CHAPTER 4

CHEMICAL EQUILIBRIUM

- Equilibrium represents the state of a process in which the measurable properties like :- temperature, pressure, color, concentration of the system do not show any change with the passage of time.
- Equilibrium is a dynamic process, chemical equilibrium can be approached from both sides.
- The state of equilibrium is not affected by the presence of catalyst. It only helps to attain the equilibrium state in less or more time.
- Equilibrium can be attained both in homogeneous & heterogenous system.

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,

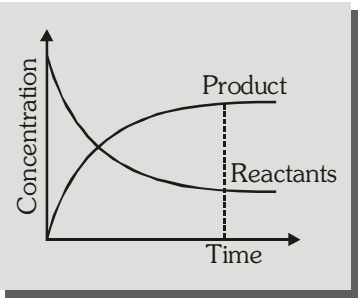
$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{K_f}{K_b}$ In terms of active mass

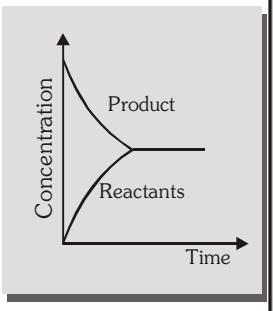
$K_P = \frac{[P_C]^c[P_D]^d}{[P_A]^a[P_B]^b}$ In terms of partial pressure

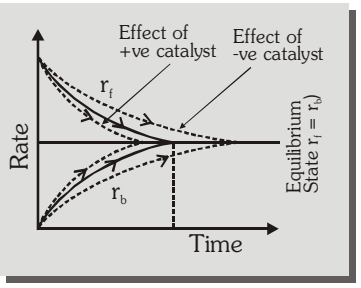
$K_X = \frac{[X_C]^c[X_D]^d}{[X_A]^a[X_B]^b}$ In terms of mole fraction

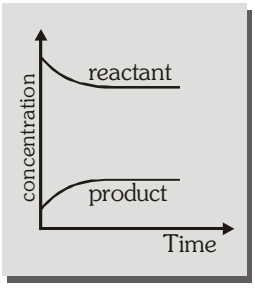
- Partial pressure of solid is taken as unity & in calculation of partial pressure of solids, their number of moles are not considered.
- $K_p = K_C(RT)^{\Delta ng}$ then $K_P = K_C$
  when $\Delta n_g = 0$ then $K_P = K_C$
  when $\Delta n_g > 0$ then $K_P > K_C$
  when $\Delta n_g < 0$ then $K_P < K_C$
- 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 increases.

CHARACTERISTICS OF EQUILIBRIUM CONSTANT

Equilibrium constant depends upon temperature & way of writing the reaction

(i) Temperature :

Let K_1 & K_2 be equilibrium constant at T_1 & T_2 then

$$\text{Log}\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^o}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

(Van't Hoff equation)

(ii) Way of writing the reaction :

For $A + B \rightleftharpoons C + D$ $K_C = K$ then

(a) $C + D \rightleftharpoons A + B$; $K'_C = \frac{1}{K}$

(b) $nA + nB \rightleftharpoons nC + nD$, $K''_C = K^n$

when n=2, then $K''_C = K^2$

$n = \frac{1}{3}$ then $K''_C = K^{1/3}$

(c) $A \rightleftharpoons B$ $K_C = K_1$

$B \rightleftharpoons C$ $K_C = K_2$

$C \rightleftharpoons D$ $K_C = K_3$ then

$A \rightleftharpoons D$ $K_C = K_1 \times K_2 \times K_3$

(d) $A \rightleftharpoons B$ $K_C = K_1$

$2C \rightleftharpoons 2B$ $K_C = K_2$

$D \rightleftharpoons C$ $K_C = K_3$ then

$A \rightleftharpoons D$ $K_C = \frac{K_1}{\sqrt{K_2} * K_3}$

- **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)**

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

- **Degree of Dissociation from Vapour pressure**

$n_1A \rightleftharpoons n_2B + n_3C$

$$\alpha = \frac{n_1}{\Delta n}\left(\frac{D_T - D_0}{D_0}\right); \Delta n = (n_2 + n_3) - (n_1)$$

D_T = theoretical vapour density = $\frac{\text{Molecular weight}}{2}$

D_0 = Observed vapour density

PHYSICAL EQUILIBRIUM

Physical reaction :

Those reactions in which change in only & only physical states of substances takes place without any chemical change.

(i) Ice-water system (melting of ice) :

$$\underset{\text{(more volume)}}{Ice_{(s)}} + Heat \rightleftharpoons \underset{\text{(less volume)}}{water_{(\ell)}}$$

It is an endothermic process & there is decrease in volume. Thus, the favourable conditions for melting of ice are high temperature, & High-pressure.

(ii) Water -Water vapour system (vapourisation of water) :

$$\underset{\text{(less volume)}}{water_{(\ell)}} \rightleftharpoons \underset{\text{(more volume)}}{vapour_{(g)}}$$

It is an endothermic process & there is increase in volume. Thus, the favourable conditions for vaporisation of water are high temperature, & low-pressure.

(iii) Solubility of gases in liquids :

$Gas_{(g)} + water_{(\ell)} \rightleftharpoons Aqueous\ solution_{(\ell)}$

When a gas dissolve in liquid, these is decrease in volume. Thus, increase in pressure will favour the dissolution of a gas in liquid.

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

S. No.	Effect due to change in		$\Delta n_g = 0$ $A \rightleftharpoons B$	$\Delta n_g > 0$ $A \rightleftharpoons 2B$	$\Delta n_g < 0$ $2A \rightleftharpoons B$
a)	Concentration	(i) ↑ [A] (ii) ↓ [A]	Forward direction Backward direction	Forward direction Backward direction	Forward direction Backward direction
b)	Pressure	(i) ↑ in pressure (ii) ↓ in pressure	Unchanged Unchanged	Backward direction Forward direction	Forward direction Backward direction
c)	Temperature	(i) ↑ in Endothermic (ii) ↑ in Exothermic	Forward direction Backward direction	Forward direction Backward direction	Forward direction Backward direction
d)	Dissociation	(i) ↑ in pressure (ii) ↑ in volume	Unchanged Unchanged	Dissociation Decreases Dissociation Increases	Dissociation Increases Dissociation Decreases
e)	Mixing of inert gas	(i) at constant P (ii) at constant V	Unchanged Unchanged	Dissociation Increases Unchanged	Dissociation Decreases Unchanged