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Deg II chem. Hons, Paper – III

Topic :- Thermodynamics

Van't Hoff's Reaction Isotherm :-

When the system is in equilibrium the free energy change is zero. Now we shall proceed to calculate the change in free energy when a chemical reaction is carried out at a constant temperature from some arbitrary concentration of reactants to some other arbitrary concentrations of the products

Consider a reaction involving four gases A, B, C and D

$$A + B \rightleftharpoons C + D$$

In this reaction amounts of A and B are decreasing and those of C and D are increasing. Subsequently the free energy of A and B are decreasing and those of C and D are increasing

The free energy of the substance A per mole at temperature T is given by

$$G_A = G^0_A + RT \log p_A$$

where p_A is the partial pressure of A and G^0_A is the free energy at some standard state ($p = 1$) and is known as the standard free energy.

Similarly the free energy of B, C and D are

$$G_B = G^0_B + RT \log p_B$$

$$G_C = G^0_C + RT \log p_C$$

$$G_D = G^0_D + RT \log p_D$$

The free energy change (ΔG) is given by

$$\Delta G = (G_C + G_D) - (G_A + G_B)$$

$$= G^0_C + RT \log p_C + G^0_D + RT \log p_D)$$

$$- (G^0_A + RT \log p_A + G^0_B + RT \log p_B)$$

$$= (G^0_C + G^0_D - G^0_A - G^0_B) + RT \log \frac{p_C \times p_D}{p_A \times p_B}$$

or $$\Delta G = \Delta G^0 + RT \log \frac{p_C \times p_D}{p_A \times p_B} \quad \text{——(1)}$$

where ΔG^0 = standard free energy change of reaction.

But at equilibrium $\Delta G = 0$

i.e. the change in free energy is zero

Therefore $$\Delta G^0 + RT \log \frac{p_C \times p_D}{p_A \times p_B} = 0$$

Where Pressures are equilibrium Pressures or $\Delta G^0 + RT \log K_p = 0$

or $\Delta G^0 = -RT \log K_p$

$\left[\text{where } K_p = \frac{p_C \times p_D}{p_A \times p_B} \right]$

Putting the value of ΔG^0 in eq-①

$$\Delta G = -RT \log K_p + RT \log \frac{p_C \times p_D}{p_A \times p_B}$$

or $-\Delta G = RT \log K_p - RT \log \frac{p_C \times p_D}{p_A \times p_B}$

Now consider the general reaction

$$n_1 A + n_2 B + \cdots \rightleftharpoons n_3 C + n_4 D +$$

By following the same procedure

$$-\Delta G = RT \log K_p - RT \log \frac{(p_C)^{n_3} \cdot (p_D)^{n_4}}{(p_A)^{n_1} \times (p_B)^{n_2}} \quad (2)$$

$$-\Delta G = RT \log K_p - RT \Sigma n \log p \quad (3)$$

Thus $-\Delta G = RT \log K_c - RT \Sigma n \log C$ — ④

Where K_c is equilibrium constant

Equation ③ and ④ are known as Van't Hoff's reaction Isotherm as the reaction is carried out at constant temperature.