}}$$
$$= \frac{\text{Weight of substance (in grams)}}{\text{Molecular weight (M_w) \times Volume (in litres)}}$$
$$= \frac{w}{M_w \times V(\text{litre})} = \frac{w \times 1000}{M_w \times V(\text{mL})}$$

79

* The active mass of solids and pure liquids is a constant quantity (unity) because it is an intensive property i.e. number of molecules present per unit volume do not change because density and molecular weight of solids and pure liquids are constant. But it does not apply for gaseous substances because for them number of molecules present per unit volume change with change in volume of vessel.

Molar concentration =
$$\frac{w}{M_w \times V(\text{litre})}$$

= $\frac{\rho}{M_w}$ (where ρ = density in gram/litre)
= $\frac{\rho}{M_w} \times 1000$ (where ρ = density in g/mL)

Active mass = $\frac{\text{density of the substance}}{\text{molecular mass of the substance}}$

Following other names of active mass can also be used :

- (i) mole/litre
- (ii) gram mole/litre
- (iii) gram molecules/litre
- (iv) molarity
- (v) Concentration
- (vi) Effective concentration
- (vii) active quantity
- (viii) n/v
- (ix) C
- (x) M
- (xi) []

Solved Examples

- **Ex.1** In any chemical reaction, equilibrium is supposed to be establish when :
 - (1) Mutual opposite reaction undergo.

(2) concentration of reactants and resulting products are equal.

(3) Velocity of mutual reactions become equal.

(4) The temperature of mutual opposite reactions becomes equal.

Ex.2 8.5 g ammonia is present in a vessel of 0.5 litre capacity then find out the active mass of ammonia?

Sol.
$$[NH_3] = \frac{8.5}{17 \times 0.5} = 1 \text{ mole / litre}$$

Ex.3 Assertion : The active mass of pure solids and pure liquids is taken unity..

Reason: The active mass of pure solids and pure liquids depends on density and molecular mass. The density and molecular mass of pure solids and pure liquids are constant.

Sol. (A)

LAW OF MASS ACTION OR LAW OF CHEMICAL EQUILIBRIUM

The law of mass action was given by Guldberg and Waage (1864). It states that the rate of a chemical reaction is directly proportional to the product of active masses of the reacting substances.

A. Derivation of equilibrium constant :

Consider a reversible homogeneous chemical reaction which has attained equilibrium state at a particular temperature : $A + B \implies C + D$

Let the active masses of A, B, C and D be [A] [B] [C] and [D] respectively at equilibrium.

According to law of mass action :

Rate of forward reaction $(R_{f}) \propto [A][B]$

Rate of backward reaction $(R_{h}) \propto [C] [D]$

 $R_f = k_f[A][B]$ and $R_b = k_b[C][D]$

Where k_{f} and k_{b} are forward and backward rate or velocity constants respectively.

At equilibrium state :

$$\begin{aligned} \mathbf{R}_{\mathrm{f}} &= \mathbf{R}_{\mathrm{b}} \\ \mathbf{k}_{\mathrm{f}}[\mathbf{A}] [\mathbf{B}] &= \mathbf{k}_{\mathrm{b}}[\mathbf{C}] [\mathbf{D}] \\ \frac{\mathbf{k}_{\mathrm{f}}}{\mathbf{k}_{\mathrm{b}}} &= \frac{\left[\mathbf{C}\right] \left[\mathbf{D}\right]}{\left[\mathbf{A}\right] \left[\mathbf{B}\right]} \quad \mathbf{K}_{\mathrm{C}} = \frac{\left[\mathbf{C}\right] \left[\mathbf{D}\right]}{\left[\mathbf{A}\right] \left[\mathbf{B}\right]}; \quad \ddots \quad \mathbf{K}_{\mathrm{C}} = \frac{\mathbf{k}_{\mathrm{f}}}{\mathbf{k}_{\mathrm{b}}} \end{aligned}$$

 K_c is known as equilibrium constant. K_c has a definite value for every chemical reaction at particular temperature.

Sol. (3)

* For a general reaction

$$\begin{split} \mathbf{m}_{1}\mathbf{A} + \mathbf{m}_{2}\mathbf{B} + \mathbf{m}_{3}\mathbf{C} & \longleftrightarrow \quad \mathbf{n}_{1}\mathbf{M} + \mathbf{n}_{2}\mathbf{N} + \mathbf{n}_{3}\mathbf{C} \\ \mathbf{K}_{C} = \frac{\left[\mathbf{M}\right]^{n_{1}}\left[\mathbf{N}\right]^{n_{2}}\left[\mathbf{O}\right]^{n_{3}}}{\left[\mathbf{A}\right]^{m_{1}}\left[\mathbf{B}\right]^{m_{2}}\left[\mathbf{C}\right]^{m_{3}}} \end{split}$$

* The equilibrium constant at a given temperature is the ratio of the rate constants of forward and



B. Relation between K_p and K_c : Consider a reversible homogeneous chemical equilibrium reaction

 $m_1A + m_2B \implies n_1C + n_2D$ According to law of mass action (L.M.A.)

$$K_{C} = \frac{[C]^{n_{1}}[D]^{n_{2}}}{[A]^{m_{1}}[B]^{m_{2}}}$$
 and $K_{P} = \frac{(P_{C})^{n_{1}}(P_{D})^{n_{2}}}{(P_{A})^{m_{1}}(P_{B})^{m_{2}}}$

For an ideal gas

PV=nRT

Where –

P = Pressure in atm

- V=Volume in litres
- n = Number of gaseous moles
- R = Gas constant
 - = 0.082 litre atm/mole/K
- T=Temperature in kelvin

$$P = \frac{n}{V} RT = active mass \times RT$$

 $\frac{n}{V} = \text{molar concentration or active mass}$ $P_{A} = [A]RT, P_{B} = [B]RT,$ $P_{C} = [C]RT, P_{D} = [D]RT$

Put all these values in K_p

So
$$K_{p} = \frac{[C]^{n_{1}} (RT)^{n_{1}} \times [D]^{n_{2}} (RT)^{n_{2}}}{[A]^{m_{1}} (RT)^{m_{1}} \times [B]^{m_{2}} (RT)^{m_{2}}}$$

 $= \frac{[C]^{n_{1}} [D]^{n_{2}}}{[A]^{m_{1}} [B]^{m_{2}}} \times \frac{(RT)^{n_{1}+n_{2}}}{(RT)^{m_{1}+m_{2}}}$
 $K_{p} = K_{C} (RT)^{(n_{1}+n_{2})-(m_{1}+m_{2})}$
 $\Delta n = (n_{1}+n_{2}) - (m_{1}+m_{2})$
 $= \text{total number of moles of gaseous}$
products – total number of moles of gaseous of gaseous reactants

 $K_{P} = K_{C} (RT)^{\Delta n}$

- * The K_C is expressed by the units (mole litre⁻¹)^{Δn} and K_P by (atm)^{Δn}.
- * Three cases may arise :
- (a) When $\Delta n = 0$ $K_p = K_C (RT)^0 = K_C$ For example : (i) $N_2 + O_2 \implies 2NO$ (ii) $H_2 + I_2 \implies 2HI$
- * K_{c} and K_{p} are unit less in this case.
- **(b)** When $\Delta n = +ve$, $K_p > K_C$ For example :
 - (i) $PCl_{5} \implies PCl_{3} + Cl_{2} \begin{pmatrix} K_{C} \rightarrow mole \ litre^{-1} \\ K_{P} \rightarrow atm \end{pmatrix}$ (ii) $2NH_{3} \implies N_{2} + 3H_{2} \begin{pmatrix} K_{C} \rightarrow mole^{2} \ litre^{-2} \\ K_{P} \rightarrow atm^{2} \end{pmatrix}$
- (c) When $\Delta n = -ve$, $K_p < K_C$ for example :

(i)
$$N_2 + 3H_2 \implies 2NH_3 \begin{pmatrix} K_C \rightarrow mole^{-2} litre^2 \\ K_P \rightarrow atm^{-2} \end{pmatrix}$$

(ii) $PCl_3 + Cl_2 \implies PCl_5 \begin{pmatrix} K_C \rightarrow mole^{-1} litre^1 \\ K_P \rightarrow atm^{-1} \end{pmatrix}$

(d) Special point: If $T = \frac{1}{R}$ then $K_P = K_C \left(\mathbb{R} \times \frac{1}{R} \right)^{\Delta n}$ or $K_P = K_C (1)^{\Delta n}$ or $K_P = K_C$ For any value of Δn

- **C.** Possible values of **K** : $K = \frac{[Product]}{[Reactant]}$
 - K = 1 when [Product] = [Reactant]
 - K > 1 when [Product] > [Reactant]
 - K < 1 when [Product] < [Reactant]

D. Application of K:

(a) Stability of reactants and products :

Stability of reactants increases when K decreases Stability of products increases when K increases

Ex : In the following reaction which one oxide is more stable.

$$2XO(g) \implies X_2(g) + O_2(g); \quad K_1 = 1 \times 10^{24}$$
$$2XO_2(g) \implies X_2(g) + 2O_2(g);$$
$$K_2 = 2.5 \times 10^{10}$$
$$\therefore \quad K_1 > K_2 \qquad \text{So the stability of } XO_2 > XO$$

(b) Time taken to attain equilibrium increases when K decreases

E. Factors affecting the equilibrium constant :

(a) The mode of representation of the reaction Consider the reversible chemical equilibrium reaction

$$A + B \rightleftharpoons C + D$$

The equilibrium constant for the reaction

$$\mathbf{K}_{\mathrm{C}} = \frac{\begin{bmatrix} \mathbf{C} \end{bmatrix} \begin{bmatrix} \mathbf{D} \end{bmatrix}}{\begin{bmatrix} \mathbf{A} \end{bmatrix} \begin{bmatrix} \mathbf{B} \end{bmatrix}}$$

If the reaction is reversed

$$C + D \rightleftharpoons A + B$$

The equilibrium constant for the reaction is

$$\mathbf{K}_{\mathbf{C}}^{'} = \frac{[\mathbf{A}][\mathbf{B}]}{[\mathbf{C}][\mathbf{D}]}$$

The equilibrium constant K'_c is actually the reciprocal of K_c

Thus, the two equilibrium constants are related

as
$$\rightarrow K_{\rm C}^{'} = \frac{1}{K_{\rm C}}$$

(b) Stoichiometry of the reaction : When a reversible reaction can be written with the help of two or more stoichiometric equation then the value of equilibrium constant will be numerically different in these cases.

For example the dissociation of NO_2 can be represented as :

(i) If reaction (1) is divided by 2 :

Then the reaction becomes :

$$NO_2 \implies \frac{1}{2}N_2 + O_2$$

$$\mathbf{K}_{\mathrm{C}}^{'} = \frac{\left[\mathbf{N}_{2}\right]^{\frac{1}{2}} \left[\mathbf{O}_{2}\right]}{\left[\mathbf{N}\mathbf{O}_{2}\right]}$$

Thus, the two equilibrium constants are related as

$$K_{\rm C}^{'} = \sqrt{K_{\rm C}}$$

So if reaction is divided by n then

$$K_{C}^{'} = \left(K_{C}\right)^{\frac{1}{n}}$$

(ii) If reaction (1) is multiplied by 2 :

Then the reaction becomes -

$$4NO_2 \implies 2N_2 + 4O_2$$

$$\mathbf{K}_{\mathrm{C}}^{'} = \frac{\left[\mathbf{N}_{2}\right]^{2} \left[\mathbf{O}_{2}\right]^{4}}{\left[\mathbf{N}\mathbf{O}_{2}\right]^{4}}$$

Thus, the two equilibrium constants are related as

$$\mathbf{K}_{\mathrm{C}}^{'} = \left(\mathbf{K}_{\mathrm{C}}\right)^{2}$$

So if reaction is multiplied by n then

$$\mathbf{K}_{\mathrm{C}}^{'} = \left(\mathbf{K}_{\mathrm{C}}\right)^{\mathrm{n}}$$

(c) If a reaction can be expressed as the sum of two or more reactions then overall K_c will be equal to the product of the individual equilibrium constants of the reactions.

Ex.
$$SO_2(g) + \frac{1}{2} O_2(g) \Longrightarrow SO_3(g) \to K_1$$

 $NO_2(g) \Longrightarrow NO(g) + \frac{1}{2} O_2(g) \to K_2$

then

$$SO_{2}(g) + NO_{2}(g) \Longrightarrow SO_{3}(g) + NO(g) \rightarrow K$$

So $K = K_{1} \times K_{2}$

(d) **Temperature** : The value of equilibrium constant changes with the change of temperature. If K_1 and K_2 be the equilibrium constants of a reaction at absolute temperatures T_1 and T_2K and ΔH is the change in enthalpy then :

$$\log K_2 - \log K_1 = \frac{\Delta H}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

(According to vant hoff equation)

If the temperature T_2 is higher than T_1

then $\frac{1}{T_1} - \frac{1}{T_2} > 0$

So
$$\log K_2 - \log K_1 = \frac{\Delta H}{2.303 R}$$

(i) When
$$\Delta H = +ve$$
 (endothermic reaction)
log $K_2 - \log K_1 > 0$

or
$$\log K_2 > \log K_1$$

 $K_2 > K_1$

The value of equilibrium constant increases when temperature increases in case of endothermic reactions.

(ii) When $\Delta H = -ve$ (exothermic reaction)

$$log K_{2} - log K_{1} < 0$$

$$log K_{2} < log K_{1}$$

$$K_{2} < K_{1}$$

The value of equilibrium constant decreases when temperature increases in the case of exothermic reactions. **F.** None affecting factors of the equilibrium constant : The value of equilibrium constant is independent of the following factors :

- (a) Concentration of reactants and products.
- (b) Pressure
- (c) Volume
- (d) The presence of a catalyst.
- (e) Presence of inert materials.

Solved Examples

Ex.4 $\operatorname{XeF}_6 + \operatorname{H}_2\operatorname{O} \Longrightarrow \operatorname{XeOF}_4 + 2\operatorname{HF} \operatorname{constant} = \operatorname{K}_1$, $\operatorname{XeO}_4 + \operatorname{XeF}_6 \Longrightarrow \operatorname{XeOF}_4 + \operatorname{XeO}_3\operatorname{F}_2 \operatorname{constant} =$ K_2 . Then equilibrium constant for the following reaction will be- $\operatorname{XeO}_4 + 2\operatorname{HF} \Longrightarrow \operatorname{XeO}_3\operatorname{F}_2 +$ $\operatorname{H}_2\operatorname{O}$ K_1

(1)
$$\frac{K_1}{K_2}$$
 (2) $K_1 + K_2$

(4) $\frac{K_1}{(K_2)^2}$

Ans. (3)

(3) $\frac{K_1}{K_2}$

- **Ex.5** If the value of K_c for $P + Q \implies R + C$ is 10^{-2} and that of k_f is 10^{-1} , the rate constant for the backward reaction will be :
 - (1) 100 times of K_c (2) equal to K_c (3) 1000 times of K_c (4) None of the above

Sol. (3)
$$K_{c} = \frac{k_{f}}{k_{b}}$$

Therefore,
$$k_b = \frac{k_f}{K_c} = \frac{10^{-1}}{10^{-2}} = 10$$

Therefore, $k_b = 10$ and $K_c = 10^{-2}$
Therefore, $k_b = 1000 \times K_c$

Ex.6 *Assertion:* In the presence of catalyst, the value of equilibrium constant K increases.

Reason :- Catalysts increases the rate of forward and backward reaction to same extent.

Ans. (D)

DISSOCIATION

$$\alpha = \frac{x}{a} \times 100$$

Where α = Degree of dissociation in percentage x = Number of dissociates moles a= Given initial number of moles

Solved Examples

Ex.7 40% of PCl₅ is not dissociated at 300°C. The reaction is carried out in a flask of 1 litre capacity. The value of K_c would be :

(1) 3.2	(2) 1.6
$(3)(3.2)^{-1}$	(4) 0.9

Ans. (4)

Ex.8 In the beginning of the reaction, $A \xrightarrow{B+C, 2} B+C, 2$ moles of A are taken, out of which 0.5 moles gets

dissociated. What is the amount of dissociation of A?

(1) 0.5	(2) 1
(3) 0.25	(4) 4.2

Sol. (3)

	$A \rightleftharpoons$	B +	C
Initial mole	2	0	0
		Initia	lly x = 0.5
At equilibrium	2 - x	Х	Х
Moles at equilibrium	12 - 0.5	0.5	0.5
Since, two moles diss	sociated int	o 0.5	
Therefore, one mole v	will dissoci	ated into	0.25

APPLICATIONS OF LAW OF MASS ACTION [RELATION OF DISSOCIATION (X) WITH VOLUME (V) AND PRESSURE (P)]

- A. HOMOGENEOUS GASEOUS REACTIONS OF TYPE-I (Δn=0) : Synthesis of HI :
- (i) The formation of HI from H_2 and I_2 is represented by following reaction

$$\begin{array}{cccc} I & I & 2 \\ H_2(g) + I_2(g) & \Longrightarrow & 2HI(g) \\ \hline \text{Initial moles} & a & b & 0 \\ \hline \text{Moles at equilibrium } (a-x) & (b-x) & 2x \end{array}$$

Let us start with 'a' moles of H_2 and 'b' moles of I_2 in a closed bulb of V volume. If at equilibrium x moles of each of H_2 and I_2 have reacted, then 2x moles of HI will be formed so active masses.

$$[H_2] = \frac{(a-x)}{V} ; [I_2] = \frac{(b-x)}{V} ; [HI] = \frac{2x}{V}$$

Applying law of mass action

$$\begin{split} K_{\rm C} = & \frac{\left[HI \right]^2}{\left[H_2 \right] \left[I_2 \right]} = \frac{\left(\frac{2x}{V} \right)^2}{\left(\frac{a-x}{V} \right) \left(\frac{b-x}{V} \right)} \\ or \quad K_{\rm C} = & \frac{4x^2}{(a-x)(b-x)} \end{split}$$

When a = b = 1, x becomes degree of formation of HI or degree of dissociation of H₂(or I₂).

$$K_{\rm C} = \frac{4x^2}{\left(1-x\right)^2}$$

Letif

$$x \ll 1$$
 then $1-x \sim$

1

So
$$K_c = 4x^2 \implies x = \sqrt{\frac{K_c}{4}}$$
 i.e.
 $\boxed{x \propto V^0}$

At equilibrium the degree of dissociation is independent to the volume.

 (ii) The equilibrium constant K_p can also be calculated considering partial pressures of reactants and products at equilibrium.

Total number of moles at equilibrium = (a-x) + (b - x) + 2x = (a + b)

If total pressure of the system at equilibrium be P then

Partial pressure of $H_2 = \frac{(a - x)}{(a + b)}P$, Partial pressure of $I_2 = \frac{(b - x)}{(a + b)}P$, Partial pressure of $HI = \frac{2x}{(a + b)}P$

$$K_{P} = \frac{\left(P_{HI}\right)^{2}}{\left(P_{H_{2}}\right)\left(P_{I_{2}}\right)} = \frac{\left(\frac{2x}{a+b}\right)P^{2}}{\left(\frac{a-x}{a+b}\right)\left(\frac{b-x}{a+b}\right)P^{2}}$$

or
$$K_{P} = \frac{4x^{2}}{(a-x)(b-x)}$$

Thus $K_p = K_c$ $x \ll 1$ then $1-x \ge 1$ Letif

So
$$K_p = 4x^2 \implies x = \sqrt{\frac{K_p}{4}}$$

i.e. $\mathbf{x} \propto \mathbf{P}^0$

At equilibrium the degree of dissociation is independent to the pressure also.

B. HOMOGENEOUS GASEOUS REACTIONS OF TYPE-II ($\Delta n > 0$)

Dissociation of PCl₅:

The dissociation of PCl₅ takes place according to (i) the equation

а

$$1 \qquad 1 \qquad 1$$
$$PCl_{5} \Longrightarrow PCl_{3} + Cl_{2}$$
$$a \qquad 0 \qquad 0$$

Initial moles

Moles at equilibrium (a-x) Х Х Let a moles of PCl₅ be taken in a closed vessel of volume V. At equilibrium x moles of PCl₅ are dissociated into x moles of each PCl₃ and Cl₂.

$$\left[\operatorname{PCl}_{5}\right] = \frac{\left(a-x\right)}{V}; \quad \left[\operatorname{PCl}_{3}\right] = \frac{x}{V}; \quad \left[\operatorname{Cl}_{2}\right] = \frac{x}{V}$$

Apply law of mass action

$$K_{C} = \frac{\left[PCl_{3}\right]\left[Cl_{2}\right]}{\left[PCl_{5}\right]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right)} = \frac{x^{2}}{(a-x)V}$$

When a = 1, x becomes degree of dissociation *

$$K_{C} = \frac{x^{2}}{(1-x)V}$$

If $x <<<1$ then $1-x \approx$
 $K_{C} \approx \frac{x^{2}}{V} \implies \qquad \boxed{x \propto \sqrt{V}}$

The degree of dissociation of PCl₅ at equilibrium is directly proportional to the square root of the volume.

1

(ii). Expression for K_p :

Let the total pressure at equilibrium be P. Total number of moles at equilibrium

$$= (a - x) + x + x = a + x$$

$$P_{PCl_5} = \left(\frac{a-x}{a+x}\right)P$$
, $P_{PCl_3} = \left(\frac{x}{a+x}\right)P$,

$$P_{Cl_2} = \left(\frac{x}{a+x}\right)P$$

Apply law of mass action

$$K_{P} = \frac{P_{PCl_{3}}.P_{Cl_{2}}}{P_{PCl_{5}}} = \frac{x^{2}P}{(a+x)(a-x)}$$

When a = 1, x becomes degree of dissociation

$$K_{P} = \frac{x^{2}P}{(1+x)(1-x)} = \frac{x^{2}P}{1-x^{2}}$$

If
$$x < < < 1$$
 then $1 - x^2 \approx 1$,

$$K_{\rm p} \approx x^2 P \Rightarrow \ x^2 \propto \frac{1}{P} \qquad \Rightarrow \qquad \boxed{x \propto \frac{1}{\sqrt{P}}}$$

The degree of dissociation of PCl_5 is inversely proportional to the square root of the total pressure at equilibrium.

С. **HOMOGENEOUS GASEOUS REACTIONS** OF TYPE-III ($\Delta n < 0$) Synthesis of Ammonia :

The formation of ammonia from nitrogen and (i) hydrogen is represented by the equation :

0

2x

 $N_2 + 3H_2 \implies 2NH_3$

Initial moles b а Moles at equilibrium (a-x) (b-3x)

Let us start with 'a' moles of N, and 'b' moles of H, in a closed vessel of Volume V. At equilibrium x moles of N₂ has combined with 3x moles of H₂ and produced 2x moles of NH₃.

 $\left[N_{2}\right] = \frac{\left(a - x\right)}{V};$ At equilibrium $[H_2] = \frac{(b-3x)}{V}$; $[NH_3] = \frac{2x}{V}$

$$K_{c} = \frac{\left[NH_{3}\right]^{2}}{\left[N_{2}\right]\left[H_{2}\right]^{3}} = \frac{\left(\frac{2x}{V}\right)^{2}}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^{3}}$$
$$= \frac{4x^{2}V^{2}}{(a-x)(b-3x)^{3}}$$
If $a = 1, b = 3$ then $K_{c} = \frac{4x^{2}V^{2}}{27(1-x)^{4}}$ If $x < < 1$ then $1-x \approx 1 \implies$
 $K_{c} = \frac{4x^{2}V^{2}}{27}$ i.e. $\boxed{x \propto \frac{1}{V}}$

At equilibrium, the degree of dissociation is reciprocal to the volume of vessel.

(ii) Expression for K_p:

Total number of moles at equilibrium

= a - x + b - 3x + 2x = a + b - 2x

If total pressure is P at equilibrium then

$$P_{N_2} = \frac{(a-x)}{(a+b-2x)}P$$
, $P_{H_2} = \frac{(b-3x)}{(a+b-2x)}P$,

Summary

D	_	2x	P
I NH ₃	-	$\overline{(a+b-2x)}$	

According to Law of mass action

$$\begin{split} K_{p} &= \frac{P^{2}{}_{NH_{3}}}{P_{N_{2}}P_{H_{2}}^{3}} = \frac{\left(\frac{2x}{a+b-2x}P\right)^{2}}{\left(\frac{a-x}{a+b-2x}P\right)\left(\frac{b-3x}{a+b-2x}P\right)^{3}}\\ K_{p} &= \frac{4x^{2}\left(a+b-2x\right)^{2}}{\left(a-x\right)\left(b-3x\right)^{3}P^{2}}\\ If a &= 1 , b = 3 \text{ then}\\ K_{p} &= \frac{16x^{2}\left(2-x\right)^{2}}{27\left(1-x\right)^{4}P^{2}}\\ If x &< < 1 \qquad \text{then } 2-x \approx 2 \text{ and } 1-x \approx 1\\ K_{p} &= \frac{64x^{2}}{27P^{2}} \end{split}$$

i.e. $\mathbf{x}^2 \propto \mathbf{P}^2 \implies \mathbf{x} \propto \mathbf{P}$

At equilibrium, the degree of dissociation is directly proportional to the pressure.

	$\Delta n=0$	$\Delta n > 0$ or +ve	$\Delta n < 0 \text{ or } -ve$
Effect	$H_2+I_2 \Longrightarrow 2HI$	$PCl_5 \longrightarrow PCl_3 + Cl_2$	$N_2 + 3H_2 \longrightarrow 2NH_3$
	$x \propto (v)^0 \propto (P)^0$	$\mathbf{x} \propto (\mathbf{v})^{1/2} \propto \left(\frac{1}{P}\right)^{1/2}$	$x \propto \left(\frac{1}{v}\right) \propto (P)$
(i) Pressure increases	x unchanged	x decreases	x increases
(ii) Volume increases	x unchanged	x increases	x decreases
(iii) Mixing of inert gas at			
(a) constant pressure	x unchanged	x increases	x decreases
(b) constant volume	x unchanged	x unchanged	x unchanged

Special point :- If inert gas mixed at constant temperature and constant volume in an equilibrium chemical reaction then total number of moles of gases are present in a container, increases i.e. total pressure of gases increases but concentration in terms of moles/ litre and partial pressure of reacting substances are unchanged so dissociation (x) unchanged.

D. Law of Mass Action as Applied to Heterogeneous Equilibrium :

In such cases the active mass of pure solids and pure liquids is taken as unity and the value of equilibrium constant is determined by the gaseous substances only. (i) The dissociation of $CaCO_3$ in closed vessel.

$CaCO_3(s) \implies CaO(s) + CO_2(g)$; $K_p = p_{CO_2}$

- (ii) $PCl_5(s) \Longrightarrow PCl_3(\ell) + Cl_2(g)$; $K_p = p_{Cl_2}$
- (iii) $2H_2O(\ell) \Longrightarrow 2H_2(g) + O_2(g)$;

 $K_{P} = (p_{H_{2}})^{2} (p_{O_{2}})$

(iv) $3Fe(s) + 4H_2O(g) \implies Fe_3O_4(s) + 4H_2(g)$

$$K_{\rm P} = \frac{\left(p_{H_2}\right)^4}{\left(p_{H_2O}\right)^4}$$

Solved Examples

- **Ex.9** Two semple of HI each of 5 g were taken seperately into vessels of volume 5 litres and 10 litres respectively at 27°C. The extent of dissociation of HI will be :-
 - (1) More in 5 litre vessel
 - (2) More in 10 litre vessel
 - (3) Equal in both vessel
 - (4) Nill in both

Sol. (3)

Ex.10 What will be the amount of dissociation, if the volume is increased 16 times of initial volume in the

reaction
$$PCl_5 \implies PCl_3 + Cl_2$$
?

(1) 4 times (2) $\frac{1}{4}$ times

(3) 2 times (4) $\frac{1}{5}$ times

Sol. (1) $x \propto \sqrt{V} = x \propto \sqrt{16}$ Thus, 4 times.

Ex.11 Assertion: – For the reaction, $N_2 + O_2 \implies 2NO$, increase in pressure at equilibrium has no effect on the reaction.

Reason :- The reaction is not accompanied by any change in number of moles of gaseous species.

Ans. (A)

LE-CHATELIER'S PRINCIPLE

A. PRINCIPLE :

According to this principle, if a system at equilibrium is subjected to a change of concentration, pressure or temperature then the equilibrium is shifted in such a way as to nullify the effect of change.

- (a) Change in concentration: In an equilibrium increasing the concentrations of reactants results in shifting the equilibrium in favour of products while increasing concentrations of the products results in shifting the equilibrium in favour of the reactants.
- (b) Change in pressure : When the pressure on the system is increased, the volume decreases proportionately i.e. the total number of moles present per unit volume increases. According to Le-Chatelier's principle, the equilibrium shifts in that direction in which there is decrease in number of moles.
- * If there is no change in number of moles of gases in a reaction then a pressure change does not affect the equilibrium.
- (c) Change in temperature : If the temperature of the system at equilibrium is increased then reaction will proceed in that direction in which heat can be used. Thus increase in temperature will favour the forward reaction for endothermic reaction.

Similarly, increase in temperature will favour the backward reaction for exothermic reactions.

Special point :- Le-Chatelier's principle is applicable for both chemical and physical equilibrium.

B. PHYSICAL EQUILIBRIUM :

Physical reaction : Those reaction in which change in only and only state of substance takes place without any chemical change is called physical reaction.

Ex:(a) Ice-water system (melting of ice):

Melting of ice is accompained by absorption of heat (endothermic) and decrease in volume

Ice (s) \rightleftharpoons water (ℓ) (H₂O) (H₂O) 1gram (1.09 mL) 1gram (1.01 mL) Hence both increase of temperature and pressure will favour the melting of ice into water.

(b) Water-water vapour system

(Vapourisation of water) :

Vapourisation of water is an endothermic and condensation of vapour into water is an exothermic reaction :

Water (ℓ) \checkmark Vapour (g)(H2O)(H2O)

- * The equilibrium shifts towards right side when the temperature is increased so rise in temperature will increase the vapour.
- * The equilibrium shifts towards left side when the pressure is increased (i.e. volume is decreased) so increase in pressure will favour the rate of condensation of vapour into water.
- * Thus favourable conditions for conversion of water into vapour are high tempeprature and low pressure.

(c) Solubility of gases :

Gas (g) + Water (ℓ)Aqueous solution (ℓ)(Solute)(Solvent)(Solution)

* Effect of pressure → Solubility of gases which dissolve in a solvents increases with a decrease in volume, and with increasing pressure.

Solved Examples

- **Ex.12** On applying pressure to the equilibrium ice \implies water, which phenomenon will happen :
 - (1) More ice will be formed
 - (2) More water will be formed
 - (3) Equilibrium will not be disturbed
 - (4) Water will evaporate

Ans. (2)

Ex.13 Which of the following conditions should be more favourable for increasing the rate of forward reaction

in the equilibrium $H_2 \implies H + H (\Delta H = +ve)$?

- (1) 2000° C temperature and 760 mm pressure.
- (2) 3500° C temperature and 100 cm pressure.
- (3) 3500° C temperature and 1 mm pressure.
- (4) All are wrong.
- **Sol.** In $H_2 \implies H + H$, heat has to be provided to dissociate H_2 into H. Therefore, the reaction is endothermic (ΔH will positive). So, temperature should be high. Since, one mole of H_2 forms two atoms of H, so volume is increasing (Δn is positive) so pressure should be low for increasing the rate of forward reaction.

Ex.14 Assertion:
$$SO_2(g) + \frac{1}{2}O_2(g) \Longrightarrow SO_3(g) + heat$$

Forward reaction is favoured at low temperature and low pressure.

Reason :- Reaction is endothermic.

Ans. (C)

FEW IMPORTANT POINTS

A. Calculation of Degree of dissociation from vapour density :

Ex.
$$PCl_5 \implies PCl_3 + Cl_2$$

$$\alpha = \frac{D_T - D_0}{D_0} \text{ or } \frac{D - d}{d}$$

Where:

 D_T or D = Principle or theoretical vapour density

 D_0 or d = Observed or practical vapour density

 α = Degree of dissociation

Vanour density -	Molecular weight
	2

Equilibrium

Reversible reaction	$PCl_5 =$	\Rightarrow PCl	$_3 + Cl_2$	Total moles	Volume at NTP	Vapour density
Let initial moles	1	0	0	1	V _T =22.4	$D_T \propto \frac{1}{V_T}$
Moles at equilibrium If α is the degree of dissociation	(1–α)	α	α	1+α	$V_0 = 22.4 (1+\alpha)$	$D_0 \propto \frac{1}{V_0}$

$$\frac{D_{T}}{D_{0}} = \frac{V_{0}}{V_{T}} = \frac{22.4(1+\alpha)}{22.4}$$

$$\frac{D_{T}}{D_{0}} = 1 + \alpha \quad \text{or} \qquad \alpha = \frac{D_{T}}{D_{0}} - 1 \quad \text{or} \quad \boxed{\alpha = \frac{D_{T} - D_{0}}{D_{0}}}$$

So for a general reversible reaction $n_1A \rightarrow$

$$\boxed{\alpha = \frac{n_1}{\Delta n} \left(\frac{D_T - D_0}{D_0} \right)}$$

When -

(i)	$\Delta n > 0$	then	$D_T > D_0$
(ii)	$\Delta n = 0$	then	$D_T = D_0$
(iii)	$\Delta n < 0$	then	$D_{T} < D_{O}$

B Reaction Quotient (Q) :

Consider a general homogeneous reversible reaction

 $A + B \rightleftharpoons C + D$

Reaction Quotient (Q) =
$$\begin{bmatrix} C \end{bmatrix} \begin{bmatrix} D \\ A \end{bmatrix}$$
,

(Applied in any condition)

Equilibrium constant
$$K = \frac{\begin{bmatrix} C \end{bmatrix} \begin{bmatrix} D \end{bmatrix}}{\begin{bmatrix} A \end{bmatrix} \begin{bmatrix} B \end{bmatrix}}$$
,

(Applied only in equilibrium state)

- (i) When Q = K then reaction is in equilibrium state.
- (ii) When Q < K then rate of forward reaction increases.
- (iii) When Q > K then rate of backward reaction increases.

Solved Examples

Ex.15 The vapour density of undecomposed N_2O_4 is 46. When heated, vapour density decreases to 24.5 due to its dissociation to NO_2 . The precentage dissociation of N_2O_4 at the final temperature is -

(1) 87	(2) 60
(3) 40	(4) 70

Sol. (1)

 $n_2B + n_3C$

Ex.16 If PCl_5 is 80% dissociated at 250° C then its vapour density at room temperature will be

(1) 56.5	(2) 104.25	
(3) 101.2	(4) 52.7	

Sol. (2) $D_T = \frac{\text{Molecular weight}}{2} = \frac{208.5}{2} = 104.25$

Vapour density at room temperature (D_T) is 104.25, which is fixed.

Ex.17 *Assertion:* For a reaction concentration quotient Q is equal to K when the reaction is in equilibrium.

Reason: If a catalyst is added to the reaction at equilibrium, the value of Q remains no longer equal to K.

Ans. (C)

IONIC EQUILIBRIUM

INTRODUCTION

Formulae:

(i) $\ln x = \log_{e} x = 2.303 \log_{10} x = 2.303 \log x$ (ii) $\log (x \times y) = \log x + \log y$ (iii) $\log \left(\frac{x}{y}\right) = \log x - \log y$ (iv) $\log x^{y} = y \log x$ **Ex.** (i) $\log 6 = \log (2 \times 3)$ $= \log 2 + \log 3$ = 0.3010 + 0.4771 = 0.7781(ii) $\log 30 = \log (3 \times 10)$ $= \log 3 + \log 10$ $= \log 0.4471 + 1 = 1.4471$ (iii) $\log 1000 = \log 10^{3}$ $= 3 \log 10$ $= 3 \times 1 = 3$

A. Some values of Log :

log 1 = 0 log 2 = 0.3010 log 3 = 0.4771 log 4 = 0.6020 log 5 = 0.699 log 6 = 0.7781 log 7 = 0.8451 log 8 = 0.9030log 9 = 0.9542

pH scale at 25°C :

log 10 = 1log 11 = 1.04log 100 = 2log 1000 = 3

Some terms which are used in ionic equilibrium :

Antilog: Antilog(x) = 10^x

Ex. Antilog $(2) = 10^2 = 100$ Antilog $(0.3010) = 10^{0.3010} = 2$ Antilog $[\log(2)] = \text{Antilog}(0.3010) = 2$

pH - Scale : Given by - Sorenson

pH Scale is called Sorenson scale.

pH scale is a measuring scale used to measure strength of acid and base and its value is equal to $-\log[H^+]$

i.e.
$$pH = -\log[H^+] = \log \frac{1}{[H^+]}$$

Ex.
$$[H^+] = 10^{-3}$$

pH = $-\log 10^{-3} = +3 \log 10 = 3$

Conclusion:

If pH = x then $[H^+] = 10^{-x}$ or Vice versa i.e. If $[H^+] = 10^{-x}$ then pH = x $pOH \rightarrow It$ is equal to $-\log [OH^-]$ i.e. $pOH = -\log [OH^-]$



Solved Examples

Ex.18 If
$$X = \frac{a}{b} \times 10^{-c}$$
, then find pX?
Sol. pX = $-\log X = -\log \left(\frac{a}{b} \times 10^{-c}\right)$
 $pX = -\left[\log \frac{a}{b} + \log 10^{-c}\right] = -\left[\log a - \log b - c\right]$
 $pX = c + \log b - \log a$

According to strength, ionic conductors are of two types –

(1) Strong electrolytes – Those ionic conductors which are completely ionized in aqueous solution are called as strong electrolytes.

Ex. Na⁺Cl⁻, K⁺Cl⁻, etc.

For strong electrolyte the value of degree of ionisation is 100% i.e. $\alpha = 1$

Ex.

- (a) Strong acid \rightarrow H₂SO₄, HCl, HNO₃, HClO₄, HBr, HI
- (b) Strong base \rightarrow

٦

(c) All Salts

(2) Weak electrolytes – Those electrolytes which are partially ionized in aqueous solution are called as weak electrolytes. For weak electrolytes the value of α is less than one.

Ex.

(a) Weak acids
$$\rightarrow$$
 HCN, CH₃COOH,
HCOOH, H₂CO₃, H₃PO₃, H₃PO₂, B(OH)₃, etc.

$$H_{3}BO_{3}$$

(boric acid)

NH₄OH, Cu(OH), (b) Weak bases \rightarrow Zn(OH)₂, Fe(OH)₃, Al(OH)₃ etc.

B.ARRHENIUS CONCEPT:

(1) According to Arrhenius when an electrolyte dissolves in aqueous solution it spilts up into two oppositely charged particles i.e. cation and anion.

- (2) In an electrolytic solution (Aqueous solution of electrolyte), total +ve charge = total -ve charge i.e. solution is electrically neutral.
- \Rightarrow In an electrolytic solution number of +ve ions may or may not be equal to the number of negative ions.
- (3) Properties of an electrolytic solution are defind by its ions.

Ex. Blue colour of $CuSO_4$ aqueous solution is due to Cu^{+2} ion (dark blue colour)

- (4) When electric current is pass in aqueous solution of electrolyte then cation shows migration towards cathode where as anion shows migration towards anode.
- (5) Ionization is the reversible reaction. In it an equilibrium is set up between unionized moles and ionized moles. This condition of the reversible ionic reaction is known as ionic equilibrium.

$$AB (Aq.) \rightleftharpoons A^{+}(Aq.) + B^{-}(Aq.)$$

According to L.M.A.

Ionisation constant $K = \frac{\left\lfloor A^+ \right\rfloor \left\lfloor B^- \right\rfloor}{\left\lceil AB \right\rceil}$

Solved Examples

Ex.19 Number of total ion's and resultant total charge in A₂B₃ electrolyte's :-

(1) Five and $+1$	(2) Five and - 1
(3) 0 and 0	(4) None of them

Sol. (4)

Ex.20 If
$$[H^+] = \frac{5}{3} \times 10^{-4}$$
 then find pH ?
Sol. pH = $-\log [H^+] = -\log \left(\frac{5}{3} \times 10^{-4}\right)$
= $-\left[\log \frac{5}{3} + \log 10^{-4}\right] = -\left[\log 5 - \log 3 - 4\right]$
= $-\left[0.699 - 0.4771 - 4\right]$
= $-\left[-3.778\right] = 3.778$

Ex.21 Asserssion : H_2SO_4 is a strong acid.

Reason : H_2SO_4 undergoes almost completely ionised in aqueous solution.

Sol. (A)

OSTWALD'S DILUTION LAW

- \Rightarrow Ostwald was the first to apply law of mass action to ionic equilibrium.
- \Rightarrow Ostwald dilution law is applicable only for weak electrolytes.

Statement : According to Ostwald when solution of weak electrolyte is diluted then degree of ionisation of solution is increased, is called dilution law.

Let

$$AB(Aq.) \Longrightarrow A^{+}(Aq.) + B^{-}(Aq.)$$

C 0 0

0

Initial

concentration

 $K_a = \frac{L}{2}$

K

•.•

 $=\overline{C(1)}$

Degree $(C - C\alpha)$ $(C\alpha)$ $(C\alpha)$ of ionisation (α)

According to L.M.A.

Ionisation constant
$$K = \frac{\begin{bmatrix} A^+ \end{bmatrix} \begin{bmatrix} B^- \end{bmatrix}}{\begin{bmatrix} AB \end{bmatrix}}$$

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

Application of Ostwald's Dilution Law :

 $K = C\alpha^2$

If
$$\alpha \le 1$$
 then $1 - \alpha \ge 1$
 $K = C\alpha^2$ or $\alpha = \sqrt{\frac{K}{C}}$

(K = constant, At constant temperature)

$$\alpha \propto \frac{1}{\sqrt{C}} \qquad (C \propto \frac{1}{V})$$
$$\alpha \propto \sqrt{V}$$

volume = dilution $\alpha \propto \sqrt{dilution}$ by dilution law dilution $\uparrow \alpha \uparrow$

At infinite dilution, $\alpha = 100\%$

Thus for weak electrolytes the degree of ionisation is directly proportional to square root of dilution or inversely proportional to square root of concentration. This law is known as Ostwald Dilution Law.

- Note : *
- (1) At infinite dilution the value of α becomes equal to one.
- (2) The value of concentration should be in terms of normality.

(a) For mono basic weak acid (HA)(b) For mono acidic weak base (BOH)(i). Ionisation constant (K_a)
HA
$$\rightleftharpoons$$
 H⁺ + A⁻Ionisation constant (K_b)Initial concentration C00At equilibrium C - C\alphaCa CaCaIf degree of ionisation is α If degree of ionisation is α If degree of ionisation is α $K_a = \frac{[H^+][A^-]}{[HA]} = \frac{C\alpha \times C\alpha}{C - C\alpha}$ $K_b = \frac{[B^+][OH^-]}{[BOH]} = \frac{C\alpha \times C\alpha}{C - C\alpha}$ $K_a = \frac{C^2 \alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$ $K_b = \frac{C^2 \alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$ \therefore $K_a = C\alpha^2$ \therefore $(1 - \alpha) \approx 1$ \therefore $K_a = C\alpha^2$ Where $K_a \rightarrow$ Ionisation constant of weak base

(ii). [H ⁺] (Concentration of H ⁺)	[OH ⁻] (Concentration of OH ⁻)
$[H^+] = C\alpha$ (1)	$[OH^{-}] = C\alpha$ (1)
$K_a = C\alpha^2$ or $\alpha = \sqrt{\frac{K_a}{C}}$ (2)	$K_b = C\alpha^2$ or $\alpha = \sqrt{\frac{K_b}{C}}$ (2)
from Eq. (1) and (2)	from Eq. (1) and (2)
$[H^+] = C \times \frac{\sqrt{K_a}}{\sqrt{C}}$	$[OH^{-}] = C \times \frac{\sqrt{K_{b}}}{\sqrt{C}}$
$[H^+] = \sqrt{K_a \times C}$	$[OH^{-}] = \sqrt{K_{b} \times C}$
(iii). $pH = -log[H^+]$ put the value of [H ⁺]	pOH = – log [OH ⁻] put the value of [OH ⁻]
$pH = -\log(\sqrt{K_a \times C}) = -\log(K_a \times C)^{\frac{1}{2}}$	$pOH = -\log(\sqrt{K_b \times C}) = -\log(K_b \times C)^{1/2}$
$pH = -\frac{1}{2} \left[\log K_a + \log C \right]$	$pOH = -\frac{1}{2} \left[\log K_{b} + \log C \right]$
$pH = -\frac{1}{2}\log K_a - \frac{1}{2}\log C$	$pOH = -\frac{1}{2}\log K_{b} - \frac{1}{2}\log C$
$pH = \frac{1}{2}pK_a - \frac{1}{2}\log C$	$pOH = \frac{1}{2}pK_{b} - \frac{1}{2}\log C$
In summary :	
1. $K_a = C\alpha^2$	1. $K_b = C\alpha^2$
2. $[H^+] = C\alpha = \sqrt{K_a \times C}$	2. $[OH^{-}] = C\alpha = \sqrt{K_b \times C}$
3. $pH = -\log[H^+]$	3. $pOH = -\log [OH^{-}]$
or $pH = \frac{1}{2}pK_a - \frac{1}{2}\log C$	or $pOH = \frac{1}{2}pK_b - \frac{1}{2}\log C$

Limitation of Ostwald Dilution Law :

- (1) It is not applicable for strong electrolytes.
- (2) It is not applicable for saturated solutions.

Factors affecting the Value of Degree of ionisation :

(1) Temperature \rightarrow On increasing temperature, ionization increases so α increases.

(2) Dilution
$$\rightarrow \alpha \propto \sqrt{\nabla}$$
 so on dilution, α increases.

- (3) Nature of electrolytes
- (i) Strong electrolytes (ii) Weak electrolytes $\alpha = 100\%$ $\alpha < 100\%$
- (4) Nature of solvent

If Dielectric constant μ of solvent increases then the value of α increases.

 $H_2O \rightarrow \mu = 81$ $D_2O \rightarrow \mu = 79$ $C_6H_6 \rightarrow \mu = 2.5$ $CCl_4 \rightarrow \mu = 0$

Solved Examples

Ex.22 For which, dilution law is applicable :

$$(1) \operatorname{NaCl}(\operatorname{SASB}) \qquad (2) \operatorname{HCl}(\operatorname{SA})$$

$$(3) CH_3 COONa(WASB)$$
 (4) None

Sol. (4)

Ex.23 Find out the value of α of 10^{-2} M HCN solution if [H⁺] = 10^{-3} .

Sol.
$$[H^+] = C\alpha$$

$$10^{-3} = 10^{-2}\alpha$$
 or $\alpha = \frac{10^{-3}}{10^{-2}} = 10^{-1}$ or $= 0.1$
 $\alpha \% = 10\%$

Ex.24 For 10^{-3} M HCN solution if α is 10% then find **c.** out K_a and pH of the solution ?

Sol. (i)
$$K_a = C\alpha^2 = 10^{-3} \times \frac{10}{100} \times \frac{10}{100} = 10^{-5}$$

(ii) $pH = \frac{1}{2}pK_a - \frac{1}{2}\log C$
 $(\because K_a = 10^{-5} \therefore pK_a = 5)$

$$pH = \frac{1}{2} \times 5 - \frac{1}{2} \log 10^{-3} = \frac{5}{2} + \frac{3}{2} = \frac{8}{2} = 4$$

Ex.25 For 10 M CH₃COOH solution if $K_a = 10^{-5}$ then find out: (i) α (ii) [H⁺] (iii) pH

Sol. (i) α (Degree of ionisation) :-

$$K_{a} = C\alpha^{2}$$

10⁻⁵ = 10\alpha^{2} or
$$\alpha^{2} = \frac{10^{-5}}{10} = 10^{-6} \text{ or } \alpha = 10^{-3}$$

- (ii) $[H^+] = C\alpha = 10 \times 10^{-3} = 10^{-2}$
- (iii) pH = $-\log [H^+] = -\log 10^{-2} = 2$
- **Ex.26** Find out the pOH of 10^{-3} M NH₄OH solution If $K_{b} = 10^{-5}$

Sol.
$$[OH^{-}] = \sqrt{K_b \times C} = \sqrt{10^{-5} \times 10^{-3}}$$

= $\sqrt{10^{-8}} = 10^{-4}$
pOH = $-\log [OH^{-}] = -\log 10^{-4} = 4 \log 10 = 4$

- **Ex.27** For 10^{-3} M H₂CO₃ if $\alpha = 10\%$ then find out the value of pH ?
- Sol. Normality = M × V.F. = $10^{-3} \times 2 = 2 \times 10^{-3}$ [H⁺] = C $\alpha = 2 \times 10^{-3} \times 0.1 = 2 \times 10^{-4}$ pH = $-\log [H^+] = -\log (2 \times 10^{-4})$ = $-\log 2 - \log 10^{-4} = -0.3010 + 4 = 3.7$

EXPLANATION OF WATER

a. Nature of water is neutral.

i.e. at 25°C
$$pH = 7$$
 and $pOH = 7$
 $\therefore pH = pOH$

b. Concentration of H⁺ and OH⁻ ions in 1 litre water $[H^+] = 10^{-7} \text{ mol } L^{-1} \text{ and } [OH^-] = 10^{-7} \text{ mol } L^{-1}$ c. Number of H⁺ and OH⁻ ions in 1 litre water Number of H⁺ ions = 10⁻⁷N_A and number of OH⁻ ions = 10⁻⁷ N_A
d. Number of H₂O moles in 1 litre water 1000/18 = 55.5 moles
e. Number of H₂O molecules in 1 litre water

= 55.5 N_A (N_A= avogadro's number)

- **f.** Molar concentration of H_2O molecules in water = 55.5 mol L⁻¹
- **g.** In water (Number of H_2O molecules : Number of H^+ ions)

= 55.5 N_A :
$$10^{-7}$$
N_A
= 55.5 × 10^{7} : 1

i.e. one H^{+} ion is obtained from 55.5 $\times ~10^{7} H_{2}O$ molecules

So degree of ionisation of water

$$\alpha = \frac{x}{a} = \frac{1}{55.5 \times 10^{+7}} = 18 \times 10^{-10} = 1.8 \times 10^{-9}$$

$$\alpha\% = 1.8 \times 10^{-7}\%$$

Hence, water is a very weak electrolyte.

K (Ionisation constant of water)

$$H_{2}O \ 1 \quad H^{+} + OH^{-}$$

$$K = \frac{\left[H^{+}\right]\left[OH^{-}\right]}{\left[H_{2}O\right]}$$

$$K = \frac{10^{-7} \times 10^{-7}}{55.5} \quad \text{or} \quad \boxed{K = 1.8 \times 10^{-16}}$$

h. Ionic product of water

Represented by
$$[K_w]$$

 $K \times [H_2O] = [H^+] [OH^-]$
 $\overline{[K_w = [H^+] [OH^-]]}$
At 25°C - $K_w = 10^{-7} \times 10^{-7} = 10^{-14}$
 $K [H_2O] = K_w \Rightarrow \overline{[K_w > K]}$ (always)
 $K_w = [H^+] [OH^-]$
taking -log on both sides
 $-\log K_w = -\log [H^+] - \log [OH^-]$
 $\overline{[pK_w = pH + pOH]}$

Nature of water is neutral so

$$[pH = pOH]$$

$$pK_{w} = pH + pH \qquad pK_{w} = pOH + pOH$$

$$2pH = pK_{w} \qquad 2 pOH = pK_{w}$$

$$pH = \frac{pK_{w}}{2} \qquad pOH = \frac{pK_{w}}{2}$$

$$\boxed{pH = pOH = \frac{pK_{w}}{2}}$$

$$At 25^{\circ}C, K_{w} = 10^{-14} \text{ or } pK_{w} = 14$$

$$pH + pOH = 14 \text{ or } pH = pOH = 7$$

i. Main Points :-

$$pH = pOH = \frac{pK_w}{2}$$

At 25°C, $pK_w = pH + pOH = 14$

j. Effect of temperature :-

 $H_2O \Longrightarrow H^+ + OH^-$

On increasing temperature rate of the forward reaction increases i.e. α increases or [H⁺] and [OH⁻] increases or [H⁺][OH⁻] increases i.e. K_w increases means pH decreases or pOH decreases.

$$T \uparrow = \alpha \uparrow = [H^+] [OH^-] \uparrow = K_w \uparrow \implies pK_w \downarrow$$

At 25° C, $K_w = 10^{-14}$

At 90° C, $K_w = (100 \times 10^{-14}) = 10^{-12}$

	At 25°C	At 90°C
K _w	10-14	10-12
рК _w	14	12
$pH = \frac{pK_w}{2} = pOH$	7	6
$[H^+] = [OH^-]$	10 ⁻⁷	10-6
pH + pOH	14	12

Important point : On increasing temperature, both [H⁺] and [OH⁻] increases equally so water remains neutral but neutral pH changes from 7 to 6 at 90°C.

Mixing of ions :

(a) Common ion effect	(b) Odd ion effect
When a weak	When a weak
electrolyte having a	electrolyte having a
common ion, is mixed	odd ion, is mixed with
with strong electrolyte	electrolyte then the
then the degree of	degree of ionization of
ionization of weak	weak electrolyte is
electrolyte is decreased.	increased. This effect
This effect is called	is effect is called
common ion effect.	common ion effect.

Common ion :

On mixing CH₃COONa with CH₃COOH solution Initially CH₃COOH \implies CH₃COO⁻ + H⁺ On mixing CH₃COONa \implies CH₃COO⁻ + Na⁺ CH₃COOH \implies CH₃COO⁻ + H⁺

Odd ion :

On mixing, NaOH with CH_3COOH solution Initially $CH_3COOH \implies CH_3COO^- + H^+$ On mixing, NaOH \implies Na^+ + OH^- \rightarrow H_2O $CH_3COOH \implies CH_3COO^- + H^+$

Solved Examples

Ex.28 Dissociation constant of water at 25° C is

(1) $10^{-14} \times (55.5)^{-1}$	(2) $10^{-7} \times (18)^{-1}$
(3) $10^{-14} \times (18)^{-1}$	(4) $10^{-7} \times (55.4)^{-1}$

Sol. (1)

- **Ex.29** What should be the number of H⁺ ions in 1 mL of distilled water, if the number of H⁺ ions in 1 L is 6.023×10^{16} ?
- Sol. Number of H⁺ ions in 1 mL distilled water

$$= \frac{6.023 \times 10^{16}}{1000} = 6.023 \times 10^{13}$$

Ex.30 *Assertion* : NaCl + HCl does not experience common ion effect.

Reason : Both NaCl and HCl are strong electrolytes.

Sol. (A)

SALTS, TYPES OF SALT AND CONJUGATE THEORY

A. SALT:

Salts are regarded as compounds made up of positive and negative ions. The positive part comes from a base while negative part from an acid. Salts are ionic compounds.

i.e. A compound formed by the combination of acid and base is known as salt.

Acid + Base \rightarrow Salt + Water HCl + NaOH \rightarrow NaCl (Salt) + H₂O Δ H = -ve

B. TYPES OF SALT

(a) Normal/general salts :- The salts formed by the loss of all possible protons. (replaceable hydrogen ions as H^+) are called normal salts. Such a salt does not contain either a replaceable hydrogen ions or a hydroxyl (OH⁻) group.

Ex.: NaCl, NaNO₃, K_2SO_4 , $Ca_3(PO_4)_2$, Na₂HPO₃, NaH₂PO₂ etc.

(b) Acid salts :- Salt formed by incomplete neutralisation of poly basic acids are called acid salts. Such salts still contain one or more replaceable hydrogen ions (H^+) .

Ex. : NaHCO₃, NaHSO₄, NaH₂PO₄, Na₂HPO₄ etc.

(c) Basic salts :- Salts are formed by incomplete neutralisation of poly acidic base are called basic salts. Such salts still contain one or more hydroxyl ion group.

Ex.: Zn(OH)Cl, Mg(OH)Cl, $Fe(OH)_2Cl$, $Bi(OH)_2Cl$ etc.

(d) **Double salts** :- The addition compounds formed by the combination of two simple salts are termed double salts. Such salts are stable in solid state only.

Ex.: $FeSO_4 \cdot (NH_4)_2 SO_4 \cdot 6H_2O$, (Ferrous ammonium sulphate)

$$K_2SO_4$$
. $Al_2(SO_4)_3$. $24H_2O$ etc.

(Potash alum)

(e) Complex salts :- These are formed by combination of simple salts or molecular compounds or complex ions are present in salt molecules. These are stable in solid state as well as in solutions.

$$\underbrace{\operatorname{FeSO}_{4} + 6\operatorname{KCN}}_{\text{Simple salt}} \longrightarrow \operatorname{K}_{4}[\operatorname{Fe}(\operatorname{CN})_{6}] + \operatorname{K}_{2}\operatorname{SO}_{4}$$

$$\operatorname{K}_{4}[\operatorname{Fe}(\operatorname{CN})_{6}] \longrightarrow 4\operatorname{K}^{+} + [\operatorname{Fe}(\operatorname{CN})_{6}]^{-4}$$

$$\underbrace{\operatorname{CoSO}_{4}}_{\operatorname{Simple}} + \operatorname{6NH}_{3}_{\operatorname{Molecular}} \longrightarrow [\operatorname{Co}(\operatorname{NH}_{3})_{6}]\operatorname{SO}_{4}_{\operatorname{Complex salt}}$$

 $[\operatorname{Co(NH_3)_6}]\operatorname{SO}_4 \longrightarrow [\operatorname{Co(NH_3)_6}]^{+2} + \operatorname{SO_4}^{-2}$

(f) Mixed salts :- The salts which furnishes more than one cation or more than one anion when dissolved in water is called a mixed salt.

$$\begin{array}{rcl} H_2SO_4 &+ NaOH &\longrightarrow & NaHSO_4 &+ & H_2O\\ acidic salt &+ & KOH &\longrightarrow & NaKSO_4\\ acidic salt &\longrightarrow & Na^+ K^+ SO_4^{-2}\\ &\longrightarrow & Na^+ K^+ SO_4^{-2}\\ (more than two radicals) \end{array}$$

(ii)
$$Ca < Cl$$
 (iii) $Na > S$ (iv) $NH_4 > PO_4$

(a) Types of general salts :

(i) SASB (ii) SAWB (iii) WASB (iv) WAWB

C. Neutralization :

- 1. In this process heat is evolved by the system, means the process is exothermic.
- 2. In this process acid and base neutralize each other therefore the evolved heat is known as heat of neutralization.

3. Heat of neutralization :

(a) When one equivalent of an acid reacts with one equivalent of a base then the evolved heat is known as heat of neutralization.

Unit of heat of neutralization \rightarrow Kilo calorie / equivalent or kJ/equivalent

(b) For strong acid and Strong base the heat of neutralization is -13.7 Kilo calories / equivalent or -57.3 kilo joules / equivalent

Ex. HCl + NaOH \rightarrow NaCl (Salt) + H₂O; Δ H of neutralization = -13.7 Kilo calories/ equivalent H⁺ + OH⁻ \rightarrow H₂O + 13.7 Kilo calories/ equivalent 1 eq. 1 eq. 1 eq. \rightarrow 13.7 Kilo calories n eq. n eq. n eq. \rightarrow 13.7 × n Kilo calories \Rightarrow Total amount of heat evolved during the neutralization.

 Δ H = (-13.7 × number of limiting equivalents) Kilo calorie

- (c) For Strong acid + weak base
 - or Weak acid + strong base
 - or Weak acid + weak base

Heat of neutralization is always less than 13.7 Kilo calorie because some heat is required to ionize weak electrolytes.

 $HCl + NH_4OH \rightarrow NH_4Cl + H_2O$

 $\Delta H = -12.9$ Kilo calories/equivalent SA WB HCN + NH₄OH \rightarrow NH₄CN + H₂O $\Delta H = -11.9$ Kilo calories/equivalent WA WB

D. Conjugate acid-base pair : Conjugate acid-base pairs means difference between two species of only one H⁺ or OH⁻ ion.

 $CH_2 COOH \implies CH_2 COO^- + H^+$ Conjugate strong base Weak acid $(K_a = 1.85 \times 10^{-5})$ or acceptor ion NH₄OH ==== $NH_{4}^{+} + OH^{-}$ Weak base Conjugate strong acid $(K_{h} = 1.85 \times 10^{-5})$ or acceptor ion HC1 \implies H⁺+ Cl⁻ Strong acid Conjugate weak base (spectator ion) Accepting tendency of $H^+ \simeq 0$ $(K_{a} \simeq \infty)$ Na⁺ + OH⁻ NaOH ====⇒ Strong base Conjugate weak acid $(K_{h} \simeq \infty)$ (spectator ion)

E. Relation between conjugate acid-base pair :-Example – $CH_2COOH \implies CH_2COO^- + H^+$ Acid conjugate base NH_4^{+} + NH₄OH ==== OH Base conjugate acid CH₃COOH CH₃COO⁻ acid conjugate base $CH_3COOH + H_2O \Longrightarrow CH_3COO^- + H_3O^+$ $CH_3COO^-+H_2O \Longrightarrow CH_3COOH + OH^ K_{a} = \frac{[CH_{3}COO^{-}][H_{3}O^{+}]}{[CH_{3}COOH]} \dots (i)$

$$K_{b} = \frac{[CH_{3}COOH][OH^{-}]}{[CH_{3}COO^{-}]}.....(ii)$$

In both the reactions H_2O in excess quantity so active mass of H_2O is one.

Now multiply the equation (i) and (ii)

 $K_a \times K_b = [H^+] [OH^-]$ we know $[H^+] \times [OH^-] = K_W$

(Ionic product of water)

$$K_a \times K_b = K_w$$

Taking -log on both sides

 $pK_a + pK_b = pK_w$

we know that for water at 25°C, $K_W = 10^{-14}$ or $pK_W = 14$

So
$$K_a \times K_b = 10^{-14}$$

or $pK_a + pK_b = 14$

Note : These relation are applicable for only conjugate acid-base pairs.

Solved Examples

Ex.31 Which salt does not an acidic salt :-

(1) HCOONa	(2) NaH_2PO_2
(3) NaHS	(4)(1) and (2) both

Sol. (4)

- **Ex.32** Calculate the no. of ions in Mohr's salt $[FeSO_4.(NH_4)_2 SO_4.6H_2O]$ or Ferrous Ammonium Sulphate
- Sol. $FeSO_4$. $(NH_4)_2SO_4 \cdot 6H_2O$ $\longrightarrow Fe^{+2} + SO_4^{-2} + 2NH_4^{+} + SO_4^{-2} + 6H_2O$ Total number of ions = 5
- **Ex.33** Assertion :- Heat of neutralisation of perchloric acid $HClO_4$ with NaOH is same as that of HCl with NaOH.

Reason :-Both HCl and $HClO_4$ are strong acids. **Sol.** (A)

HYDROLYSIS OF SALTS

Salt hydrolysis is defined as the process in which water reacts with salt to form acid and base. i.e. change in concentration of H^+ and OH^- ions of water.

Water + Salt \implies Acid + Base

A. Hydrolysis of strong acid and strong base [SA – SB] types of salt –

Ex. NaCl, BaCl₂, Na₂SO₄, KClO₄, BaSO₄, NaNO₃, KBr, KCl etc.

 $NaCl + H_2O \implies NaOH + HCl$

 $Na^+ + Cl^- + H_2O \implies Na^+ + OH^- + H^+ + Cl^-$

 $H_2O \perp H^+ + OH^-$ (It is not salt hydrolysis)

(i) Hydrolysis of salt of [SA-SB] is not possible.

(ii) Aqueous solution of these type of salt is neutral in nature. (pH = pOH = 7)

- (iii) pH of the solution is 7.
- (iv) No effect on litmus paper.

B. Hydrolysis of strong acid and weak base

[SA - WB] types of salt – Ex. CaSO₄, NH₄Cl, (NH₄)₂SO₄, Ca(NO₃)₂, ZnCl₂, CuCl₂, CaCl₂, AgCl, AgI, AgNO₃ etc NH₄Cl + H₂O \implies NH₄OH + HCl WB SA NH₄⁺+Cl⁻ + H₂O \implies NH₄OH + H⁺ + Cl⁻ NH₄⁺ + H₂O \implies NH₄OH + H⁺

- (i) In this type of salt hydrolysis, cation reacts with H₂O therefore called as cationic hydrolysis.
- (ii) Solution is acidic in nature as $[H^+]$ is increased.
- (iii) pH of the solution is less than 7.
- (iv) Solution turns blue litmus paper red.
 - $K_{h} = Hydrolysis constant$
 - $K_w =$ Ionic product of water
 - $K_a = Ionisation constant of acid$
 - $K_{\rm b}$ = Ionisation constant of base
 - h = Degree of hydrolysis
 - C = Concentration of salt (concentration of ions)
- (a) Relation between K_h , K_w and K_b $B^+ + H_2O \implies BOH + H^+$ $NH_4^+ + H_2O \implies NH_4OH + H^+$

Hydrolysis constant $[K_h]$

$$K_{h} = \frac{[NH_{4}OH][H^{+}]}{[NH_{4}^{+}]}$$
(1)

For weak Base

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

$$K_{b} = \frac{\left[NH_{4}^{+}\right]\left[OH^{-}\right]}{\left[NH_{4}OH\right]} \qquad \dots \dots \dots (2)$$

For water $H_2O \ 1 \ H^+ + OH^ K_w = [H^+] [OH^-]$ (3) Now mutiplying Eq. (1) and (2) = Eq. (3)

(b) Degree of hydrolysis – Represented by h $NH_4^+ + H_2O \implies NH_4OH + H^+$

Initial concentration of salt

C 0 0

$$C-Ch$$
 Ch Ch

$$K_{h} = \frac{\left[NH_{4}OH\right]\left[H^{+}\right]}{\left[NH_{4}^{+}\right]} = \frac{Ch \times Ch}{C - Ch}$$
$$= \frac{C^{2}h^{2}}{C(1-h)} = \frac{Ch^{2}}{(1-h)}$$

Since $h \ll 1$ then $(1-h) \approx 1$

(c) **pH of the solution :** $pH = -\log [H^+]$

$$[\mathrm{H}^{+}] = \mathrm{Ch} = \mathrm{C} \sqrt{\frac{\mathrm{K}_{\mathrm{W}}}{\mathrm{K}_{\mathrm{b}} \times \mathrm{C}}} \qquad \Longrightarrow \qquad$$

$$[\mathrm{H}^{+}] = \sqrt{\frac{\mathrm{K}_{\mathrm{W}} \times \mathrm{C}}{\mathrm{K}_{\mathrm{b}}}} \qquad \dots \dots \dots (8)$$

taking-log on both sides

$$-\log [\mathrm{H}^+] = -\log \sqrt{\frac{\mathrm{K}_{\mathrm{W}} \times \mathrm{C}}{\mathrm{K}_{\mathrm{b}}}} \quad \Rightarrow$$

$$pH = -\log\left(\frac{K_{W} \times C}{K_{b}}\right)^{\frac{1}{2}}$$

$$pH = -\frac{1}{2} \left[\log K_{W} + \log C - \log K_{b} \right]$$

$$pH = -\frac{1}{2} \log K_{W} - \frac{1}{2} \log C - \frac{1}{2} \left(-\log K_{b} \right)$$

$$pH = \frac{1}{2} pK_{W} - \frac{1}{2} \log C - \frac{1}{2} pK_{b}$$

$$pH = 7 - \frac{1}{2} pK_{b} - \frac{1}{2} \log C \qquad \dots \dots \dots (9)$$

- C. Hydrolysis of weak acid and strong base [WA-SB] types of salt – Ex. CH₃ COONa, HCOONa, KCN, NaCN, K_2CO_3 , BaCO₃, K_3PO_4 etc. CH₃ COONa + H₂ O \rightleftharpoons CH₃ COOH + NaOH CH₃ COO⁻+Na⁺ + H₂O \rightleftharpoons CH₃ COOH + Na⁺ + OH⁻ CH₃ COO⁻+H₂O \rightleftharpoons CH₃ COOH + OH⁻
- (i) In this type of salt hydrolysis, anion reacts with water therefore called as anionic hydrolysis.
- (ii) Solution is basic in nature as [OH⁻] increases.
- (iii) pH of the solution is greater than 7.
- (iv) Solution turns red litmus paper blue.

(a) Relation between
$$K_h$$
, K_w and K_a
 $CH_3COO^- + H_2O \implies CH_3COOH + OH^-$

For weak acid
CH₃COOH
$$\implies$$
 CH₃COO⁻ + H⁺

$$K_{a} = \frac{\left[CH_{3}COO^{-}\right]\left[H^{+}\right]}{\left[CH_{3}COOH\right]} \qquad \dots \dots (2)$$

For water

$$H_2O \perp H^+ + OH^-$$

 $K_w = [H^+] [OH^-]$ (3)
Now multiply eq. (1) × eq. (2) = eq. (3)

$$\frac{[CH_{3}COOH][OH^{-}]}{[CH_{3}COO^{-}]} \times \frac{[CH_{3}COO^{-}][H^{+}]}{[CH_{3}COOH]}$$

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

$$K_{h} \times K_{a} = K_{W}$$

$$\overline{K_{h}} = \frac{K_{W}}{K_{a}}$$
.....(4)

(b) Degree of hydrolysis (h): $CH_3COO^- + H_2O \Longrightarrow CH_3COOH + OH^-$ Initial concentration of salt

$$\begin{array}{ccc} C & 0 & 0 \\ C-Ch & Ch & Ch \end{array}$$

$$K_{h} = \frac{\left[CH_{3}COOH\right]\left[OH^{-}\right]}{\left[CH_{3}COO^{-}\right]} = \frac{Ch \times Ch}{C - Ch} = \frac{C^{2}h^{2}}{C(1-h)}$$

$$K_{h} = \frac{Ch^{2}}{\left(1 - h\right)}$$

Since $h \ll 1$ then $(1-h) \approx 1$

$$h^2 = \frac{K_h}{C}$$
 or $h = \sqrt{\frac{K_h}{C}}$ (6)

(c) **pH of the solution** $[OH^-] = Ch$

$$[OH^{-}] = C \times \sqrt{\frac{K_{w}}{K_{a} \times C}} \quad \text{or}$$

$$[OH^{-}] = \sqrt{\frac{K_{w} \times C}{K_{a}}}$$

$$\therefore \quad K_{w} = [OH^{-}] [H^{+}]$$

$$\vdots \quad [H^{+}] = \frac{K_{w}}{[OH^{-}]} = \frac{K_{w}}{\sqrt{\frac{K_{w} \times C}{K_{a}}}}$$

$$[H^{+}] = \sqrt{\frac{K_{w} \times K_{a}}{C}} \quad \dots \dots (8)$$

taking – log on both sides

$$-\log [H^{+}] = -\log \sqrt{\frac{K_{W} \times K_{a}}{C}}$$
$$pH = -\log \left(\frac{K_{W} \times K_{a}}{C}\right)^{\frac{1}{2}}$$
$$pH = -\frac{1}{2} [\log K_{W} + \log K_{a} - \log C]$$

D. Hydrolysis of weak acid and weak base (WA - WB) type of salt : Ex. CH_3COONH_4 , AgCN, NH_4CN , $CaCO_3$, $[NH_4]_2CO_3$, $ZnHPO_3$ etc. $CH_3COONH_4 + H_2O \implies CH_3COOH + NH_4OH$

$$CH_{3}COO^{-} + NH_{4}^{+} + H_{2}O \Longrightarrow$$

 $CH_{3}COOH + NH_{4}OH$

• Solution is almost neutral but it may be acidic or basic depending upon the nature of acid and base and pH of the solution is near to 7.

(a) Relation between K_{h}, K_{w}, K_{a} and K_{b}

$$CH_{3}COO^{-} + NH_{4}^{+} + H_{2}O \iff CH_{3}COOH + NH_{4}OH$$

$$CH_{3}COOH - NH_{4}OH$$

$$K_{h} = \frac{\left[CH_{3}COO^{-}\right]\left[NH_{4}^{+}\right]}{\left[CH_{3}COO^{-}\right]\left[NH_{4}^{+}\right]} \quad \dots \dots \dots (1)$$

For weak base $NH_4OH \perp NH_4^+ + OH^-$

For weak acid CH₃COOH 1 CH₃COO⁻ +H⁺

$$K_{a} = \frac{\left[CH_{3}COO^{-}\right]\left[H^{+}\right]}{\left[CH_{3}COOH\right]} \qquad \dots \dots (3)$$

For water $H_2O \perp H^+ + OH^ K_w = [H^+] [OH^-]$ (4) Multipy Eq. (1) × Eq. (2) × Eq. (3) = Eq. (4)

$$\frac{[CH_{3}COOH][NH_{4}OH]}{[CH_{3}COO^{-}][NH_{4}^{+}]} \times \frac{[NH_{4}^{+}][OH^{-}]}{[NH_{4}OH]} \times \frac{[CH_{3}COO^{-}][H^{+}]}{[CH_{3}COOH]} = [H^{+}][OH^{-}]$$

$$K_{h} \times K_{b} \times K_{a} = K_{W}$$

$$K_{h} = \frac{K_{W}}{K_{a} \times K_{b}}$$
.....(5)

(b) Degree of hydrolysis (h) -

$$CH_{3}COO^{-} + NH_{4}^{+} + H_{2}O \Longrightarrow$$

 $CH_{3}COOH + NH_{4}OH$

Initial concentration of salt

 $\begin{array}{cccc} C & C & 0 & 0 \\ C-Ch & C-Ch & Ch & Ch \end{array}$

$$\mathbf{K}_{h} = \frac{\left[\mathbf{CH}_{3}\mathbf{COOH}\right]\left[\mathbf{NH}_{4}\mathbf{OH}\right]}{\left[\mathbf{CH}_{3}\mathbf{COO}^{-}\right]\left[\mathbf{NH}_{4}^{+}\right]} = \frac{\mathbf{Ch} \times \mathbf{Ch}}{(\mathbf{C} - \mathbf{Ch})(\mathbf{C} - \mathbf{Ch})}$$

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

Since $h \ll 1$ then $(1-h) \approx 1$

$$\therefore \quad \boxed{K_h = h^2} \qquad \dots \dots \dots (6)$$

or
$$h^2 = \frac{K_W}{K_a \times K_b}$$
 or $h = \sqrt{\frac{K_W}{K_a \times K_b}}$ (7)

(c) **pH of the solution** from equation(3)

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

$$\begin{bmatrix} H^{+} \end{bmatrix} = \frac{K_{a} \times [CH_{3}COO^{-}]}{[CH_{3}COO^{-}]}$$

$$= \frac{K_{a} \times Ch}{C - Ch} = \frac{K_{a} \times h}{1 - h}$$
Since $h <<<<1$ then $(1 - h) \approx 1$

$$\begin{bmatrix} H^{+} \end{bmatrix} = K_{a} \times h$$

$$\begin{bmatrix} Now put the value of h from eq. (5) \end{bmatrix}$$

$$= K_{a} \times \sqrt{\frac{K_{w}}{K_{a} \times K_{b}}} \begin{bmatrix} H^{+} \end{bmatrix} = \sqrt{\frac{K_{w} \times K_{a}}{K_{b}}} \\ \dots \dots (8)$$
taking - log on both sides $-\log [H^{+}]$

$$= -\log \left(\frac{K_{w} \times K_{a}}{K_{b}}\right)^{\frac{1}{2}}$$

$$pH = -\frac{1}{2} [\log (K_{w} \times K_{a}) - \log K_{b}]$$

$$pH = -\frac{1}{2} [\log K_{w}] - \frac{1}{2} [\log K_{a}] - \frac{1}{2} [-\log K_{b}]$$

$$pH = +\frac{1}{2} pK_{w} + \frac{1}{2} pK_{a} - \frac{1}{2} pK_{b}$$

$$\boxed{pH = 7 + \frac{1}{2}pK_{a} - \frac{1}{2}pK_{b}} \qquad \dots \dots (9)$$

Note : Degree of hydrolysis of weak acid and weak base [WA–WB] type salt does not depend on the concentration of salt.

For WA - WB types of salt :

		$K_a > K_b$	$K_b > K_a$	$K_a = K_b$
1.	Hydrolysis	Cationic-anionic	Anionic-cationic	Neutral hydrolysis
2.	Nature	Acidic	Basic	Neutral
3.	pН	pH<7	pH>7	pH=7

Summary:

Type of salts	$K_{h} = \frac{K_{W}}{weak}$	$h = \sqrt{\frac{K_h}{C}}$	$[\mathrm{H}^+]$	pН
SA SB	-	-	-	7
WA SB	$K_{\rm h} = \frac{K_{\rm W}}{K_{\rm a}}$	$h = \sqrt{\frac{K_{\rm W}}{K_{\rm a}} \times C}$	$\sqrt{\frac{K_{W} \times K_{a}}{C}}$	$7 + \frac{1}{2} pK_a + \frac{1}{2} \log C$
SA WB	$K_{\rm h} = \frac{K_{\rm W}}{K_{\rm b}}$	$h = \sqrt{\frac{K_{W}}{K_{b} \times C}}$	$\sqrt{\frac{K_{\rm W} \times C}{K_{\rm b}}}$	$7 - \frac{1}{2} pK_{b} - \frac{1}{2} \log C$
WA WB	$K_{\rm h} = \frac{K_{\rm W}}{K_{\rm a} \times K_{\rm b}}$	$h = \sqrt{\frac{K_{W}}{K_{a} \times K_{b}}}$	$\sqrt{\frac{K_{\rm W} \times K_{\rm a}}{K_{\rm b}}}$	$7 + \frac{1}{2} pK_{a} - \frac{1}{2} pK_{b}$

Solved Examples

Ex.34 What is the pH of 1 M CH₃COONa solution? Ka of acetic acid = 1.8×10^{-5} , K_w= 10^{-14} mol² L⁻² (1) 2.4 (2) 3.6

(3) 4.8	(4) 9.4

Sol. (4)

Ex.35 Calculate the degree of hydrolysis of a mixture containing $0.1N \text{ NH}_4\text{OH}$ and 0.1N HCN

If
$$K_a = 10^{-5}$$
 and $K_b = 10^{-5}$

$$h = \sqrt{\frac{K_{w}}{K_{a} \times K_{b}}} = \sqrt{\frac{10^{-14}}{10^{-5} \times 10^{-5}}} = \sqrt{10^{-14} \times 10^{+10}}$$
$$= \sqrt{10^{-4}} = 10^{-2}$$

Ex.36 *Assertion* : An aqueous solution of NH_4NO_3 is acidic in characters.

Reason : NH_4NO_3 in an aqueous solution undergoes anionic hydrolysis.

Ans. (C)

SOLUBILITY AND SOLUBILITY PRODUCT (K_{sp})

A. SOLUBILITY

(a) Definition

(i). At constant temperature the maximum number of moles of solute which can be dissolved in a solvent to obtain 1 litre of solution (i.e. saturated solution) is called solubility.

$$S(M) = \frac{\text{Number of moles of solute}}{\text{Volume of solution } (L)} \quad S = \frac{x}{M_w \times V_L} \text{ mol } L^{-1}$$

(ii). The maximum weight of solute which can be dissolved in a given amount of solvent is known as solubility.

(b) Important points :-

Solubility does not depend on amount of substances and volume of solution where as depends on the following-

- (i). Temperature
- (ii). Presence of common ion
- (iii). Nature of solvent

(Molecular wt. of AgCl = 143.5)

(Molecular wt. of $BaSO_4 = 233$)

• Solubility can be expressed in terms of molarity.

В. SOLUBILITY PRODUCT(K_{m}):

(a) At constant temperature product of concentrations of ions in a saturated solution of substance is called solubility product of that substance. (Saturated solution is that solution in which further dissolution of even a small amount of salt is not possible).

Ex. (i) Let solubility of AgCl

	AgCl	
is S mol L ⁻¹	a	

0 S After saturation a-S

0

S

According to L.M.A.

Solubility product at saturation in terms of concentration of ions $K_{sp} = [Ag^+][Cl^-]$ Solubility product in terms of solubility

$$K_{sp} = (S) (S)$$
$$K_{sp} = S^2$$

Ex. (ii) Ksp for CaCl,

 $CaCl_2 \implies Ca^{+2} + 2Cl^{-1}$ 0 Initially 0 S 2SLet solubility of CaCl, a-Sis S mol L-1

Solubility product in terms of concentration of ions $Ksp = [Ca^{+2}] [Cl^{-}]^2$

In terms of solubility

 $K_{sn} = (S) (2S)^2$ $K_{sp} = 4S^3$

Ex. (iii) Ksp for AlCl₃

 $AlCl_3 \Longrightarrow Al^{+3} + 3Cl^{-1}$ 0 0 Initially а Let solubility of AlCl₃ a - SS **3**S is S mol L⁻¹ Solubility product in terms of concentration of ions $K_{sp} = [Al^{+3}] [Cl^{-}]^{3}$ In terms of solubility $K_{sn} = (S) (3S)^3$ $K_{sp} = 27S^4$

(b) General form

$$\begin{array}{ccc} AxBy & & & \\ a & & 0 & 0 \\ a-S & & xS & yS \end{array}$$

 $\mathbf{K}_{sp} = [\mathbf{A}^{+y}]^{x} [\mathbf{B}^{-x}]^{y}$ $= [xs]^x \times [ys]^y = x^x \cdot s^x \cdot y^y \cdot s^y$ $K_{sp} = x^x y^y S^{(x+y)}$ \Rightarrow Ag⁺ + Cl⁻ **Ex.** (i) Al₂(SO₄)₃ $K_{sp} = 2^2 \times 3^3 \times (S)^{2+3} = 4 \times 27 \times S^5$ $= 108 \text{ S}^{5}$

а

(ii) Na, KPO_4 $K_{_{SD}} = 2^2 \times 1^1 \times 1^1 (S)^{2+1+1} = 4S^4$ (iii) NaKRbPO₄

$$K_{sp} = 1^{1} \times 1^{1} \times 1^{1} \times 1^{1} \times (S)^{1+1+1+1} = S^{4}$$

Solved Examples

Ex.37 If solubility product of the base $M(OH)_3$ is 2.7×10^{-11} , the concentration of OH^{-1} will be

(1) 3×10^{-3}	(2) 3×10^{-4}
$(3) 10^{-3}$	$(4) \ 10^{-11}$

Sol. (1)

Ex.38 Compound AB gets 80% ionised. What should be the solubility of AB, calculate if its solubility product is 6.4×10^{-9} ?

Sol. AB
$$\iff$$
 A⁺ B⁻
s 0.8s 0.8s
K_{sp} = [A⁺] [B⁻]
6.4 × 10⁻⁹ = 0.8s × 0.8s
0.64 s² = 6.4 × 10⁻⁹ or
s² = $\frac{6.4 \times 10^{-9}}{0.64} = 10^{-8}$
∴ s = 10⁻⁴

Ex.39 Assertion : For a sparingly soluble salt, K_{sp} is the maximum dissolved value of solute in a solution.

Reason: K_{sp} corresponds to the ionic product of the salt in a saturated solution.

PPLICATION OF SOLUBILITY

PRODUCT (K_{sn})

- A. To find out the solubility (S) :
 - (i) K_{sn} of AB (Mono-mono, di-di, tri-tri valency) type salt -
 - Ex. NaCl, BaSO₄, CH₃COONa, CaCO₃, NaCN, KCN, NH_4CN , NH_4Cl etc.

$$AB(s) \iff A^{+} + B^{-}$$

$$1 \qquad 0 \qquad 0$$

$$1 \qquad s \qquad s$$

$$K_{sp} = [A^{+}] [B^{-}]$$

$$K_{sp} = s^{2} \quad \text{or} \quad s = \sqrt{K_{sp}}$$

- (ii) K_{sp} of AB₂ or A₂B (Mono-di or di-mono valency) type salt –
- **Ex.** CaCl₂, CaBr₂, K₂S, (NH₄)₂SO₄, K₂SO₄, K_2CO_3 etc. $AB_2(s) \implies A^{+2} + 2B^{-1}$ 0 1 0 1 2s S $K_{sn} = [A^{+2}] [B^{-}]^2$ $\mathbf{K}_{sn} = \mathbf{s} \times (2\mathbf{s})^2 = \mathbf{s} \times 4\mathbf{s}^2 = 4\mathbf{s}^3$ $s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
- (iii) K_{sp} of AB₃ or A₃B (Mono-tri or tri-mono valency) type salt -

Ex. FeCl₃, AlCl₃, K₃PO₄ etc.
AB₃(s)
$$\implies$$
 A⁺³ + 3B⁻
1 0 0
1 s 3s
K_{sp} = $[A^{+3}][B^{-}]^{3} = s \times (3s)^{3} = 27s^{4}$
s = $\left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}$

(iv)
$$\mathbf{K}_{sp} \text{ of } \mathbf{A}_2 \mathbf{B}_3 \text{ or } \mathbf{A}_3 \mathbf{B}_2 \text{ (Di-tri or tri-di valency)}}$$

type salt –
Ex. $Al_2(SO_4)_3$, $Ba_3(PO_4)_2$ etc.
 $A_2B_3(s) \implies 2A^{+3} + 3B^{-2}$
 $1 \qquad 0 \qquad 0$
 $1 \qquad 2s \qquad 3s$
 $\mathbf{K}_{sp} = [A^{+3}]^2 [B^{-2}]^3$
 $= 2s \times 2s \times 3s \times 3s \times 3s = 108s^5$
 $s = \left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$

B. Common ion effect on solubility :

Important point :- Solubility of substances always decreases in the presence of common ion.

Find out the solubility of AgCl in the presence **Ex.** (i) of C NaCl solution?

AgCl
$$\implies$$
 Ag⁺ + Cl⁻
S S S
(Let solubility of AgCl is S mol L⁻¹)
K_{sp} = [Ag⁺] [Cl⁻]
K_{sp} = S²
In NaCl solution
NaCl \implies Na⁺ + Cl⁻
C C C
[Cl⁻] = C
Let solubility of AgCl in the presence of NaC

21 solution is S' mol L⁻¹.

$$\begin{array}{cccc} \text{AgCl} & \Longrightarrow & \text{Ag}^+ & + & \text{Cl}^- \\ \text{S'} & \text{S'} & \text{S'+C} \end{array}$$

According to L.M.A.

 $K_{sp} = [Ag^+]' [Cl^-]'$ $K_{sn} = S' (S' + C) = S'^{2+}S'C$

(Neglecting the higher power terms of S') K = S' C

$$\frac{K_{sp}}{S' = \frac{K_{sp}}{C}}$$

Ex. (ii) Find out the solubility of CaCl, solution in the Ex. (iii) Find out the solubility of NaCl in the presence presence of C NaCl solution? of C CaCl₂ solution ?

CaCl	$_2 $	$Ca^{+2}+$	2Cl-
S		S	2S
[Let solub	ility of Ca	Cl ₂ is S me	ol L-1]
K _{sp}	$= [Ca^{+2}]$	[Cl [_]] ²	
	$= 4S^{3}$		

For NaCl solution

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

$$C \qquad C \qquad C \qquad [Cl^-] = C$$

Let solubility of $CaCl_2$ in the presence of NaCl solution is S' mol L⁻¹.

$$\begin{array}{cccc} {\rm CaCl}_2 & \mathchoice{\longrightarrow}{\leftarrow}{\leftarrow}{\leftarrow} & {\rm Ca^{+2}} & + & 2{\rm Cl^-} \\ {\rm S'} & {\rm S'} & 2{\rm S'+C} \end{array}$$

According to L.M.A.

$$\begin{split} K_{sp} &= [Ca^{+2}]' \ [Cl^{-}]'^2 \\ K_{sp} &= S' \ (2S'+C)^2 \ = S' \ (4S'^2+4S'C+C^2) \\ K_{sp} &= 4S'^3+4S'^2C+S'C^2 \ (Neglecting the higher power terms of S') \end{split}$$

$$S' = \frac{K_{sp}}{C^2}$$

$$\begin{array}{ccc} \operatorname{CaCl}_2 & \Longrightarrow & \operatorname{Ca^{+2+}} & 2\operatorname{Cl^-} \\ \operatorname{C} & \operatorname{C} & 2\operatorname{C} \end{array}$$

Let solubility of NaCl in the presence of CaCl, solution is S' mol L⁻¹.

According to L.M.A.

 $K_{sp} = [Na^+]' [Cl^-]'$ $K_{sp} = S' (S' + 2C) = S'^2 + 2S'C$ (Neglecting the higher power terms of S')

K_{sp} S' = 2C

C. Group precipitation :

(i) $K_{sp} > []$ [] \Rightarrow Unsaturated precipitation (ii) $K_{sp} = []$ [] \Rightarrow Saturated (iii) $K_{sp} < []$ []

No

 \Rightarrow Super saturated

 \Rightarrow precipitation

Group	Radicals	Condition for precipitation (Group reagent)	Forms of precipitation
Zero	NH_4^+, K^+, Na^+	1-2 drops of CH ₃ COOH	_
First	$Ag^{+},Hg^{+1},(Hg_{2}^{+2}),$	By mixing of dilute HCl	Chloride
	Pb ⁺²		AgCl,Hg ₂ Cl ₂ ,PbCl ₂
Second	Pb ⁺² Hg ⁺² ,Cu ⁺² ,Cd ⁺²	H_2S gas passed in	Sulphide
	Sn ⁺² ,Sn ⁺⁴ ,As ⁺³ ,Sb ⁺³	the presence of	PbS,HgS, CuS,CdS,
	Bi ⁺³	acidic medium	SnS , SnS_2 , As_2S_3 ,
			Sb_2S_3, Bi_2S_3
Third	$Al^{+3}, Fe^{+3}, Cr^{+3}$	NH_4OH mixed in	Hydroxide
		the presence of NH_4Cl	$Al(OH)_3$, $Fe(OH)_3$, $Cr(OH)_3$
Fourth	Mn ⁺² ,Co ⁺² ,Ni ⁺²	H_2S gas passed in	Sulphide
	Zn^{+2}	presence of	MnS,CoS, NiS, ZnS
		basic medium	
Fifth	$Ba^{+2}, Sr^{+2}, Ca^{+2}$	$(NH_4)_2 CO_3$ mixed in the	Corbonate
		presence of NH ₄ Cl	BaCO ₃ ,SrCO ₃ , CaCO ₃
Sixth	Mg ⁺²	By mixing of Na ₂ HPO ₄	Hydrogen phosphate (MgHPO ₄)

(iv) Important points :

- (a). $Hg^{+1}(us) \rightarrow Unstable in aqueous solution.$ [Stable in dimer form $(Hg_2^{+2}) \Rightarrow Hg_2Cl_2$] $Hg_2Cl_2 \implies Hg_2^{+2} + 2Cl^-$ S S 2S $K_{sp} = [Hg_2^{+2}] [Cl^-]^2$ $= (S) (2S)^2$ $K_{sp} = 4S^3$]
- (b). $Hg^{+2}(ic) \rightarrow HgCl_{2} \rightarrow stable in aqueous solution$ $HgCl_{2} \iff Hg^{+2} + 2Cl^{-}$ S S 2S $K_{sp} = 4S^{3}$
- (c). For precipitation of II group, H_2S gas is passed in acidic medium to decrease S^{-2} concentration by common ion effect. So that ionic product of cations of group II and S^{-2} ions exceed the solubility product of their corresponding metal sulphides. Therefore only the cations of group II gets precipitated. But the sulphides of the cation of the other groupes (III, IV & V) are not precipitated under these conditions because their solubility products are quite high.

When H_2S gas is directly passed through solution then IVth group is also precipitated with IInd group.

 $H_2S \implies 2H^+ + S^{-2}$ $Ksp_{II} < Ksp_{IV} < [radicals of II^{nd} and IV group]$ $[S^{-2}]$

When H_2S gas pass in acidic medium [H⁺] then only IInd group radicals are precipitated.

 $H_2S \implies 2H^+ + S^{-2}$

 $Ksp_{_{\rm II}}{<}[radicals \, of \, {\rm II^{nd}} \, and \, {\rm IV} \, group] \, [S^{-2}]{<} Ksp_{_{\rm IV}}$

(d). For precipitation of group III, NH₄OH is added in the presence of NH₄Cl to decrease the concentration of OH⁻ by common ion effect so ionic product of cations of group III and hydroxides ions exceed the solubility product of their corresponding metal hydroxides and only group III cations will precipitated. On the other hand cations of group IV, V and VI, which require large concentration of OH⁻ due to their high solubility product, will not be precipitated. (e). In IV group, H₂S gas is passed in basic medium to increase S⁻² ion concentration by odd ion effect, so that the ionic product of cations of group IV and S⁻ ² ions exceed the solubility product of their corresponding metal sulphide and hence gets precipitated.

$$\begin{array}{cccc} H_2S & \mathchoice{\longleftarrow}{\leftarrow}{\leftarrow} & \hline 2H^+ & + & S^{-2} \\ NH_4OH & \mathchoice{\longleftarrow}{\leftarrow}{\leftarrow} & NH_4^{+} & + & OH^- & H_2O \end{array} \end{array} \begin{array}{c} Odd \ ion \\ effect \end{array}$$

So $[S^{-2}]^{\uparrow}$ $Ksp_{IV} \leq [Radicals of group IV] [S^{-2}]$

(f). In V group, order of K_{sp} and precipitation is – BaCO₃ < SrCO₃ < CaCO₃

D. Precipitation of soap and salt (NaCl)

(i) Precipitation of NaCl (common salt):

For the precipitation of NaCl, HCl gas passed in saturated solution of NaCl to increase the concentration of Cl⁻ ion by common ion, so ionic product of concentration of Na⁺ and Cl⁻ ion is more than Ksp of NaCl and NaCl easily precipitated.

Saturated solution of NaCl $K_{sp} = [Na^+] [Cl^-]$ By passing of HCl gasHCl \iff H⁺ + Cl⁻due to common ion $K_{sp} < [Na^+] [Cl^-] \uparrow$

(ii) Precipitation of soap :

For precipitation of soap, NaCl mixed in saturated solution of soap to increase the concentration of Na^+ ion by common ion. So ionic product of concentration of Na^+ and strearate ions is more than Ksp of soap and soap is easily precipitated.

Ex. $C_{17}H_{35}COONa$ (Sodium stearate) Saturated solution of $C_{17}H_{35}COONar$ $K_{sp} = [C_{17}H_{35}COO^{-}]$ [Na⁺] By mixing of NaCl solution NaCl \implies Na⁺ + Cl⁻ due to common ion $K_{sp} < [C_{17}H_{35}COO^{-}]$ [Na⁺] \uparrow

Solved Examples

Ex.40 Solubility products of $M(OH)_3$ and $M(OH)_2$ are 10^{-23} and 10^{-14} respectively. Which will be precipitated first on adding NH_4OH , if M^{+2} and M^{+3} both the ions are in solution ?

$$(1) M^{+2}$$

(2) M^{+3}

(3) Both M^{+2} and M^{+3} together

(4) Precipitation will not take place.

Sol. (2)

Ex.41 Solubility of CaCl₂ is 4×10^{-8} , then find out its K_{sp} and its new solubility in the presence of 10^{-2} M Ca(OH)₂.

Sol.
$$\operatorname{CaCl}_{2} \rightleftharpoons \operatorname{Ca}^{+2} + 2\operatorname{Cl}^{-}$$

1 s 2s
(Initial solubility=s)
 $K_{sp} = 4s^{3} = 4(4 \times 10^{-8})^{3} = 256 \times 10^{-24}$ (i)
 $\operatorname{Ca(OH)}_{2} \rightleftharpoons \operatorname{Ca}^{+2} + 2\operatorname{OH}^{-}$
C 0 0
0 C 2C
 $\operatorname{CaCl}_{2} \rightleftharpoons \operatorname{Ca}^{+2} + 2\operatorname{Cl}^{-}$
1 s' +C 2s'
(New solubility=s')
 $K_{-} = [\operatorname{Ca}^{+2}]^{+}[\operatorname{Cl}^{-}]^{2}$

$$= [s' + C] [2s']^2 = 4s'^3 + 4s'^2C$$

(s'³=negligible)

$$K_{sp} = 4s'^2C$$

From equation (i) and (ii)

$$s'^{2} = \frac{K_{sp}}{4C} = \frac{256 \times 10^{-24}}{4 \times 10^{-2}} = 64 \times 10^{-22}$$
$$s' = 8 \times 10^{-11} \text{ mol } \text{L}^{-1}$$

Ex.42 Assertion : In acidic medium, Zn^{2+} is not precipitated by S^{-2} ions.

Reason : Common ion effect reduced the concentration of S^{-2} ions to the minimum value.

.....(ii)

Sol. (A)

FEW IMPORTANT POINTS

- A. Various forms of K_W
 - (a) $K_W = [H^+] [OH^-]$ for water $[H^+] = [OH^-]$
 - (b) $K_W = [H^+]^2$
 - (c) $K_W = [OH^-]^2$
 - (d) $K_W = [H_3O^+] [OH^-]$

(e)
$$K_W = [H_3O^+]^2 \{ [H_3O^+] = [H^+] \}$$

Hydronium Proton

ion

B. Isohydric solution –

If different–different solution has same pH are called isohydric solution.

Sp. point :– Isohydric conditions for two given weak acids HA_1 and HA_2 which has concentration C_1 and C_2 and ionisation constants are Ka_1 and Ka_2 respectively.

Then $[H^+]_1 = \sqrt{Ka_1C_1}$ and $[H^+]_2 = \sqrt{Ka_2C_2}$ According to given condition for isohydric solution pH of different solution is same.

Hence
$$[H^+]_1 = [H^+]_2$$

 $\sqrt{Ka_1 C_1} = \sqrt{Ka_2 C_2}$
 $\boxed{Ka_1 C_1 = Ka_2 C_2}$ or $\boxed{\frac{Ka_1}{V_1} = \frac{Ka_2}{V_2}}$ \therefore $\boxed{C \propto \frac{1}{V}}$

C. Strength of Acids and Bases :-

We known Strength of acid ∞ [H⁺]

If there are two weak acids HA_1 and HA_2 which has concentration C_1 and C_2 , degree of ionisation α_1 and α_2 and ionisation constants Ka_1 and Ka_2 respectively then ratio of their strength of acids.

We know
$$[H^+] = C\alpha = \sqrt{KaC}$$

So
$$\frac{\text{Strength of weak acid} \text{HA}_1}{\text{Strength of weak acid} \text{HA}_2}$$

$$=\frac{[H^+]_1}{[H^+]_2}=\frac{C_1\alpha_1}{C_2\alpha_2}=\frac{\sqrt{Ka_1C}}{\sqrt{Ka_2C}}$$

 $if C_1 = C_2$

Strength of weak acid HA_1 _	Ka ₁
Strength of weak acid HA_2	$\sqrt{\text{Ka}_2}$

Thus the relative strength of two acids of equimolar concentration can be compared by taking square root of the ratio of their ionisation constants. **D.** Resultant concentration :- When two non reactive electrolytes AB and CD which has concentration C_1 and C_2 and volume V_1 and V_2 respectively are mixed in one container then total volume of container is $(V_1 + V_2)$ and resultant concentration of each electrolyte is-

Resultant concentration of AB \implies C'₁ = $\frac{C_1 V_1}{V_1 + V_2}$

Resultant concentration of CD \Rightarrow C'₂ = $\frac{C_2 V_2}{V_1 + V_2}$

If volume of both electrolytes are equal

i.e.
$$V_1 = V_2 = V$$

then resultant concentration of each electrolyte is becomes half of initial concentration.

$$C'_{1} = \frac{C_{1}V}{V+V} = \frac{C_{1}}{2},$$
 $C'_{2} = \frac{C_{2}V}{V+V} = \frac{C_{2}}{2}$
 $C'_{1} = \frac{C_{1}}{2}$ and $C'_{2} = \frac{C_{2}}{2}$

Sp. Point : 'n' different solutions of non reactive different electrolytes are mixed in equal volume then

resultant concentration of each electrolyte is $\frac{1}{n}$ times.

Solved Examples

- **Ex.43** pH values of two acids A and B are 4 and 5. The strengths of these two acids are related as :-
 - (1) The strengths of the two acids cannot be compared.
 - (2) Acid B is 10 times stronger than acid A.
 - (3) Strength of acid A : Strength of acid B = 4 : 5
 - (4) Acid A is 10 times stronger than acid B.

Sol. (4)

- **Ex.44** Equal amounts of 0.004 M CaCl₂ and 0.002 M Na₂SO₄ are mixed. Find out, whether CaSO₄ will be precipitated or not, if K_{sp} of CaSO₄ is 2.5 × 10⁻⁵?
- **Sol.** When equal amounts of $CaCl_2$ and Na_2SO_4 are mixed then the concentration becomes half.

$$[Ca^{+2}] = \frac{[CaCl_2]}{2} = \frac{0.004}{2} = 0.002 \text{ M} \text{ and}$$

$$[\mathrm{SO}_4^{-2}] = \frac{0.002}{2} = 0.001 \text{ M}$$

Ionic product = $[Ca^{+2}] \times [SO_4^{-2}]$ = (0.002) × (0.001) = 2 × 10⁻⁶

Hence ionic product of $CaSO_4$ is 2×10^{-6} , which is less than its solubility product. Therefore, precipitation will not take place.

pH INTRODUCTION

- pH of some important substance :-
- (i) Blood \longrightarrow 7.4
- (ii) Tear \longrightarrow 7.4
- (iii) Gastric Juice \longrightarrow 1 to 3
- (iv) Soft drink \longrightarrow 2 to 4
- (v) Acidic rain $\longrightarrow 6$
- (vi) Milk \longrightarrow 6.3 to 6.6

(vii) Water $\longrightarrow 7$

TYPES OF pH

- (i) pH of SA and SB. $[H^+] = C$, $[OH^-] = C$
- (ii) pH of WA and WB. $[H^+] = C\alpha$, $[OH^-] = C\alpha$
- (iii) pH of very dilute solution.

(Consider H^+ & OH $^-$ of H_2O also)

- (iv) pH of salt solution.
 - (a) SA SB Type Salt (always 7)
 - (b) SA WB Type Salt (<7)
 - (c) WA SB Type Salt (>7)
 - (d) WA WB Type Salt (Almost 7)

(v) **pH of mixture of acid and base.**

(a) pH of mixture of acids :

 $N_1V_1 + N_2V_2 + N_3V_3 + \dots = NV$

V = Volume of final solution

$$= V_1 + V_2 + V_3 + \dots$$

N=Normality of final solution

= [H⁺] in final solution.

(b) pH of mixture of base : $N_1V_1 + N_2V_2 + N_3V_3 + \dots = NV$ V = Volume of final solution $= V_1 + V_2 + V_3 + \dots$ N = Normality of final solution $= [OH^-] in final solution.$ (c) pH of mixture of acids and bases : For acid : $N_1V_1 + N_2V_2 + N_3V_3 + \dots = (NV)_{Acid}$ For base : $N_1V_1 + N_2V_2 + N_3V_3 + \dots = (NV)_{Base}$ If $(NV)_{Acid} > (NV)_{Base}$ then solution is acidic. $NV = (NV)_{Acid} - (NV)_{Base}$ and $[H^+] = N$ If $(NV)_{Base} > (NV)_{Acid}$ then solution is basic. $NV = (NV)_{Base} - (NV)_{Acid}$ and $[OH^-] = N$

BUFFER SOLUTION

INTRODUCTION

A. Definition :

Those solution which have resistive nature for pH change are called Buffer Solution.

B. Properties of buffer solution :

- (i) pH of buffer solution is never depends on their concentration and dilution. (water add or escape).
- (ii) When some amount of strong acid and strong base are mixed in buffer solution then pH of buffer solution is almost unchange.

Special point :-

Change in pH of a solution due to change in concentration of present free H^+ or OH^- ions.

TYPES OF BUFFER SOLUTION

- (A). Simple buffer solution
- (B). Mixed buffer solution :-
 - (i) Acidic buffer solution
 - (ii) Basic buffer solution

A. Simple buffer solution :-Aqueous solution of weak acid-weak base (WA – WB) types of salt. Ex. CH₃COONH₄, NH₄CN, AgCN etc. $pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$ CH₃COO⁻+ NH₄⁺ + H₂O \rightleftharpoons CH₃COOH + NH₄OH. Case 1. When mixing of acid [H⁺] CH₃COO⁻ + H⁺ \rightleftharpoons CH₃COOH NH₄OH + H⁺ \rightleftharpoons NH₄⁺ + H₂O Case 2. When mixing of base [OH⁻] NH₄⁺ + OH⁻ \rightleftharpoons NH₄OH

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

- **B.** Mixed buffer solution :
- (i) Acidic buffer solution :- Aqueous solution of mixture of weak acid and salt of same weak acid with any type of strong base is called acidic buffer solution.
 - Ex. CH₃COOH + CH₃COONa WA WASB
 - Weak acid + Strong base
 - 1. When $N_1 V_1 = N_2 V_2 \Longrightarrow Salt (WASB)$
 - 2. When $N_1V_1 > N_2V_2 \Rightarrow$ Acidic buffer solution (WA+WASB salt)

 $[CH_3 COOH + CH_3 COONa]$ $[CH_3 COOH + CH_3 COO^-]$

Na⁺(Spectator ion)

Case 1.

When mixing of acid [H⁺]

 $CH_3COO^- + H^+ \implies CH_3COOH$

Case 2.

When mixing of base [OH-]

 $CH_{3}COOH + OH^{-} \Longrightarrow CH_{3}COO^{-} + H_{2}O$

ie. in aqueous solution if weak acid and its conjugate are present then it is definitely acidic buffer solution.

a. pH of acidic buffer solution :

CH₃ COONa CH, COOH +Salt Acid + $CH_{3}COO^{-}] + Na^{+}$ [CH₃COOH + Acid Conjugate $CH_3COOH \implies CH_3COO^- + H^+$ $\mathbf{K}_{a} = \frac{\left[\mathbf{CH}_{3}\mathbf{COO^{-}}\right]\left[\mathbf{H}^{+}\right]}{\left[\mathbf{CH}_{3}\mathbf{COOH}\right]}$ or $[H^+] = \frac{\text{Ka}[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{\text{Ka}[\text{Acid}]}{[\text{Conjugate}]}$ taking-log on both sides $pH = pKa - log \frac{[Acid]}{[Conjugate]}$ or $pH = pKa + log \frac{[Conjugate]}{[Acid]}$ **Henderson's equation :** [Salt]

$$pH = pKa + \log \frac{[Call]}{[Acid]}$$

- **b. pH range of acidic buffer solution :** CH₃ COOH CH₃ COONa
 - 1 : 10 $pH=pKa + \log \frac{10}{1}$ pH = pKa + 110 : 1 pH = pKa - 1

So pH range

pH = pKa ± 1

(c) Maximum buffer action condition of acidic buffer solution :

CH₃COOH CH₃COONa

$$1 \qquad : \qquad 1 \qquad pH = pK_a + \log \frac{1}{1}$$
$$pH = pKa$$

(ii) Basic buffer solution :

Definition : Aqueous solution of mixture of weak base and salt of same weak base with any type of strong acid is called basic buffer solution.

Ex. $NH_4OH + NH_4Cl$ $[NH_4^+] = [NH_4Cl]$

 $[NH_4OH + NH_4^+] + Cl^-[Spectator]$

Case 1. When mixing of acid [H⁺]

 $\mathrm{NH_4OH} + \mathrm{H^+} \Longrightarrow \mathrm{NH_4^+} + \mathrm{H_2O}.$

Case 2. When mixing of base [OH⁻] $NH_4^+ + OH^- \rightleftharpoons NH_4OH$

(a) pOH of basic buffer solution :

 $[NH_4OH + NH_4Cl]$

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

$$K_{b} = \frac{\left[NH_{4}^{+}\right]\left[OH^{-}\right]}{\left[NH_{4}OH\right]} \text{ or }$$

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

taking-log on both sides

$$pOH = pK_{b} + \log \frac{\left[NH_{4}^{+}\right]}{\left[NH_{4}OH\right]}$$

Henderson's equation :

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

(b) pOH range of basic buffer solution :

$$NH_4OH : NH_4Cl$$

$$1 : 10$$

$$10 : 1$$

$$pOH = pK_b \pm 1$$

(c) Maximum buffer action condition of basic buffer solution :

$$NH_4OH : NH_4Cl$$

$$1 : 1$$

$$pOH = pK_b$$

BUFFER CAPACITY

Definition :- It is defined as the number of moles of acid (or base) require by one litre of a buffer solution for changing its pH by one unit.

Buffer capacity =

Number of equivalents of acid or base added per litre Change in pH of buffer solution

Solved Examples

Ex.45 When 2 moles of HCl is added to 1 L. of an acidic buffer solution, its pH changes from 3.9 to 3.4. Find its buffer capacity.

Sol. B.C. = $\frac{2}{0.5} = 4$

INDICATOR

INTRODUCTION

- A. **Definition :-** Those compound or substance which indicate the nature of solution by changes their self colour.
- **B.** Types of indicators :
- (a) Acidic indicator (HIn)

Ex. Phenolphthalein (HPh)

HPh		$\mathrm{H}^{\!\scriptscriptstyle +}$	+	Ph⁻
colourless				pink

(b) Basic indicator (InOH)

Ex. Methyl orange (MeOH) MeOH \rightleftharpoons Me⁺ + OH⁻ yellow orange red

OSTWALD THEORY OF INDICATORS

- (i) According to this theory, all the indicators are weak organic acid or base.
- (ii) Every indicator has light colour in its unionised form and dark colour in ionised form.
- (iii) Every indicator works in opposite medium (it means if it is acidic then it will work in basic medium and vice versa) it means colour change in opposite medium due to their unionised form is change in ionised form.

Case 1. HPh
$$\rightleftharpoons$$
 H⁺ + Ph⁻
In acidic medium [H⁺] [HPh] > [Ph⁻]
Colourless
Case2. HPh \rightleftharpoons H⁺ + Ph⁻
In basic medium [OH⁻] [Ph⁻] > [HPh]
Pink colour

(a) pH of acidic indicator -

$$HIn \Longrightarrow H^+ + In^-$$

Acidic indicator [HPh]

 $\mathbf{F}_{\mathbf{w}}$

$$\mathbf{K}_{\mathrm{I}} = \frac{\left[\mathbf{H}^{+}\right]\left[\mathbf{In}^{-}\right]}{\left[\mathbf{HIn}\right]}$$

$$[\mathrm{H}^{+}] = \frac{\mathrm{K}_{\mathrm{I}}[\mathrm{H}\mathrm{In}]}{[\mathrm{In}^{-}]}$$

Taking – log on both sides $pH = pK_1 - log [HIn] + log [In^-]$

$$pH = pK_{I} + log \frac{\left[In^{-}\right]}{\left[HIn\right]}$$

$$pH=pK_1 + log \frac{[Ionised form]}{[Unionised form]}$$

(b) pOH of basic indicator -InOH \implies In⁺ + OH⁻

$$\mathbf{K}_{\mathrm{I}} = \frac{\left[\mathrm{In}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{In}\mathrm{OH}\right]}$$

$$pOH = pK_1 + log \frac{[lonised form]}{[Unionised form]}$$

[HIn] : [In⁻]
1 : 10
10 : 1

$$pH = pK_1 \pm 1$$

(d)	pOH range of	basic ir	ndicator :	(e) Neutral condition for indicators
	[InOH]	:	$[In^+]$	(No working condition)
	1	:	10	For acidic indicator For basic indicators
	10	:	1	[HIn] : [In-] [InOH] : [In+]
	pOH = pK	1 ± 1		1 : 1 1 : 1
				$pH = pK_1$ $pOH = pK_1$

S.No.	Name of indicator	Colour in acidic	Colour in basic	Working pH range
	medium	medium	of indicators	
1.	Methyl orange (MeOH)	Orange red	Yellow	3.1 to 4.5
2.	Methyl red	Red	Yellow	4.2 to 6.2
3.	Phenol red	Yellow	Red	6.2 to 8.2
4.	Phenolphthalein (HPh)	Colourless	Pink	8.2 to 10.2

ACID-BASE TITRATION

S.No.	Type of titration	pH range of titration Suitable indicators
1.	SA/SB.	3 – 11 All indicators (MeOH, HPh etc.)
2.	SA/WB	3-7 Methyl orange (MeOH) and methyl red
3.	WA/SB7 – 11	Phenolphthalein (HPh)
4.	WA/WB	6.5 – 7.5 Phenol red

Important points of titration :

- (i). Titration is always possible in two opposite solution. (i.e. one is acidic and other is basic).
- (ii). For any titration only that indicator is suitable if their working pH range is in pH range of titration.
- (iii). At the end point of titration equivalents of acids and bases are always same.
- (iv). At the end point, nature of solution depends on the type of titration.

SA/SB	-	Neutral $(pH = 7)$
SA/WB	-	Acidic
WA/SB	-	Basic
WA/WB	-	Any one possible

BENZENOID AND QUINONOID THEORY OF INDICATORS

- (i). According to this theory, all indicators are aromatic compounds.
- (ii). Unionised form of indicator is called benzenoid form and ionised form is called quinonoid form.



Benzenoid form (Unionised form)

Quinonoid form (Ionised form)

- (iii). Every indicator has light colour in its benzenoid form and dark colour in quinonoid form.
- (iv). Every indicator works in opposite medium due to their benzenoid form (unionised form) is changes in quinonoid form (ionised form).
 - (a)



ACID AND BASE

INTRODUCTION

The earliest classification of substances into acids and bases was bases upon the characteristic properties possessed by each one of them. For example,

Acid was defined as a substance whose aqueous solution possesses the following characteristic properties:

(i) conducts electricity,

(ii) reacts with active metals like zinc, magnesium etc. to give hydrogen,

- (iii) turns blue litmus red.
- (iv) has a sour taste.

(v) whose acidic properties disappear on reaction with a base.

Base was defined as a substance whose aqueous solution possessed the following characteristic properties:

(i) conducts electricity,

(ii) reacts with active metals like zinc, magnesium etc. to give hydrogen,

(iii) turns red litmus blue,

(iv) has a bitter taste

 $\left(v\right)$ whose basic properties are destroyed on reaction with an acid.

The above definitions of acids and bases are called operational definitions as they are based certain operations (i.e. tests) to be performed on the substances. However, these have been replaced by conceptual definitions (put forward by Arrhenius, Bronsted-Lowry and Lewis) which go into the causes of the observed behaviour, based upon structure and composition of the substances.

ARRHENIUS CONCEPT (1884)

(a) Acid:- According to this concept, those substances which produce free H⁺ ions in aqueous solution are called acid.

Ex. HCl, HNO₃, H_2SO_4 , H_3PO_4 , H_2CO_3 , H_2S , CH₃COOH etc.

$$\begin{split} & \text{HCl} + \text{H}_2\text{O} \longrightarrow \text{H}^+(\text{aq.}) + \text{Cl}^-(\text{aq.}) \\ & \text{H}_2\text{SO}_4 + \text{H}_2\text{O} \longrightarrow 2\text{H}^+(\text{aq.}) + \text{SO}_4^{-2}(\text{aq.}) \\ & \text{CH}_3\text{COOH} + \text{H}_2\text{O} \longrightarrow \end{split}$$

$$CH_3COO^-(aq.) + H^+(aq.)$$

 (b) Base :- Those substances which produce free OHions in aqueous solution are called base.
 Ex. NaOH, KOH, Cs(OH), Rb(OH), NH₄OH,

Ex. NaOH, KOH, Cs(OH), KO(OH), NH_4OH , Ba(OH)₂, Ca(OH)₂, Al(OH)₃ etc.

 $NaOH + H_2O \longrightarrow Na^+ (aq.) + OH^- (aq.)$ $Ba(OH)_2 + H_2O \longrightarrow Ba^{+2} (aq.) + 2OH^- (aq.)$ $Al(OH)_3 + H_2O \longrightarrow Al^{+3} (aq.) + 3OH^- (aq.)$

- (c) Nature of water :- According to this concept nature of water is neutral and act as a solvent.
- (d) Neutralisation Reaction :- Those reactions in which acid and base react together to form water molecule are called neutralisation reactions.
 - i.e. $Na^+ + OH^- + H^+ + Cl^- \longrightarrow NaCl + H_2O$ $H^+ + OH^- \longrightarrow H_2O$

(e) Strength of acids and bases :- This concept explains the strength of acids and bases depending upon the basis of degree of ionisation.

Ex. For strong electrolytes $\alpha \simeq 100\%$ For weak electrolytes $\alpha < 100\%$

- (f) Advantage :- This concept explains the acids and bases practically. i.e. To find out the pH, ionisation constant, hydrolysis constants, heat of neutralisation etc.
- (g) Disadvantage :-
 - (i) It explains the behaviour of acids and bases only in aqueous (water) solvents.
 - (ii) It does not explain the stability of proton (H^+) .

(iii) It does not explain the conjugate acid-base theory.

(iv) It does not explain the acidic and basic behaviour of aprotic acid and base for example - SO_2 , CO_2 , $SiCl_4$, $AlCl_3$ etc.

Solved Examples

- **Ex.46** Gaseous hydrogen chloride is a very poor conductor of electricity but a solution of hydrogen chloride in water is a good conductor. This is due to the fact that :-
 - (1) Water is a good conductor of electricity
 - (2) Hydrogen chloride ionises in water
 - (3) A gas cannot conduct electricity but a liquid can
 - (4) HCl does not obey Ohm's law where as the solution does

Sol. (2)

- **Ex.47** Which is acid in the following pairs according to Arrhenius concept?
 - (i) HCl(g) and HCl (aq)
 - (ii) CH₃COOH(1) and CH₃COOH(aq)
- Sol. (i) HCl(aq.)

(ii) CH₃COOH(aq.)

BRONSTED-LOWRY CONCEPT (1923)

It is based upon the exchange of proton.

(a) Acid :- According to this concept those substances which have tendency to donate the proton (H⁺) by any method in any solvent are called acids.

Ex.

- (i) HCl, HNO₃, H₂SO₄, H₂CO₃, H₂S, CH₃COOH, H₃PO₃ etc.
- (ii) HS^- , HCO_3^- , HSO_4^- , $H_2PO_4^-$, HPO_4^{-2} , H_2O etc.
- (iii) NH_4^+ , H_3O^+ , PH_4^+ , $CH_3COOH_2^+$ etc.

(vi)
$$[Al(H_2O)_6]^{+3}$$
, $[Ag(H_2O)_2]^{+1}$, $[Fe(H_2O)_6]^{+3}$ etc.
(a) $HCl(Acid) + H_2O(Solvent) \longrightarrow$

(b) $HS^{-}(Acid) + H_2O(Solvent) \longrightarrow H_3O^{+} + S^{-2}$

(c)
$$NH_4^+(Acid) + H_2O(Solvent) \longrightarrow NH_3^+ + H_3O^+$$

(d)
$$[Al(H_2O)_6]^{+3}(Acid) + H_2O(Solvent) \longrightarrow$$

 $[Al(H_2O)_5OH]^{+2} + H_3O^{+}$

(b) **Base :-** Those substances which have tendency to accept the proton by any method in any solvent are called the bases.

Ex.

- (i) NaOH, KOH, Rb(OH), Cs(OH), Ba(OH)₂, Ca(OH)₂, NH₄OH, Al(OH)₃ etc.
- (ii) HS^- , HCO_3^- , HSO_4^- , $H_2PO_4^-$, HPO_4^{-2} , H_2O etc.
- (iii) NH_3 , RNH_2 , R_2NH , R_3N , $C_6H_5NH_2$, C_5H_5N , H_2N-NH_2 etc.

(iv)
$$O^{-2}$$
, SO_4^{-2} , CO_3^{-2} , CI^- , Br^- , I^- , CN^- etc.

0

(a) NaOH (Base) +
$$H_2O$$
 (Solvent) \longrightarrow

$$H^{-} \xrightarrow{+NaOH_{2}^{+}} Na^{+} + H_{2}O$$

(b)
$$HS^{-}(Base) + H_2O(Solvent) \longrightarrow H_2S + OH^{-1}$$

(c) NH_3 (Base) + H_2O (Solvent) \longrightarrow $NH_4^+ + OH^-$

(d)
$$CO_3^{-2}(Base) + H_2O(Solvent) \longrightarrow HCO_3^{-} + OH^{-1}$$

Equilibrium

- (c) Nature of water :- According to this concept nature of water is amphoteric or amphiprotic i.e. water can act as both acid and base.
- (i) HCl (Acid) + H₂O (Base) \longrightarrow Cl⁻ + H₃O⁺
- (ii) $NH_3(Base) + H_2O(Acid) \longrightarrow NH_4^+ + OH^-$
- (d) Neutralisation Reaction :- According to this concept those reaction in which acid and base react together and convert into their respective conjugate acid and base are called neutralisation reactions.
 Ex.



(e) Strength of acids and bases :- This concept explain the strength of acid and base depending upon the basis of relative tendency to accept or donate the proton.

(i) HClO ₄	(ii)	HI
(iii) HBr	(iv)	H_2SO_4
(v) HCl	(vi)	HNO ₃
(vii) H ₃ O ⁺	(viii)	HSO_4^-
(ix) H ₃ PO ₄	(x)	HF
(xi) CH ₃ COOH	(xii)	H_2CO_3
(xiii) H ₂ S	(xiv)	NH_4^+
(xv) HCN	(xvi)	C ₆ H ₅ OH
(xvii) H-OH	(xviii)	C ₂ H ₅ –OH
$(xix)C_6H_5NH_2$	(xx)	NH ₃
(xxi) R–NH ₂	(xxii)	CH_4
(xxiii) H.		

Ex.

(i)	HCl + $H_2O \rightleftharpoons$	Cl^- + H_3O^+
	Strong acid	Strong base
	Weak base	Weak acid
(ii)	$CH_3COOH + H_2O$	\implies CH ₃ COO ⁻ + H ₃ O ⁺

Weak acid Strong base Weak base

Strong acid

- (iii) NH₃ + NH H,O Weak base Weak acid Strong acid Strong base (iv) HCl + CH₂COOH \implies Cl⁻+ CH₂COOH₂+ Weak acid Weak base Strong acid Strong base (v) $HCl + NH_3$ Cl- + NH_{4}^{+} Strong acid Strong base Weak base Weak acid (vi) $CH_3COOH + NH_3 \implies CH_3COO^- + NH_4^+$
- (vi) $CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$ Strong acid Strong base Weak base Weak acid

Types of solvent :

(a) Protogenic or acidic solvent :- They have a tendency to generate or donate the protons.

Ex. CH_3COOH , HCl, HNO_3 , H_2SO_4 etc.

(b) Protophilic or basic solvent :- They have a tendency to accept the protons.

Ex. NH₃, CH₃OH, RNH₂ etc.

(c) Amphiprotic or amphoteric solvents :- They have the tendency to accept or donate the protons or they are either protophilic or protogenic.

Ex. H_2O , HS^- , C_2H_5OH , HSO_4^- , HCO_3^- etc.

(d) Aprotic solvents :- They neither donate nor accept the protons.

Ex. C_6H_6 , CCl_4 , $CHCl_3$, BrF_3 , NO_2 , $COCl_2$ etc.

(e) Ampholyte solvents:-Those solvents in which the same molecule acts as proton donor and proton acceptor.

Ex. (i)



Special point :- Every ampholyte is amphoteric but every amphoteric is not ampholyte. (i) Compounds whose central atom of the second second

Ex. H₂O (amphoteric)

(f) Advantage :-

- (i) It explain the behaviour of acids and bases in any type of solvent.
- (ii) It explain the stability of proton (H^+) .
- (g) Disadvantage :-
 - (i) It does not explain the acid and base practically.
 - (ii) According to this concept every acid and base reaction is a neutralisation reaction which is not true.
 - (iii) It fails to explain the acidic and basic behaviour of aprotic acids and bases also.

For ex. SO₂, SO₃, CO₂, AlCl₃, SiCl₄, etc.

Solved Examples

Ex.48 In the process : $NH_3 + NH_3 \implies NH_2^- + NH_4^+$, The nature of ammonia is:-

(1)Acidic	(2) Basic
(3) Amphoteric	(4) None

Sol. (3)

Ex.49 Which of the following behave both as Bronsted acid as well as Bronsted bases ?

H₂O, HCO₃⁻, H₂SO₄, H₃PO₄, HS⁻, NH₃ **Sol.** H₂O, HCO₃⁻, HS⁻, NH₃

Ex.50 Assertion : Cl⁻ is weaker base than $^{\ominus}OC_{2}H_{5}$.

Reason : Cl⁻ is conjugate base of stronger acid, HCl.

Sol. (A)

LEWIS CONCEPT (1939)

(a) Lewis acid :- According to this concept those species which have self tendency to accept the lone pair of electrons are called acids. i.e. Lewis acid is an electron pair acceptor (electrophilic).

 $H^+ +: \ddot{O}_x H^- \longrightarrow H: \ddot{O}_x H$ Acid Base (i) Compounds whose central atom have an incomplete octect (electron deficient)

Ex. BF₃, BBr₃, BCl₃, BI₃, B(CH₃)₃, B(OH)₃, AlCl₃, GeCl₃ etc.

$$\stackrel{-\delta}{F} \stackrel{+\delta}{\longleftarrow} \stackrel{-\delta}{B} \stackrel{-\delta}{\longrightarrow} \stackrel{-\delta}{F} \\ \downarrow \\ F^{-\delta}$$

 (ii) Compounds whose central atom have vacant dorbitals and can accept one or more pair of lone electrons.

Ex. SF₄, SF₆, SnCl₂, SnCl₄, PX₃, PX₅, GeX₄, TeX₄, IF₅, IF₇, etc.



(iii) Molecules with a multiple bond between atoms of different electronegativities.

Ex. CO₂, SO₂, SO₃ etc.

$$\overrightarrow{O} = \overrightarrow{C} = \overrightarrow{O}$$
 $\overrightarrow{O} = \overrightarrow{S} = \overrightarrow{O}$
 $\overrightarrow{O} = \overrightarrow{S} = \overrightarrow{O}$
 $\overrightarrow{O} = \overrightarrow{S} = \overrightarrow{O}$
 $\overrightarrow{O} = \overrightarrow{C} = \overrightarrow{O} + \overrightarrow{OH^{-}} \longrightarrow \overrightarrow{O} - \overrightarrow{C} = \overrightarrow{O} \longrightarrow \overrightarrow{HCO_{3}^{-}}$
Lewis acid Lewis base |
 \overrightarrow{OH}
SO₂ + H.O $\longrightarrow \overrightarrow{H.SO_{2}}$

Lewis acid Lewis base

(iv) Cations :-

Ex. Ag^+ , Na^+ , Li^+ , Al^{+3} , Be^{+2} , Mg^{+2} , I^+ , Cl^+ , H^+ etc.

False cations :-

Ex. NH_4^+ , H_3O^+ , $\operatorname{CH}_3\operatorname{COOH}_2^+$, PH_4^+ etc. Ex. $\operatorname{Ag}^+ + 2 : \operatorname{NH}_3 \rightleftharpoons [\operatorname{Ag}(:\operatorname{NH}_3)_2]^+$ $\operatorname{Cu}^{+2} + 2 (:\operatorname{H}_2O)_2 \longrightarrow [\operatorname{Cu}(:\operatorname{H}_2O)_4]^{+2}$ (v) Elements which have six electrons in their outermost shell or valence shell.

O-Family (O, S, Se, Te)

Po-Radioactive element

$$\begin{array}{l} SO_3^{-2} + \begin{tabular}{l} $SO_3^{-2} + \begin{tabular}{l} $O_3 \end{tabular} \longrightarrow \end{tabular} O \end{tabular} \\ Base & Acid \end{array}$$

(b) Lewis base :- Those species which have self tendency to donate the lone pair of electrons are called bases. i.e. a base is an electron pair (lone pair) donor (nucleophile).

Classification of Lewis bases :-

(i) Those species whose central atom have lone pair of electrons and have self tendency to donate them –

Ex.
$$\ddot{N}H_3$$
, $R - \ddot{N}H_2$, $R_2 - \ddot{N}H$, $C_6H_5 - \ddot{N}H_2$,
 $C_5H_5 - \ddot{N}$, $H_2\ddot{N} - \ddot{N}H_2$,
 $H - \ddot{O} - H$, $R - \ddot{O} - H$, $R - \ddot{O} - R$, $R - \ddot{S} - R$,
 $R - \ddot{S} - H$, etc.

Explain: $R \xrightarrow{-\delta} C \xleftarrow{R} R$ +I +I

(Electron density on O, increases due to +I effect)

(ii) Anions –

Ex. O^{-2} , SO_4^{-2} , CO_3^{-2} , CI^- , Br^- , F^- , I^- , N^{-3} , P^{-3} , NO_3^- , S^{-2} , CN^- , etc.

- (c) Nature of water :- According to this concept nature of water is basic i.e. water is a base.
- (d) Neutralisation Reaction :- According to this concept those reactions in which acid and base react together to form a co-ordinate bond between them are called neutralisation reactions.

Ex.

$$F_3 B + NH_3$$
 $[F_3 B NH_3]$

Lewis acid Lewis base

$$H^{+} + NH_{3} \qquad [H \quad NH_{3}]^{+} \qquad NH_{4}^{+}$$
$$H^{+} + H_{2}O^{+} \qquad \left[H \quad O_{H}^{+}\right] \qquad H_{3}O^{+}$$

$$Ag^{+} + 2NH_{3}$$
 $[H_{3}N Ag NH_{3}]^{+}$
 $[Ag (NH_{3})_{2}]^{+}$

Strength of acids and bases :- This concept explain the strength of acids and bases depending upon the basis of self tendency. To accept or donate the lone pair of electrons (e^{-}) .

Ex. SO₂ < SO₃ (Strong acid)

(f) Advantage :-

(e)

(a) This concept explains the acid and base without any solvent.

(b) This concept explains those acids and bases which are not explained by other concepts.

(g) Disadvantage :-

(a) This concept fails to explain the acid and base practically.

(b) According to this concept forming of coordinate bond in neutralisation reaction of acid and base is a slow process, whereas neutralisation reaction of acids and bases is actually fast process.

(c) This concept fails to explain the real acids and bases

Ex. HCl, HNO₃, H₂SO₄, NaOH, KOH, etc.

Special point :- All the lewis bases are bronsted bases but all the lewis acids are not bronsted acids.

Solved Examples

Ex.51 Lewis base is :-

$(1) \mathrm{NH}_3$	(2) CO ₂
(3) BCl ₃	(4) K ⁺

Sol. (1)

- **Ex.52** How does Lewis theory explain the acidic character of CO₂?
- **Sol.** According to Lewis concept, CO_2 is Lewis acid because carbon atom is attached to more electronegative oxygen atoms on both sides by double bonds. It can easily accept an electron pair from the Lewis base such as OH⁻ ion.

$$OH^- + O = C = O$$

Lewis base Lewis acid
 OH
 $O = C - O^-$ or HCO_3^-
Bicarbonate ion

CLASSIFICATION OF ACIDS AND BASES

- A. Classification of all the acids :-
 - (a) Oxy acids :- Nonmetal + O HNonmetal ---O - H
 - (i) When nonmetals are different then –
 Acidic character ∞ Electronegativity (E.N.)



- (a) $H_3BO_3 < H_2CO_3 < HNO_3 < H_2SO_4 < HClO_4$
- (b) $HIO_4 < HBrO_4 < HClO_4$
- (c) $HAsO_3 < HPO_3 < HNO_3$

(ii) When non metals are same then : Acidic character ∞ oxidation number (O.N.)

- (a) $H_{NO_2}^{+3} < H_{NO_3}^{+5}$
- (b) $H_2 \overset{+4}{SO}_3 < H_2 \overset{+6}{SO}_4$
- (c) $HOCI < HCIO_2 < HCIO_3 < HCIO_4$
- (d) $H_3^{+5}PO_4 < H_3^{+3}PO_3 < H_3^{+1}PO_2$ (exception)
- (b) Hydrides :-







- **Ex.** (i) HF < HCl < HBr < HI(ii) $NH_3 < PH_3 < AsH_3$ (iii) $CH_4 < NH_3 < H_2O < HF$
- (c) Acidic anhydrides :-

Ex.
$$H_2SO_3 \xrightarrow{-H_2O} SO_2$$

 $H_2SO_4 \xrightarrow{-H_2O} SO_3$
 $2HNO_2 \xrightarrow{-H_2O} N_2O_3$
 $2HNO_3 \xrightarrow{-H_2O} N_2O_5$
 $2HCIO_4 \xrightarrow{-H_2O} Cl_2O_7$
 $2H_3PO_4 \xrightarrow{-3H_2O} P_2O_5$
 (HPO_3)
 $2 \times CH_3COOH \xrightarrow{-H_2O} (CH_3CO)_2O$



Special point :-Acidic order of acidic anhydrides is same as the acidic order of their oxy acids.

- **Ex.** $N_2O_3 < N_2O_5$ (Acidic order) $Cl_2O < Cl_2O_3 < Cl_2O_5 < Cl_2O_7$ (Acidic order)
- (d) Organic acid :-

- (i) If R shows + I effect → then acidic character decreases.
- (ii) If R shows−I effect → then acidic character increases.
- (e) For Cations :-

Acidic character \propto Charge density (+)

$$\propto \frac{1}{\text{Size of cation}}$$

 \propto Electronegativity (E.N.)

∝ Oxidation number (O.N.)

Ex. (i) $Li^+ < Ca^{+2} < Al^{+3}$

(ii)
$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$$

(iii)
$$Be^{+2} > Mg^{+2} > Ca^{+2} > Sr^{+2} > Ba^{+2}$$

(f) Acidic character in terms of H^+ , OH^- , K_a and K_b :-

Acidic character \propto [H⁺] $\propto \sqrt{K_a}$

B. Classification of all the bases :-

(a) Hydroxides :-

М —∕—О —— Н

(Metal)

Basic character $\propto \frac{1}{\text{Electronegativity of metal}}$

LiOH	Be(OH) ₂		B(OH) ₃	. 1
NaOH	Mg(OH) ₂		Al(OH) ₃	Electronegativity
КОН	Ca(OH) ₂	d-block	Ga(OH) ₃	Basic strength
RbOH	Sr(OH) ₂		In(OH) ₃	V
CsOH	Ba(OH) ₂		Tl(OH) ₃	

Electronegativity Basic strength

i.e. CsOH is the strongest base.

Ex.

(i) LiOH < NaOH < KOH < RbOH < CsOH

(ii)
$$Be(OH)_2 \le Mg(OH)_2 \le Ca(OH)_2 \le Sr(OH)_2 \le Ba(OH)_2$$

(b) Basic anhydrides :-

Ex. 2NaOH
$$\xrightarrow{-H_2O}$$
 Na₂O

$$2\text{LiOH} \xrightarrow{-H_2O} \text{Li}_2O$$

 $Ba(OH)_2 \xrightarrow{-H_2O} BaO$

 $2\mathrm{Al(OH)}_{3} \xrightarrow{-3\mathrm{H}_{2}\mathrm{O}} \mathrm{Al}_{2}\mathrm{O}_{3}$

(Amphoteric oxide)

Special point :- Basic order of basic anhydrides is same as the basic order of their metal hydroxides.

(c) Organic Base :-

(i) If R shows + I effect \longrightarrow then basic characters are increases.

(ii) If R shows – I effect \longrightarrow then basic characters are decreases.

Ex. $C_6H_5NH_2 < NH_3 < CH_3NH_2 < C_2H_5NH_2 < C_3H_7NH_2$ (Basic order)

(d) For anions :-

Basic character \propto Charge density (-)

$$\propto \frac{1}{\text{Size of anion}}$$

$$\frac{1}{\text{Oxidation number}}$$

Ex. (i)
$$F^- < O^{2-} < N^{-3}$$

(ii) $F^- > Cl^- > Br^- > l^-$

(e) Basic characters in terms of OH⁻, H⁺, K_{b} and K_{a} :-

α

Basic character \propto [OH⁻] $\propto \sqrt{K_{b}}$

Basic cha	racter 1	ìſ	[OH-]	↑	or
рОН↓	or	pH↑		or	$[\mathrm{H}^{\scriptscriptstyle +}] \checkmark $
Basic cha	racter ↑	if	K_{b} \uparrow		or
pK _b ↓	or	pK_a^{\uparrow}		or	$K_a \downarrow$

Solved Examples

Ex.53 Least pKa value is for this acid :-

(1) F₃CCOOH

(2) CH₃COOH

- (3) (CH₃)₂CHCOOH
- (4) ClCH₂.COOH

Ex.54 Arrange the following in required order :

- (i) NH₃, C₆H₅NH₂, C₂H₅NH₂, CH₃NH₂ (increasing basic strength)
- (ii) KOH, Ga(OH)₃, Ca(OH)₂ (increasing basic strength)
- Ex.55 *Assertion* :- HBr is a stronger acid than HI.

Reason :– Bond energy of HI is smaller than that of HBr.

Sol. (D)

B.

POLYACIDIC BASE AND POLYBASIC ACIDS

A. Polyacidic base :

$$Al(OH)_{3} \iff Al^{+3} + 3OH^{-} \longrightarrow K_{b}$$

$$Al(OH)_{3} \iff [Al(OH)_{2}]^{+1} + OH^{-} \longrightarrow K_{b_{1}}$$

$$[Al(OH)_{2}]^{+1} \iff [Al(OH)]^{+2} + OH^{-} \longrightarrow K_{b_{2}}$$

$$[Al(OH)]^{+2} \iff Al^{+3} + OH^{-} \longrightarrow K_{b_{3}}$$

$$K_{b} = K_{b_{1}} \times K_{b_{2}} \times K_{b_{3}}$$

$$taking -log on both sides$$

$$pK_{b} = pK_{b_{1}} + pK_{b_{2}} + pK_{b_{3}}$$

$$i.e. \quad \overline{K_{b_{1}} > K_{b_{2}} > K_{b_{3}}} r [pK_{b_{1}} < pK_{b_{2}} < pK_{b_{3}}]$$

$$Polybasic acid :$$

$$H_{3}PO_{4} \iff 3H^{+} + PO_{4}^{-3} \longrightarrow K_{a}$$

$$H_{3}PO_{4} \iff H_{2}PO_{4}^{-1} + H^{+} \longrightarrow K_{a_{1}}$$

$$H_{2}PO_{4}^{-1} \iff HPO_{4}^{-2} + H^{+} \longrightarrow K_{a_{2}}$$

$$HPO_{4}^{-2} \iff PO_{4}^{-3} + H^{+} \longrightarrow K_{a_{3}}$$

$$K_{a} = K_{a_{1}} \times K_{a_{2}} \times K_{a_{3}}$$

taking-log on both sides

 $pK_a = pK_{a_1} + pK_{a_2} + pK_{a_3}$

 $\overline{|K_{a_1} > K_{a_2} > K_{a_3}|}$ r $pK_{a_1} < pK_{a_2} < pK_{a_3}$

Solved Examples

Ex.56 In the dissociation , $H_2A \xleftarrow{K_1} H^+ + HA^-$

$$HA^{-} \xleftarrow{K_{2}} H^{+} + A^{-2}$$

(1) K₁ is equal to K₂
 (2) K₁ is smaller than K₂
 (3) K₁ is greater than K₂
 (4) K₁ is negligible

Ans. (3)

Ex.57 Calculate the pH of 2.0×10^{-4} M H₃X Solution assuming first dissociation to be 100%, second to be 50% and third to be neglegible :

Sol. First dissociation :

$$H_3X \implies H_2X^- + H^+$$

 $\therefore \quad H^+ \text{ ion concentration} = 2 \times 10^{-4} \text{ M}$ Second dissociation :

 $H_{2}X^{-} \Longrightarrow HX^{-} + H^{+}$

H⁺ ion concentration

$$= C\alpha = 2 \times 10^{-4} \times 0.5$$

- : Third dissociation is negligible
- :. $[H^+] = 2 \times 10^{-4} + 10^{-4} = 3 \times 10^{-4}$ pH = 4 - log3 = 3.52