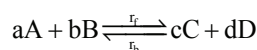


**CHEMICAL EQUILIBRIUM**

Consider a reversible reaction,

**At Equilibrium State**

Rate of forward reaction ( $r_f$ ) = rate of backward reaction ( $r_b$ )

So, at equilibrium,

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{K_f}{K_b} \quad \text{In terms of active mass}$$

$$K_p = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b} \quad \text{In terms of partial pressure}$$

$$K_X = \frac{[X_C]^c [X_D]^d}{[X_A]^a [X_B]^b} \quad \text{In terms of mole fraction}$$

$$K_p = K_C (RT)^{\Delta n_g}$$

while determining  $\Delta n_g$  take only gaseous species.

The active mass of solid and pure liquid is a constant quantity (unity) because it is an intensive property.

**Unit of Equilibrium Constant**

$$K_C = (\text{mol L}^{-1})^{\Delta n_g}; K_p = (\text{atm})^{\Delta n_g}$$

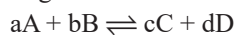
Application of  $K_C$  or  $K_p$

- ❖ More is the value of  $K_p$  or  $K_C$  more is the extent of reaction.
- ❖ Stability of reactant increases when value of  $K$  decreases.
- ❖ Stability of Product increases when value of  $K$  increases.

**Characteristics of Equilibrium Constant**

**Predicting the direction of reaction:** Reaction Quotient ( $Q$ ) is expressed in the same way as for equilibrium constant, except that the concentrations may not necessarily be at equilibrium.

In general for the reversible reaction:



$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$Q = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b} \quad (\text{in terms of pressure})$$

If  $Q = K_{eq}$  then system is in equilibrium

If  $Q > K_{eq}$  then system proceed in backward direction to attain equilibrium.

If  $Q < K_{eq}$  then system proceed in forward direction to attain equilibrium.

$$\text{Degree of dissociation } (\alpha) = \frac{\text{No. of moles of reactant dissociated}}{\text{No. of mole of reactant present initially}}$$

## Le-Chatelier's Principle

If a system at equilibrium is subjected to a change of any one of the factors such as concentration, pressure or temperature then the equilibrium is shifted in such a way so as to nullify the effect of change.

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

**Table: Factors Affecting Equilibria**

Effect due to change in		$\Delta n_g = 0$ $A \rightarrow B + \text{Heat}$	$\Delta n_g > 0$ $A \rightarrow 2B + \text{Heat}$	$\Delta n_g < 0$ $2A \rightarrow B + \text{Heat}$
Concentration	(i) $\uparrow [A]$	Forward direction	Forward direction	Forward direction
	(ii) $\downarrow [A]$	Backward direction	Backward direction	Backward direction
Pressure	(i) $\uparrow$ in pressure	Unchanged	Backward direction	Forward direction
	(ii) $\downarrow$ in pressure	Unchanged	Forward direction	Backward direction
Temperature	(i) $\uparrow$ in Endothermic	Forward direction	Forward direction	Forward direction
	(ii) $\uparrow$ in Exothermic	Backward direction	Backward direction	Backward direction
Dissociation	(i) $\uparrow$ in pressure	Unchanged	Dissociation Decreases	Dissociation Increases
	(ii) $\uparrow$ in volume	Unchanged	Dissociation Increases	Dissociation Decreases
Mixing of inert gas	(i) at constant P	Unchanged	Dissociation Increases	Dissociation Decreases
	(ii) at constant V	Unchanged	Unchanged	Unchanged

## IONIC EQUILIBRIUM

ACID BASE THEORIES (Arrhenius Concept)	
Acid	Base
Which produce $H^+$ ion in aqueous solution. e.g. $HCl$ , $H_2SO_4$ , $HClO_4$ , $H_3PO_4$ , $CH_3COOH$ but $H_3BO_3$ is not a Arrhenius acid. <b>Major Limitation:</b> Defined only in water solvent.	Which produce $OH^-$ ion in aqueous solution. e.g. $NaOH$ , $Mg(OH)_2$ , $Ba(OH)_2$

Bronsted – Lowry Concept	
<b>Acid:</b> Which gives $H^+$ in any solvent. <b>Base:</b> Which accepts $H^+$ in any solvent $\begin{array}{c} \text{HCl} + \text{NH}_3 \rightarrow \text{Cl}^- + \text{NH}_4^+ \\ \text{Acid} \quad \text{Base} \quad \text{Conjugate Base} \quad \text{Conjugate Acid} \end{array}$ <b>Major Limitation:</b> Does not explain acidic behaviour of aprotic acids e.g. $SO_2$ , $CO_2$ , $AlCl_3$ , $SiCl_4$	To find conjugate base of any Acid $\rightarrow$ Remove one $H^+$ To find conjugate acid of any Base $\rightarrow$ add one $H^+$ Water is Amphiprotic solvent (can accept as well as lose $H^+$ ) $H_2O \rightarrow H^+ + OH^-$ $H_2O + H^+ \rightarrow H_3O^+$

Lewis Theory	
Acid	Base
Types of Lewis acid	Types of Lewis Base
Lewis acid is an electron pair acceptor.	Lewis base is an electron pair donor.
1. <b>Having Incomplete octet:</b> $BF_3$ , $BCl_3$ , $B(OH)_3$ , $AlCl_3$ etc. 2. <b>Having vacant d-orbitals:</b> $SF_4$ , $SF_6$ , $SnCl_2$ , $SnCl_4$ etc. 3. <b>Having multiple bonds between atoms of different EN:</b> $CO$ , $SO_2$ , $SO_3$ etc. 4. <b>Cations</b> $Ag^+$ , $Li^+$ , $Al^{3+}$ , $Mg^{2+}$ <b>False cations (which cannot act as Lewis acid):</b> $NH_4^+$ , $H_3O^+$ , $PH_4^+$ etc.	1. Neutral molecule having lone pair $\ddot{N}H_3$ , $R - \ddot{N}H_2$ , $R_2 - \ddot{N}H$ , $H - \ddot{O} - H$ , $R - \ddot{O} - R$ etc. 2. <b>Anions:</b> $O^{2-}$ , $SO_4^{2-}$ , $CO_3^{2-}$ , $Cl^-$ , $Br^-$ , $I^-$ , $CH_3COO^-$ etc. All the Lewis bases are Bronsted bases but all the Lewis acids are not Bronsted acids. All Arrhenius acids are Bronsted acid but it is not so for bases.

Ostwald's dilution law	
ostwald's dilution law (Only for weak electrolytes) $\alpha \propto \sqrt{\text{dilution}}$ dilution $\uparrow \Rightarrow \alpha \uparrow$ Explanation of water $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$ $K_w$ = Ionic product of water $\text{p}K_w = \text{pH} + \text{pOH}$ $K$ = dissociation constant of water $K = \frac{K_w}{[\text{H}_2\text{O}]} [\therefore [\text{H}_2\text{O}] = 55.5]$	for pure water 1. $[\text{H}^+] = [\text{OH}^-]$ 2. $\text{pH} = \text{pOH}$ 3. $(\text{pH})_{\text{pure water}} = \frac{\text{p}K_w}{2}$ pH of an acidic solution is always less than pH of pure water. pH of an basic solution is always greater than pH of pure water.

## Hydrolysis of Salts

Salt	Hydrolysis	Resulting solution	Hydrolysis constant ( $K_h$ )	Degree of hydrolysis (h)	pH
Weak acid and Strong base	Anionic	Alkaline $\text{pH} > 7$	$k_w / k_a$	$h = \sqrt{\frac{K_h}{C}}$	$\text{pH} = \frac{1}{2}[\text{p}K_w + \text{p}K_a + \log C]$
Strong acid and Weak base	Cationic	Acidic $\text{pH} < 7$	$k_w / k_b$	$h = \sqrt{\frac{K_h}{C}}$	$\text{pH} = \frac{1}{2}[\text{p}K_w - \text{p}K_b - \log C]$
Weak acid and Weak base	Anionic and Cationic both	Neutral, $\text{pH} = 7$ (If $K_a = K_b$ )	$k_w / (k_a \cdot k_b)$	$h = \sqrt{K_h}$	$\text{pH} = \frac{1}{2}[\text{p}K_w + \text{p}K_a - \text{p}K_b]$

## Buffer Solutions

The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called **buffer solutions**.

Buffers are classified into two categories:

- ❖ **Simple buffers:** These are the solutions of salts of weak acid and weak base. For example,  $\text{CH}_3\text{COONH}_4$  (ammonium acetate).
- ❖ **Mixed buffers:** These are the mixtures of two solutions. These are further of two types:
  - + **Acidic buffers:** These are the solutions of mixtures of weak acid and salt of this weak acid with strong base. For example,  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ . They have pH value lesser than 7.
  - + **Basic buffers:** These are the solutions of mixtures of weak base and salt of this weak base with strong acid. For example,  $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ . They have the pH value more than 7.
- ❖ pH of an acidic buffer:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = \text{p}K_a + \log \frac{[\text{Conjugate Base}]}{[\text{Weak Acid}]}$$

- ❖ pOH of an basic buffer:

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} = \text{p}K_b + \log \frac{[\text{Conjugate Acid}]}{[\text{Weak Base}]}$$

→ (Henderson - Hasselbalch equation)

$$\text{Buffer capacity} = \frac{\text{No. of moles acid or base added per litre of buffer}}{\text{Change in pH}}$$

The range of pH over which the buffer solutions remain effective is called **buffer range**.

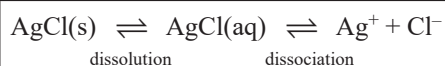
Buffer	Buffer range in pH
Acidic	$\text{p}K_a \pm 1$
Basic	$(\text{p}K_w - \text{p}K_b) \pm 1$

- ❖ Buffer capacity =  $\frac{\text{No. of moles of acid/base added per litre}}{\text{change in pH of buffer solution}}$
- ❖ Maximum buffer action when  $[\text{salt}] = [\text{acid}]$
- ❖ pH of Amphiprotic species: ( $\text{NaHPO}_4$ ,  $\text{NaHCO}_3$ ) which can donate as well as accept  $\text{H}^+$ ;  $\text{pH} = \frac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2}$

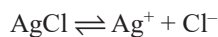
## Solubility (s) and Solubility Product ( $K_{sp}$ )

### Solubility

The maximum amount of solute that can be dissolved in a particular amount of solvent at a given temperature is called solubility(s). It is generally expressed in molarity.



### Solubility Product ( $K_{sp}$ )



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

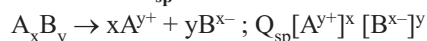
depends only on temperature.

### Expressions of $K_{sp}$ : $\text{A}_x\text{B}_y \rightarrow x\text{A}^{y+} + y\text{B}^{x-}$

$$\text{General form } K_{sp} = [\text{A}^{y+}]^x [\text{B}^{x-}]^y$$

$$\text{In terms of 'S': } K_{sp} = (xS)^x (yS)^y$$

### Ionic Product [ $Q_{sp}$ ]



In  $Q_{sp}$  the concentration taken are at any time but in  $K_{sp}$  the concentration are at equilibrium time/saturation time.

### Application

1. If  $Q_{sp} < K_{sp}$  [unsaturated]
2. If  $Q_{sp} = K_{sp}$  [saturated]
3. If  $Q_{sp} > K_{sp}$  [super saturated/ppt. will form]

### Effect of Common Ion

Presence of common ion decreases the solubility but has no effect on  $K_{sp}$  as it depends only on temperature.

### Effect of Odd Ion

Presence of odd ion increases the solubility but has no effect on  $K_{sp}$ .

### Acid-Base Titration

Type of titration	pH range of titration	Suitable indicators
SA/SB.	3-11	All indicators (MeOH, HPh etc.)
SA/WB	3-7	Methyl orange (MeOH) and methyl red
WA/SB	7-11	Phenolphthalein (HPh)
WA/WB	6.5-7.5	Phenol red