CHAPTER

7

Equilibrium

Chemical Equilibrium

Consider a reversible reaction,

$$aA + bB \underset{r_b}{\overset{r_f}{\rightleftharpoons}} cC + dD$$

At Equilibrium State

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

So, at equilibrium,

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

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

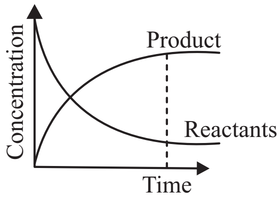
$$K_X = \frac{[X_C]^c[X_D]^d}{[X_A]^a[X_B]^b}$$ In terms of mole fraction

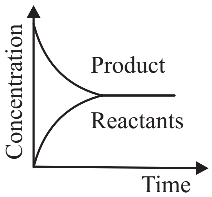
$K_P = K_C(RT)^{\Delta n_g} = K_X P^{\Delta n_g}$

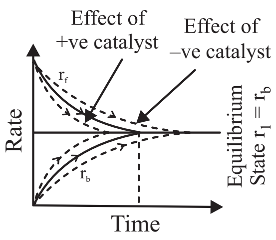
While determining Δn_g take only gaseous species.

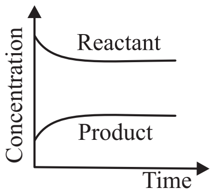
The active mass of solid & pure liquid is a constant quantity (unity) because it is an intensive property.

Graphs









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 increase.

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:

$$aA + bB \rightleftharpoons cC + dD$$

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

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

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.

Degree of dissociation (α)

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

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 as to nullify the effect of change.

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

Chemical Equilibrium

Effect due to change in		$\Delta n_g = 0$ $A \rightleftharpoons B$	$\Delta n_g > 0$ $A \rightleftharpoons 2B$	$\Delta n_g < 0$ $2A \rightleftharpoons B$
Concentration	(i) ↑ [A]	Forward direction	Forward direction	Forward direction
	(ii) ↓ [A]	Backward direction	Backward direction	Backward direction
Pressure	(i) ↑ in pressure	Unchanged	Backward direction	Forward direction
	(ii) ↓ in pressure	Unchanged	Forward direction	Backward direction
Temperature	(i) ↑ in Endothermic	Forward direction	Forward direction	Forward direction
	(ii) ↑ in Exothermic	Backward direction	Backward direction	Backward direction
Dissociation	(i) ↑ in pressure	Unchanged	Dissociation Decreases	Dissociation Increases
	(ii) ↑ 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

Relationship between Equilibrium Constant K, Reaction Quotient Q and Gibbs Energy G

$\Delta G = \Delta G^\circ + RT \ln Q$ …(i) where, ΔG° = Standard free energy difference between the products and reactant, T = Absolute temperature in kelvin, R = Universal gas constant.

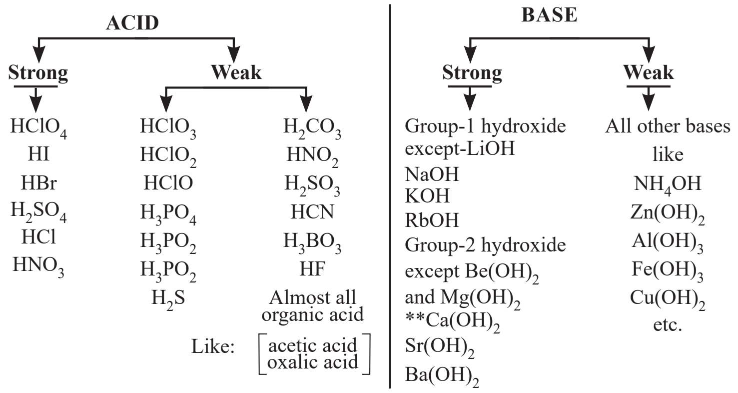
At equilibrium, when $\Delta G = 0$ and $Q = K_c$, then equation (i) becomes

$0 = \Delta G^\circ + RT \ln K_c$ or $\Delta G^\circ = -RT \ln K_c$ or $\ln K_c = -\Delta G^\circ/RT$

Case I: If $\Delta G^\circ < 0$, then $(-\Delta G^\circ/RT)$ is positive, i.e., $e^{(-\Delta G^\circ/RT)} > 1$ hence $K_c > 1$, which implies a spontaneous reaction, i.e., the reaction proceeds in the forward reaction.

Case II: If $\Delta G^\circ > 0$, then $(-\Delta G^\circ/RT)$ is negative, i.e., $e^{(-\Delta G^\circ/RT)} < 1$, hence $K_c < 1$, which implies a non-spontaneous reaction or the reaction proceeds in the forward direction to a very small extent i.e., only a very small quantity of product is formed.

Ionic Equilibrium

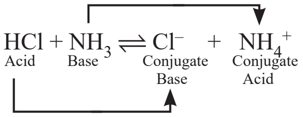


Acid Base Theories (Arrhenius Concept)	
Acid	**Base**
Which produce H^+ ion in aqueous solution. e.g. HCl, H_2SO_4, $HClO_4$, H_3PO_4, CH_3COOH but **H_3BO_3 is not an Arrhenius acid.** **Major Limitation:** Defined only in water solvent.	Which produce OH^- ion in aqueous solution. e.g. NaOH, $Mg(OH)_2$, $Ba(OH)_2$

Bronsted – Lowry Concept

Acid: Which gives H^+ in any solvent.

Base: Which accepts H^+ in any solvent



$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{NH_3} \rightleftharpoons \underset{\text{Conjugate Base}}{Cl^-} + \underset{\text{Conjugate Acid}}{NH_4^+}$$

Major Limitation: 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 → Remove one H^+
- To find conjugate acid of any Base → add one H^+
- Water is Amphiprotic solvent (can accept as well as lose H^+)

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

$H_2O + H^+ \rightleftharpoons H_3O^+$

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.	**Having Incomplete octet:** BF_3, BCl_3, $B(OH)_3$, $AlCl_3$ 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.	**Having vacant d-orbitals:** SF_4, SF_6, $SnCl_2$, $SnCl_4$ etc.	**2.**	**Anions:** $O^{2–}$, $SO_4^{2–}$, $CO_3^{2–}$, $Cl^–$, $Br^–$, $I^–$, $CH_3COO^–$ 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.
3.	**Having multiple bonds between atoms of different EN:** CO, SO_2, SO_3 etc.		
4.	**Cations** Ag^+, Li^+, Al^{+3}, Mg^{2+} **False cations (which cannot act as Lewis acid):]** NH_4^+, H_3O^+, PH_4^+ etc.		

Ostwald Dilution Law

OSTWALD'S DILUTION LAW

(Only for weak electrolytes)

$\alpha \propto \sqrt{\text{dilution}}$ dilution $\uparrow \Rightarrow \alpha \uparrow$

Explanation of water

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

K_w = Ionic product of water

$pK_w = pH + pOH$

K_w = dissociation constant of water

$$K = \frac{K_w}{[H_2O]} [\because [H_2O] = 55.5]$$

FOR PURE WATER

1. $[H^+] = [OH^-]$
2. $pH = pOH$
3. $(pH)_{\text{pure water}} = \dfrac{pK_w}{2}$

- ✦ pH of an acidic solution is always less than pH of pure water.
- ✦ pH of a 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 pH > 7	k_w / k_a	$h = \sqrt{\frac{K_h}{C}}$	$pH = \frac{1}{2}[pK_w + pK_a + \log C]$
Strong acid and Weak base	Cationic	Acidic pH < 7	k_w / k_b	$h = \sqrt{\frac{K_h}{C}}$	$pH = \frac{1}{2}[pK_w - pK_b - \log C]$
Weak acid and Weak base	Anionic and Cationic both	Neutral, pH = 7 (If $K_a = K_b$)	$k_w / (k_a \cdot k_b)$	$h = \sqrt{K_h}$	$pH = \frac{1}{2}[pK_w + pK_a - pK_b]$

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, CH_3COONH_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, $CH_3COOH + CH_3COONa$. 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, $NH_4OH + NH_4Cl$. They have the pH value more than 7.
- pH of an acidic buffer:

$$pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]} = pK_a + \log\frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

- pH of a basic buffer:

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

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

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

Buffer	**Buffer range in pH**
Acidic	$pK_a \pm 1$
Basic	$(pK_w - pK_b) \pm 1$

Solubility (s) & 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.

$$\boxed{AgCl(s) \underset{\text{dissolution}}{\rightleftharpoons} AgCl(aq) \underset{\text{dissociation}}{\longrightarrow} Ag^+ + Cl^-}$$

Solubility Product (K_{sp})

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

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

K_{sp} depends only on temperature.

Expressions of K_{sp} : $A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$

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

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

Ionic Product [Q_{sp}]

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}\ ;\ Q_{sp}[A^{y+}]^x\,[B^{x-}]^y$$

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

Key Tips

- Buffer capacity $= \dfrac{\text{No. of moles of acid/base added per litre}}{\text{change in pH of buffer solution}}$
- Maximum buffer action when [salt] = [acid]
- pH of Amphiprotic species: ($NaHPO_4$, $NaHCO_3$) which can donate as well as accept H^+; $pH = \dfrac{pKa_1 + pKa_2}{2}$