B. Sc. Sem. Part I

Subject :- Physical Chemistry (T.Y.)
Paper :- Chemical Equilibrium

[illegible]
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Expression of Equilibrium constant in terms of Partial Pressure :-

When all the reactants and products are gases we can formulate the equilibrium constant expression in terms of partial pressure. The relationship between the partial pressure (P) of any gas in the equilibrium mixture and the molar concentration derived from ideal gas equation

$$PV = nRT$$

or

$$P = \left(\frac{n}{V}\right) RT$$

The quantity n/V is the number of moles of the gas per unit volume and is simply the molar concentration. So we,

$$P = [\text{Molar Concentration}] \times RT$$

i.e. the partial pressure of a gas in the equilibrium mixture is directly proportional to its molar concentration at a given temperature. Therefore we can write the equilibrium constant expression in terms of partial pressure instead of molar concentration. Thus, for a general reaction

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

the equilibrium law or the equilibrium condition may be written as

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \quad \text{--- (1)}$$

where K_p is the equilibrium constant in terms of partial pressures and is constant at a given temperature.

Relationship between K_p and K_c :-

For a given reaction K_p and K_c are not [illegible] [illegible]. It is possible to derive a relationship between them [illegible] [illegible] provided the gases in the reaction obey the ideal gas law. Let us consider a general reaction.

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

where all reactants and products are gases we can write the equilibrium constant expression in terms of partial pressure [illegible].

$$K_p = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b}$$

Since the ideal gas law partial pressure is given by $p = \frac{n}{V}RT$

where n is the number of moles [illegible] [illegible] [illegible] is equal to the molar concentration of the gas

$$p = CRT$$

Thus the partial pressures of individual gases A, B, C and D are

$p_A = [A]RT$, $p_B = [B]RT$, $p_C = [C]RT$

and $p_D = [D]RT$

On substituting these values in above equation we get

$$K_p = \frac{([C]RT)^c ([D]RT)^d}{([A]RT)^a ([B]RT)^b}$$

$$= \frac{[C]^c [D]^d}{[A]^a [B]^b} \frac{(RT)^{c+d}}{(RT)^{a+b}}$$

or $K_p = $ [illegible] $=$ [illegible]

or $K_p = K_c \times$ [illegible]

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

where Δn [illegible]

[illegible]

[illegible]

Example 1: [illegible]

[illegible]

[illegible]

When Δn is positive [illegible] K_p will be greater than K_c

Example 2: [illegible]

[illegible]

When Δn is negative [illegible] K_p will be less than K_c

Example 3: [illegible]

[illegible]

[illegible]

[illegible]

[illegible]

$$[illegible]$$

$$[illegible]$$

[illegible]

$$[illegible]$$

$$[illegible]$$

[illegible]

$$[illegible]$$

$$[illegible]$$

Characteristics of Equilibrium Constant (K_c)

Following are some of the properties of the equilibrium constant K_c and K_p:

1. The expressions for K_c and K_p are applicable to [illegible] systems which are [illegible].
2. Equilibrium constant for a particular reaction [illegible] has a definite constant value which varies with temperature only.
3. The value of equilibrium constant is independent of the initial concentrations of reactants and products.
4. The equilibrium constant is a true constant and does not vary with [illegible] whether [illegible] are present [illegible] with a reactant or a product.
5. Value of equilibrium constant is not affected by catalyst. Catalyst simply helps in attaining equilibrium [illegible].
6. The value of equilibrium constant predicts the extent to which reaction [illegible]. If K is large, the equilibrium lies to the right and the formation of products is large. If K is small, the equilibrium lies to the left and [illegible] i.e. formation of reactants will be favoured.
7. By convention, the equilibrium constant is written [illegible] [illegible] [illegible] [illegible].

Thermodynamic Derivation of the Equilibrium Constant (— [illegible] equilibrium constant and free energy change)

By using the laws of thermodynamics, a relation may be derived that is applicable to general reaction:

$aA + bB \rightleftharpoons cC + dD$

we know that the chemical potential of a substance in a solution is related to its activity by the expression

$$\mu = \mu^\circ + RT \ln a \quad \text{—— [illegible]}$$

where μ° is the chemical potential of the pure substance in the standard state of unit activity, R is gas constant and T the absolute temperature.

For 'x' mole of substance A, we can write using eq [illegible] thus

$x\mu_A = x(\mu^\circ_A + RT \ln a_A)$

Similarly $y\mu_B = y(\mu^\circ_B + RT \ln a_B)$

$l\mu_L = l(\mu^\circ_L + RT \ln a_L)$ and

$m\mu_M = m(\mu^\circ_M + RT \ln a_M)$

The change in free energy for the reaction is given by

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

Substituting the above values we get

$$\Delta G = [l\mu_L + m\mu_M] - [x\mu_A + y\mu_B]$$

$$= \{l(\mu^\circ_L + RT \ln a_L) + m(\mu^\circ_M + RT \ln a_M)\} - \{x(\mu^\circ_A + RT \ln a_A) + y(\mu^\circ_B + RT \ln a_B)\}$$

$$= \{[l\mu^\circ_L + m\mu^\circ_M] - [x\mu^\circ_A + y\mu^\circ_B]\} + RT \ln \frac{a_L^l \, a_M^m}{a_A^x \, a_B^y}$$

or $$\Delta G = \Delta G^\circ + RT \ln \left[\frac{a_L^l \, a_M^m}{a_A^x \, a_B^y}\right] \quad \text{—— [illegible]}$$

where ΔG° stands for the difference in free energy of the products and the reactants when all are in their respective standard states [illegible]

$\Delta G^\circ = [l\mu^\circ_L + m\mu^\circ_M] - [x\mu^\circ_A + y\mu^\circ_B]$

In equation [illegible] the term $\frac{a_L^l \, a_M^m}{a_A^x \, a_B^y}$ stands for

the reaction quotient of activities of the reaction and equation [illegible] may be divided by T. The equation [illegible] now becomes

$$\Delta G = \Delta G^\circ + RT \ln J \quad \text{---- [illegible]}$$

This equation is called van't Hoff Reaction Isotherm. Again, for the reaction at equilibrium, $\Delta G = 0$ provided the pressure and the temperature are constant. Condition of equilibrium equation [illegible] becomes

$$0 = \Delta G^\circ + RT \ln J$$

or $$\Delta G^\circ = -RT \ln J$$

or $$\Delta G^\circ = -RT \ln \left(\frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b} \right) \quad \text{---- [illegible]}$$

Since ΔG° is the free energy of the reaction in the standard state and is constant at a given temperature, then as the gas constant R and the temperature T are constant, then the factor $\frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b}$ will be constant, i.e.

$$\frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b} = \text{constant} = K_p \quad \text{---- [illegible]}$$

where K_p is nothing but the equilibrium constant and is called the thermodynamic equilibrium constant of a reaction. Then the equation [illegible] becomes

$$\Delta G^\circ = -RT \ln K_p \quad \text{---- [illegible]}$$

or $$\Delta G^\circ = -2.303\, RT \log K_p \quad \text{---- [illegible]}$$

The equations [illegible] and [illegible] are also called van't Hoff isotherm. It may be used to calculate the change in free energy of a reaction in the standard state (ΔG°) when knowing the value of K_p and vice versa.

---- To be continued