

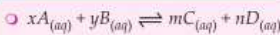
# CONCEPT MAP

# EQUILIBRIUM

## Chemical Equilibrium

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

### Law of Chemical Equilibrium



$$K_c = \frac{[C]^m [D]^n}{[A]^x [B]^y}$$



$$K_p = \frac{(p_C)^m (p_D)^n}{(p_A)^x (p_B)^y}$$

### 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

$$K_c' = K_1 \times K_2 \times K_3 \dots K_n$$

### 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.  
 $C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_2(g)$

## Physical Equilibrium

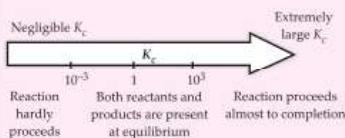
Involves physical changes

### Phase Transformation Processes

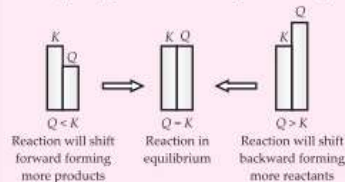
- Solid-Liquid Equilibrium:**  $r_{\text{Melting of ice}} = r_{\text{Freezing of water}}$
- Liquid-Gas Equilibrium:**  $r_{\text{Evaporation}} = r_{\text{Condensation}}$
- Solid-Gas Equilibrium:**  $r_{\text{Sublimation}} = r_{\text{Condensation}}$
- Solid-Solution Equilibrium:**  $r_{\text{Dissolution}}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

### 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:
  - $Q_c > K_c$  [Reverse reaction is favoured.]
  - $Q_c < K_c$  [Forward reaction is favoured.]
  - $Q_c = K_c$  [Reaction is in equilibrium.]



### 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.]

### Factors Affecting Equilibrium

#### Le-Chatelier's principle

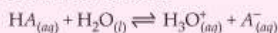
- Change in Concentration:** If concentration of any reactant or product is increased, the equilibrium will shift in a direction where it is being consumed.
- Change in Temperature:** If temperature is increased, reaction will proceed in the direction where heat is absorbed.
- Change in Pressure:** If 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:



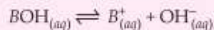
$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$K_a$  = ionisation constant,

$$pK_a = -\log K_a$$

As  $K_a$  increases,  $pK_a$  decreases and acidity increases.

#### Ionisation of Bases:



$$K_b = \frac{[B^+][OH^-]}{[BOH]} = \frac{C\alpha^2}{1-\alpha}$$

$$pK_b = -\log K_b$$

As  $K_b$  increases,  $pK_b$  decreases and basicity increases.

### Buffer Solution

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

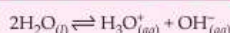
- Acidic Buffer:** Mixture of weak acid + salt of this weak acid with strong base. e.g.  $CH_3COOH + CH_3COONa$

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

- Basic Buffer:** Mixture of weak base and salt of this weak base with strong acid. e.g.  $NH_4OH + NH_4Cl$

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

### Ionic Product of Water



$$K_w = [H_3O^+][OH^-] = 1 \times 10^{-14} \text{ M}^2$$

$$\therefore [OH^-] = [H^+] = 1.0 \times 10^{-7} \text{ M at } 298 \text{ K}$$

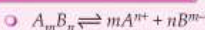
### pH

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

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

$$pK_w = pH + pOH = 14$$

### Solubility Product



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

- $K_{ip} > K_{sp}$  Precipitation occurs.
- $K_{ip} < K_{sp}$  Precipitation does not occur.
- $K_{ip} = K_{sp}$  Solution is saturated.

### Relation between Solubility and Solubility Product

$$\left. \begin{aligned} K_{sp} &= [mS]^m [nS]^n \\ &= m^m S^m \cdot n^n S^n \\ &= m^m \cdot n^n \cdot (S)^{m+n} \end{aligned} \right\} \text{ [where S is solubility.]}$$

### 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.,  $CH_3COONH_4, AlPO_4$