B. Sc. 2nd sem (Generic)

Chapter : Chemical Equilibrium

Vant Hoff Isotherm :- Free energy change in Chemical reactions.

Consider a reaction →

$$aA + bB \longrightarrow cC + dD.$$

We know that →

$$G = G^\circ + RT \ln P \quad \text{——— (1)}$$

Let, G_A, G_B, G_C and G_D be the free energy per mole of A, B, C and D at the respective pressures P_A, P_B, P_C and P_D. Also, let G_A°, G_B°, G_C° and G_D° be the standard free energy of A, B, C and D respectively.

From equation (1), we can write the free energies of various gases from A to D at their respective pressures as :-

$$aG_A = aG_A^\circ + nRT \ln P_A \quad \text{——— (2)}$$

$$bG_B = bG_B^\circ + nRT \ln P_B \quad \text{——— (3)}$$

$$cG_C = cG_C^\circ + nRT \ln P_C \quad \text{——— (4)}$$

$$dG_D = dG_D^\circ + nRT \ln P_D \quad \text{——— (5)}$$

The free energy change of the reaction ΔG is written as :

$$\Delta G = \Delta G_{products} - \Delta G_{reactants}$$

$$= cG_C + dG_D - aG_A - bG_B$$

Substituting the values from eqn (2) to (5), we get –

$$\Delta G = \left(cG_C^\circ + dG_D^\circ - aG_A^\circ - bG_b^\circ\right) + RT\ln\frac{(P_C)^c \times (P_D)^d}{(P_A)^a \times (P_B)^b}$$

$$\Rightarrow \Delta G = \Delta G^\circ + RT\ln\left\{\frac{(P_C)^c \times (P_D)^d}{(P_A)^a \times (P_B)^b}\right\} \quad \text{——— (6)}$$

We know that at equilibrium, the free energy change is zero, i.e. $\boxed{\Delta G = 0}$

So, from the above expression, we get –

$$0 = \Delta G^\circ + RT\ln\left\{\frac{(P_C)^c \times (P_D)^d}{(P_A)^a \times (P_B)^b}\right\}$$

$$-\Delta G^\circ = RT\ln\left\{\frac{(P_C)^c \times (P_D)^d}{(P_A)^a \times (P_B)^b}\right\}$$

$$\because \quad K_P = \frac{(P_C)^c \times (P_D)^d}{(P_A)^a \times (P_B)^b}$$

$$\therefore \quad -\Delta G^\circ = RT\ln K_P$$

or $\boxed{\Delta G^\circ = -RT\ln K_P}$

Substituting the value of ΔG° in eqn (6), we get –

$$\Delta G = -RT\ln K_P + RT\ln\frac{(P_C)^c\,(P_D)^d}{(P_A)^a (P_B)^b}$$

$$\Rightarrow -\Delta G = -RT\ln K_P - RT\ln\frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

This equation is eqn as Vant Hoff Isotherm.