CONCEPT MAP EQUILIBRIUM

Chemical Equilibrium

- Involves chemical changes
  $A + B \rightleftharpoons C + D$
  Rate of forward reaction = Rate of reverse reaction
- Also called dynamic equilibrium

Types of Chemical Equilibrium

- **Homogeneous Equilibrium :** All the reactants and products are in the same phase.
  $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
- **Heterogeneous Equilibrium :** Reactants and products are in two or more different phases.
  $C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$

Law of Chemical Equilibrium

- $aA_{(aq)} + bB_{(aq)} \rightleftharpoons mC_{(aq)} + nD_{(aq)}$
  $K_c = \frac{[C]^m [D]^n}{[A]^a [B]^b}$
- $aA_{(g)} + bB_{(g)} \rightleftharpoons mC_{(g)} + nD_{(g)}$
  $K_p = \frac{(p_C)^m (p_D)^n}{(p_A)^a (p_B)^b}$

Relation between K_p and K_c

- $K_p = K_c(RT)^{\Delta n}$
  - If $\Delta n = 0$, $K_p = K_c$
  - If $\Delta n = +ve$, $K_p > K_c$
  - If $\Delta n = -ve$, $K_p < K_c$
- Equilibrium constant for the reverse reaction (K_c')
  $K_c' = \frac{1}{K_c}$
- Equilibrium constant for the reaction which is divisible by n
  $K_c' = \sqrt[n]{K_c}$
- Equilibrium constant for the reaction which is multiplied by n
  $K_c' = (K_c)^n$
- Equilibrium constant for the reaction taking place in n steps
  $K_c' = K_1 \times K_2 \times K_3 \ldots K_n$

Physical Equilibrium

Involves physical changes

Phase Transformation Processes

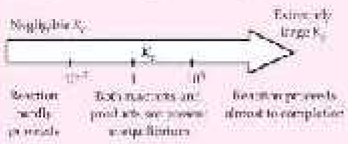
- **Solid-Liquid Equilibrium :** $r_{\text{Melting of ice}} = r_{\text{Freezing of water}}$
- **Liquid-Gas Equilibrium :** $r_{\text{Evaporation}} = r_{\text{Condensation}}$
- **Solid-Gas Equilibrium :** $r_{\text{Sublimation}} = r_{\text{Condensation}}$
- **Solid-Solution Equilibrium :** $r_{\text{Dissolution}} = r_{\text{Crystallisation}}$
- **Gas-Solution Equilibrium :** $m \propto p$ [Henry's law]

Relation between Gibbs Free Energy and Equilibrium Constant

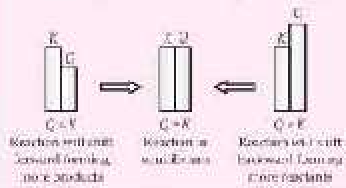
- At equilibrium
  $\Delta G^\circ = -RT \ln K$; $K = e^{-\Delta G^\circ/RT}$
  - If $\Delta G^\circ < 0$ then $K > 1$
    [Forward reaction is favoured.]
  - If $\Delta G^\circ > 0$ then $K < 1$
    [Reversed reaction is favoured.]
  - If $\Delta G^\circ = 0$, then $K = 1$
    [Reaction is in equilibrium.]

Applications of Equilibrium Constants

- Predicting the extent of reaction :
  - $K_c > 10^3$ [Forward reaction is favoured.]
  - $K_c < 10^{-3}$ [Reverse reaction is favoured.]
  - $10^{-3} < K_c < 10^3$ [Both reactants and products are present in equilibrium.]



- Predicting the direction of reaction :
  - $Q > K_c$ [Reverse reaction is favoured.]
  - $Q < K_c$ [Forward reaction is favoured.]
  - $Q = K_c$ [Reaction is in equilibrium.]



Factors Affecting Equilibrium

Le-Chatelier's principle

- **Change in Concentration:** If concentration of any reactant or product is increased, the equilibrium will shift in a direction where it is being consumed.
- **Change in Temperature:** If temperature is increased, reaction will proceed in the direction where heat is absorbed.
- **Change in Pressure :** If pressure is increased, then equilibrium will shift in a direction where number of moles reduces.
- **Addition of Inert Gas:**
  - **At Constant Volume :** No change in equilibrium
  - **At Constant Pressure:** Equilibrium will shift towards greater number of moles.
- **Catalyst :** No change in equilibrium. It helps in attaining the equilibrium quickly.

Ionic Equilibrium

Involves ionisation processes

Ionisation

- **Ionisation of Acids :**
  $HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$
  $K_a = \frac{[H_3O^+][A^-]}{[HA]}$
  K_a = ionisation constant
  $pK_a = -\log K_a$
  As K_a increases, pK_a decreases and acidity increases.
- **Ionisation of Bases :**
  $BOH_{(aq)} \rightleftharpoons B^+_{(aq)} + OH^-_{(aq)}$
  $K_b = \frac{[B^+][OH^-]}{[BOH]} = \frac{C\alpha^2}{1-\alpha}$
  $pK_b = -\log K_b$
  As K_b increases, pK_b decreases and basicity increases.

Ionic Product of Water

$2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$
$K_w = [H_3O^+][OH^-] = 1 \times 10^{-14}\ M^2$
$\therefore$ $[OH^-] = [H^+] = 1.0 \times 10^{-7}$ M at 298 K

pH

- $pH = -\log[H_3O^+] = -\log[10^{-7}] = 7$

Solution	$[H^+]$	$[OH^-]$	pH	pOH
Acidic	$>10^{-7}$	$<10^{-7}$	<7	>7
Basic	$<10^{-7}$	$>10^{-7}$	>7	<7
Neutral	10^{-7}	10^{-7}	7	7

- $pK_w = pH + pOH = 14$

Hydrolysis of Salts

It is a process in which a salt reacts with water to give acid and base.

- **Salt of Strong Base and Strong Acid :**
  Neutral solution, e.g., NaCl, KCl
- **Salt of Weak Base and Strong Acid :**
  $K_h = \frac{K_w}{K_b}$; $pH = \frac{1}{2}[pK_w - pK_b - \log C]$
  e.g., NH_4Cl, $CuSO_4$
- **Salt of Strong Base and Weak Acid :**
  $K_h = \frac{K_w}{K_a}$; $pH = \frac{1}{2}[pK_w + pK_a + \log C]$
  e.g., CH_3COONa, Na_3PO_4
- **Salt of Weak Acid and Weak Base :**
  $K_h = \frac{K_w}{K_a \times K_b}$; $pH = \frac{1}{2}[pK_w + pK_a - pK_b]$
  e.g., CH_3COONH_4, $AlPO_4$

Solubility Product

- $A_mB_n \rightleftharpoons mA^{n+} + nB^{m-}$
  $K_{sp} = [A^{n+}]^m [B^{m-}]^n$
  - $K_{ip} > K_{sp}$, Precipitation occurs.
  - $K_{ip} < K_{sp}$, Precipitation does not occur.
  - $K_{ip} = K_{sp}$, Solution is saturated.

Relation between Solubility and Solubility Product

$K_{sp} = [mS]^m [nS]^n$
$= m^m S^m \cdot n^n S^n$
$= m^m \cdot n^n \cdot (S)^{m+n}$
[where S is solubility]

Buffer Solution

It is a solution which resists change in pH on dilution or with the addition of small amounts of acid or alkali.

- **Acidic Buffer :** Mixture of weak acid + salt of this weak acid with strong base e.g. $CH_3COOH + CH_3COONa$
  $pH = pK_a + \log\frac{[Salt]}{[Acid]}$
- **Basic Buffer :** Mixture of weak base and salt of this weak base with strong acid e.g. $NH_4OH + NH_4Cl$
  $pOH = pK_b + \log\frac{[Salt]}{[Base]}$