

## 5. CHEMICAL EQUILIBRIUM

**At equilibrium :**

- (i) Rate of forward reaction = rate of backward reaction
- (ii) Concentration (mole/litre) of reactant and product becomes constant.
- (iii)  $\Delta G = 0$ .

(iv)  $Q = K_{eq}$ .

**Equilibrium constant (K) :**

$$K = \frac{\text{rate constant of forward reaction}}{\text{rate constant of backward reaction}} = \frac{K_f}{K_b}$$

**Equilibrium constant in terms of concentration ( $K_c$ ) :**

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

**Equilibrium constant in terms of partial pressure ( $K_p$ ) :**

$$K_p = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b}$$

**Equilibrium constant in terms of mole fraction ( $K_x$ ) :**

$$K_x = \frac{x_C^c x_D^d}{x_A^a x_B^b}$$

**Relation between  $K_p$  &  $K_c$  :**

$$K_p = K_c (RT)^{\Delta n}$$

**Relation between  $K_p$  &  $K_x$  :**

$$K_p = K_x (P)^{\Delta n}$$

$$* \quad \log \frac{K_2}{K_1} = \frac{\Delta H}{2.303 R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]; \Delta H = \text{Enthalpy of reaction}$$

**Relation between equilibrium constant & standard free energy change :**

$$\Delta G^\circ = -2.303 RT \log K$$

**Reaction Quotient (Q) :**

$$\text{The values of expression } Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

**Degree of Dissociation ( $\alpha$ ) :**

$\alpha$  = no. of moles dissociated / initial no. of moles taken  
= fraction of moles dissociated out of 1 mole.

**Note : % dissociation =  $\alpha \times 100$**

**Observed molecular weight and Observed Vapour Density of the mixture :**

$$\text{Observed molecular weight of } A_n(g) = \frac{\text{molecular weight of equilibrium mixture}}{\text{total no. of moles}}$$

$$\alpha = \frac{D - d}{(n-1)d} = \frac{M_T - M_0}{(n-1)M_0}$$

## External factor affecting equilibrium :

### Le Chatelier's Principle:

If a system at equilibrium is subjected to a disturbance or stress that changes any of the factors that determine the state of equilibrium, the system will react in such a way as to minimize the effect of the disturbance.

#### Effect of concentration :

- \* If the concentration of reactant is increased at equilibrium then reaction shift in the forward direction .
- \* If the concentration of product is increased then equilibrium shifts in the backward direction

#### Effect of volume :

- \* If volume is increased pressure decreases hence reaction will shift in the direction in which pressure increases that is in the direction in which number of moles of gases increases and vice versa.
- \* If volume is increased then, for  
 $\Delta n > 0$  reaction will shift in the forward direction  
 $\Delta n < 0$  reaction will shift in the backward direction  
 $\Delta n = 0$  reaction will not shift.

#### Effect of pressure :

- \* If pressure is increased at equilibrium then reaction will try to decrease the pressure, hence it will shift in the direction in which less no. of moles of gases are formed.

#### Effect of inert gas addition :

##### (i) Constant pressure :

If inert gas is added then to maintain the pressure constant, volume is increased. Hence equilibrium will shift in the direction in which larger no. of moles of gas is formed

- $\Delta n > 0$  reaction will shift in the forward direction
- $\Delta n < 0$  reaction will shift in the backward direction
- $\Delta n = 0$  reaction will not shift.

##### (ii) Constant volume :

Inert gas addition has no effect at constant volume.

#### Effect of Temperature :

Equilibrium constant is only dependent upon the temperature.

If plot of  $\ln K$  vs  $\frac{1}{T}$  is plotted then it is a straight line with slope =  $-\frac{\Delta H^\circ}{R}$ , and intercept =  $\frac{\Delta S^\circ}{R}$

- \* For endothermic ( $\Delta H > 0$ ) reaction value of the equilibrium constant increases with the rise in temperature
- \* For exothermic ( $\Delta H < 0$ ) reaction, value of the equilibrium constant decreases with increase in temperature
- \* For  $\Delta H > 0$ , reaction shifts in the forward direction with increase in temperature
- \* For  $\Delta H < 0$ , reaction shifts in the backward direction with increases in temperature.
- \* If the concentration of reactant is increased at equilibrium then reaction shift in the forward direction .
- \* If the concentration of product is increased then equilibrium shifts in the backward direction

#### Vapour Pressure of Liquid :

Relative Humidity =  $\frac{\text{Partial pressure of H}_2\text{O vapours}}{\text{Vapour pressure of H}_2\text{O at that temp.}}$

#### Thermodynamics of Equilibrium :

$$\Delta G = \Delta G^\circ + 2.303 RT \log_{10} Q$$

Vant Hoff equation-  $\log \left( \frac{K_1}{K_2} \right) = \frac{\Delta H^\circ}{2.303R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$