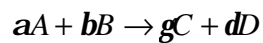


Lecture No:2

3. Chemical Equilibrium in a Mixture

Consider a closed system at constant T and P. It consists of a mixture of chemical species which react according to the equation;



The reaction continues advancing until the free energy of the system reaches a minimum value. At equilibrium; $G = G_{\min}$ and $\Delta G = 0$.

The change in the free energy of the system is;

$$dG = -SdT + VdP + \sum m_i dn_i$$

Since T and P are constant, this equation reduces to;

$$dG = \sum m_i dn_i = m_A dn_A + m_B dn_B + m_C dn_C + m_D dn_D$$

If the degree of extent is x , then the number of moles present are;

$$n_A = n_{0A} - ax$$

$$n_B = n_{0B} - bx$$

$$n_C = n_{0C} + gx$$

$$n_D = n_{0D} + dx$$

Differentiating these equations, we obtain;

$$dn_A = -a \cdot dx$$

$$dn_B = -b \cdot dx$$

$$dn_C = g \cdot dx$$

$$dn_D = d \cdot dx$$

Using these relations and dividing both sides by dx ;

$$\Delta G = \left(\frac{dG}{dx} \right)_{T,P} = gm_C + dm_D - am_A - bm_B$$

For any chemical reaction, the free energy change due to reaction is;

$$\Delta G = \sum_{\text{products}} n_i m_i - \sum_{\text{reactants}} n_i m_i$$

3.1 Chemical Equilibrium in a Mixture of Ideal Gases

If A, B, C and D are all ideal gases, ΔG may be calculated as;

$$\Delta G = (g m_C^o + d m_D^o - a m_A^o - b m_B^o) + RT(g \ln p_C + d \ln p_D - a \ln p_A - b \ln p_B)$$

The sum in the first parenthesis is the standard reaction free energy ΔG^o . It is a function only of temperature. Then, combining the logarithmic terms, we may write the free energy change as;

$$\Delta G = \Delta G^o + RT \ln \frac{p_C^g p_D^d}{p_A^a p_B^b}$$

The ratio is called the quotient of pressures. At equilibrium, $\Delta G = 0$, then the above equation becomes;

$$\Delta G^o = -RT \ln K_p$$

K_p is the pressure equilibrium constant. It is the quotient of equilibrium partial pressures.

The mole fraction equilibrium constant is;

$$K_x = \frac{x_C^g x_D^d}{x_A^a x_B^b} \quad \text{and} \quad K_p = K_x P^{\Delta n}$$

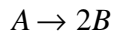
Δn is the sum of the mole numbers of the products minus the sum of the mole numbers of the reactants. If $\Delta n \neq 0$ then K_x depends upon pressure.

The concentration equilibrium constant is K_c . It is the quotient of equilibrium concentrations. K_c is a function only of temperature;

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

3.2 Calculation of K_p

In the calculation of the equilibrium constant, we use a , degree of dissociation. It is defined as the fraction dissociated per mole of the reactant.



For the above reaction;

Initial number of moles : $(n_A)_o = n$ and $(n_B)_o = 0$

Number of moles at equilibrium : $n_A = n - na$ and $n_B = 2na$

Mole fractions at equilibrium : $x_A = \frac{(1-a)}{(1+a)}$ and $x_B = \frac{2a}{(1+a)}$

The pressure equilibrium constant : $K_p = \frac{4a^2 P}{1-a^2}$

3.3 Temperature Dependence of K_p

$$\ln K_p = -\frac{\Delta G^\circ}{RT}$$

Differentiating the above equation with respect to temperature and by using the Gibbs-Helmholtz equation, we obtain van't Hoff equation;

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$$

If the reaction is endothermic, K_p increases with an increase in temperature. If the reaction is exothermic, K_p decreases with an increase in temperature.

Van't Hoff's equation can be expressed in a form convenient for plotting;

$$\ln K_p = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \text{Constant}$$

A plot of $\ln K_p$ versus $1/T$ gives a line with a slope equal to $-\Delta H^\circ/R$. Since ΔH° is constant over moderate ranges of temperature, the plot is linear.

If ΔH° is constant, integrating the above equation between the limits, we have;

$$\ln K_p = \ln(K_p)_o + \frac{\Delta H^\circ}{R} \left(\frac{1}{T_o} - \frac{1}{T} \right)$$

From the knowledge of ΔH° and a known value of $(K_p)_o$ at any temperature T_o , we can calculate K_p at any other temperature.

If ΔH° is not constant, it can be expressed as a power series in T;

$$\ln K_p = \frac{A}{T} + B + C \ln T + DT + ET^2 + \dots$$