## [IV] Thermodynamic Derivation of Law of Mass Action

The law of mass action can be derived from two concepts, viz., chemical potential concept and equilibrium box concept.

**(1) Chemical potential concept :** The chemical potential ($\mu$) of $i^{th}$ component in a mixture is defined as,

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{P, T, n_1, n_2, \ldots}$$

where $n_1, n_2, \ldots$ etc. represent the number of moles of constituent components of the mixture.

Consider the following reversible reaction :

$$n_1A + n_2B \rightleftharpoons m_1C + m_2D$$
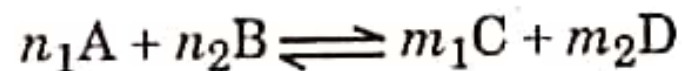
Suppose all the reactants and products are in the gaseous states and behave as ideal gases. The Gibbs potential, i.e., Gibbs free energy of reactants is given by

$$G_{reactants} = n_1 \mu_A + n_2 \mu_B$$

where $\mu_A$ and $\mu_B$ are the chemical potentials of the constituents A and B, respectively. Similarly, the Gibbs potential of the products is given by

$$G_{products} = m_1 \mu_C + m_2 \mu_D$$

The pressure and temperature remain constant in each case. We know that the free energy of the reaction is equal to the difference between the free energy of the products and that of reactants, i.e.,

$$\Delta G_{reaction} = G_{products} - G_{reactants}$$
$$= (m_1 \mu_C + m_2 \mu_D) - (n_1 \mu_A + n_2 \mu_B) \qquad \ldots (5)$$

When the reaction attains equilibrium, $\Delta G_{reaction} = 0$, so from equation (5),

$$(m_1 \mu_C + m_2 \mu_D) - (n_1 \mu_A + n_2 \mu_B) = 0 \qquad \ldots (6)$$

The chemical potential of the $i^{th}$ component in the gaseous reaction is given by

$$\mu_i = \mu_i^\circ + RT \ln p_i \qquad \ldots (7)$$

where $\mu_i^\circ$ is the standard chemical potential and $p_i$ is the partial pressure of $i^{th}$ component.

From equations (6) and (7), we get

$$[m_1 (\mu_C^\circ + RT \ln p_C) + m_2 (\mu_D^\circ + RT \ln p_D)] - [n_1 (\mu_A^\circ + RT \ln p_A)$$
$$+ n_2 (\mu_B^\circ + RT \ln p_B)] = 0$$

or

$$RT \ln \left( \frac{p_C^{m_1} \cdot p_D^{m_2}}{p_A^{n_1} \cdot p_B^{n_2}} \right) = -[(m_1 \mu_C^\circ + m_2 \mu_D^\circ) - (n_1 \mu_A^\circ + n_2 \mu_B^\circ)]$$
$$= -[G_{products}^\circ - G_{reactants}^\circ] = -\Delta G_{reaction}^\circ \qquad \ldots (8)$$

or

$$\frac{p_C^{m_1} \cdot p_D^{m_2}}{p_A^{n_1} \cdot p_B^{n_2}} = e^{-\Delta G_{reaction}^\circ / RT} \qquad \ldots (9)$$

The right hand side of equation (9) is constant, because $\Delta G_{reaction}^\circ$ depends only on temperature and $R$ is a constant. Therefore,

$$\frac{p_C^{m_1} \cdot p_D^{m_2}}{p_A^{n_1} \cdot p_B^{n_2}} = \text{constant} = K_p \qquad \ldots (10)$$

Since partial pressures are proportional to molar concentration of the components, so from equation (10), we have

$$\frac{[C]^{m_1} \cdot [D]^{m_2}}{[A]^{n_1} \cdot [B]^{n_2}} = K_C \qquad \ldots (11)$$

Equations (10) and (11) represent the expressions for equilibrium constant as obtained from law of mass action and chemical equilibrium.