

# 5. Chemical Equilibrium

➤  $K_C = \frac{[B]}{[A]} = \text{mol L}^{-1}$

➤  $K_p = \frac{P_B}{P_A} = \text{Partial Pressure}$

➤  $K_x = \frac{X_B}{X_A} = \text{mole fraction}$

➤  $K_p = K_C(RT)^{\Delta n_g}$  where  $\Delta n_g = n_p - n_r$

➤ **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]

➤ **Free Energy Change ( $\Delta G$ )**

a) If  $\Delta G = 0$  then reversible reaction would be in equilibrium,  $K_C = 1$

b) If  $\Delta G = (+)$  ve then equilibrium will be displaced in backward direction;  $K_C < 1$

c) If  $\Delta G = (-)$  ve then equilibrium will shift in forward direction;

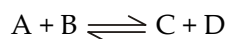
$$K_C > 1$$

➤ (a)  $K_C$  unit  $\rightarrow (\text{moles/lit})^{\Delta n}$

(b)  $K_p$  unit  $\rightarrow (\text{atm})^{\Delta n}$

➤ **Reaction Quotient and Equilibrium Constant**

Consider the following reversible reaction



➤  $\therefore Q_C = \frac{[C][D]}{[A][B]}$

**Case I :** If  $Q_C < K_C$  then :

[Reactants] > [Products] then the system is not at equilibrium

**Case II :** If  $Q_C = K_C$  then :

The system is at equilibrium.

**Case- III :** If  $Q_C > K_C$  then :

[Products] > [Reactants]

The system is not at equilibrium.

➤  $\Delta G$  of a reaction under any set of conditions is related to its value under standard conditions, i.e.  $\Delta G^\circ$  by the equation

$$\Delta G = \Delta G^\circ + 2.303 RT \log Q$$

➤ Under equilibrium conditions, for same number of moles of reactants and products

$$Q = K_p = K_C = K \text{ and } \Delta G = 0$$

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

➤ We have replaced  $K_p$  by  $K$  called thermodynamic equilibrium constant

## Significance of $\Delta G^\circ$

Significance of  $\Delta G^\circ$  can be explained from the following points

(i) If  $\Delta G^\circ < 0$ ,  $\log K > 0$ ,  $\Rightarrow K > 1$

Hence, reaction is spontaneous in forward direction.

(ii) Hence  $\Delta G^\circ < 0$ ,  $\log K > 0$ ,  $\Rightarrow K < 1$

Hence, reaction is non-spontaneous or a reaction proceeds in the forward direction to such a small extent that a very small amount of the product is formed.

(iii) If  $\Delta G^\circ = 0$ ,  $\log K = 0$ ,  $\Rightarrow K = 1$

hence, it represents equilibrium.

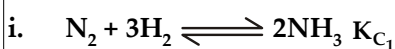
(iv) If  $\Delta G^\circ$  is large negative number,

$K \gg 1$ , the forward reaction is nearly complete.

(v) If  $\Delta G^\circ$  is a very small positive number,

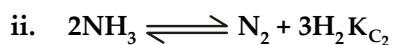
$K \ll 1$ , then reverse reaction is nearly complete.

➤ **Mole of Representation of Reversible reaction.**



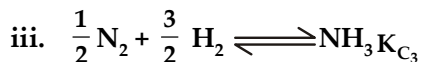
$$K_{C1} = \frac{1}{K_{C2}}$$

$$K_{C1} = \frac{1}{K_{C3}^2}$$



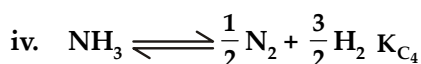
$$K_{C_1} = \frac{1}{K_{C_4}^2}$$

$$K_{C_2} = K_{C_5}$$



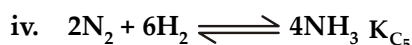
$$K_{C_2} = \frac{1}{K_{C_3}^2}$$

$$K_{C_3} = \frac{1}{K_{C_4}}$$



$$K_{C_4} = \frac{1}{K_{C_5}}$$

$$K_{C_2} = K_{C_4}$$



### ► Le-Chatelier's principle

- Increase of reactant conc. (Shift reaction forward)
- Decrease of reactant conc. (Shift reaction backward)
- Increase of pressure (from more moles to less moles)

- Decrease of pressure (from less moles to more moles)
- For exothermic reaction decrease in temp. (Shift forward)
- For endothermic increase in temp. (Shift forward)

### ► Effect of Temperature on Equilibrium Constant

According to Von't Hoff Equation,

$$k = Ae^{-\Delta H/RT}$$

Where,  $K$  = rate constant,  $E_a$  = activation energy,  $R$  = gas constant,  $T$  = absolute temperature and  $e$  = exponential constant.

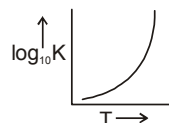
$$\log \frac{k_2}{k_1} = -\frac{\Delta H}{2.303R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

where,  $T_2 > T_1$

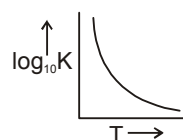
**First case :** When  $\Delta H = 0$ ;  $K_2 = K_1$ .

**Second case :** When  $\Delta H = +Ve$ ;  $K_2 > K_1$

**Thirds Case :** When  $\Delta H = -ve$ ;  $K_1 > K_2$



a) Endothermic reaction  
(Plots of logK versus T)



b) Exothermic reaction