Van't Hoff Isotherm:

It is a quantitative relationship of free energy change in a chemical reaction.

Let us consider a chemical reaction,

$$aA + bB \rightleftharpoons cC + dD$$

Where a, and b are number of moles of reactant A and B c and d are number of moles of Product C and D.

The free energy per mole is given by the expression,

$$G_1 = G^0 + RT \ln P \quad \text{——— (1)}$$

Let the free energy per mole of A, B, C and D are G_A, G_B, G_C and G_D at the respective Pressures P_A, P_B, P_C and P_D.

And their Standard free energy is G^0_A, G^0_B G^0_C and G^0_D

So, from equation (1) the free energy per mole of A at Pressure P_A will be given as

$$a G_A = a G^0_A + aRT \ln P_A$$

Similarly $b G_B = b G^0_B + bRT \ln P_B$

$$c G_C = c G^0_C + cRT \ln P_C$$

$$d G_D = d G_D + dRT \ln P_D$$

Now the change in free energy during the chemical reaction,

$$\Delta G_1 = \sum \Delta G_{Product} - \sum \Delta G_{Reactant}$$

$$\Delta G_1 = (cG_C + dG_D) - (aG_A + bG_B)$$

$$= \{(cG^0_C + cRT \ln P_C + dG^0_D + dRT \ln P_D) - (aG^0_A + aRT \ln P_A + bG^0_B + bRT \ln P_B)\}$$

$$\Delta G_1 = (cG^0_C + dG^0_D - aG^0_A - bG^0_B) + RT \ln \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b} \quad \text{——— (2)}$$

If the reaction is at equilibrium then $\Delta G_1 = 0$

$$\therefore \quad -\Delta G^0 = RT \ln \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b}$$

Continue

or, $\Delta G^0 = -RT \ln K_p$ ——— (3)

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

On Putting the value of ΔG^0 from equation (3) to equation (2) we have,

$$\Delta G = -RT \ln K_p + RT \ln \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b}$$

or, $$-\Delta G = RT \ln K_p - RT \ln \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b}$$

$$-\Delta G = RT \ln K_p - RT \sum n \ln P \quad \text{——— (4)}$$

This equation is known as Vant Hoff isotherm.