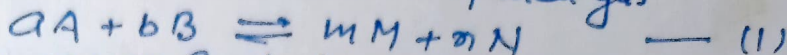


Thermodynamic Derivation of Law of Mass action.

Let us consider a reversible reaction of ideal gas



The chemical potential or Gibb's free energy of reactant containing a moles of A and b moles of B then the expression is as,

$$G_{\text{Reactants}} = a\mu_A + b\mu_B$$

where μ_A and μ_B are the chemical potentials of reactant A and B respectively.

Similarly for the product

$$G_{\text{Product}} = m\mu_M + n\mu_N$$

Now the difference between free energy is as follows

$$\Delta G = G_{\text{Product}} - G_{\text{Reactant}}$$

$$\text{or } \Delta G = (m\mu_M + n\mu_N) - (a\mu_A + b\mu_B) \quad \text{--- (2)}$$

At the point of equilibrium, $\Delta G = 0$

So, the above eqⁿ can be written as.

$$0 = (m\mu_M + n\mu_N) - (a\mu_A + b\mu_B) \quad \text{--- (3)}$$

$$\text{or } (m\mu_M + n\mu_N) - (a\mu_A + b\mu_B) = 0 \quad \text{--- (3)}$$

The chemical potential of the i^{th} species in a gaseous state is given as, $\mu_i = \mu_i^{\circ} + RT \ln P_i$ --- (4)

where P_i is the partial pressure of the i^{th} component.

and μ_i° is its standard chemical potential.

On the basis of eqⁿ (4)

$$\mu_M = \mu_M^{\circ} + RT \ln P_M, \mu_N = \mu_N^{\circ} + RT \ln P_N, \mu_A = \mu_A^{\circ} + RT \ln P_A,$$

$$\text{and } \mu_B = \mu_B^{\circ} + RT \ln P_B \dots \dots \dots$$

Now substituting this value in eqⁿ (3) we have

$$[m(\mu_M^{\circ} + RT \ln P_M) + n(\mu_N^{\circ} + RT \ln P_N)] - [a(\mu_A^{\circ} + RT \ln P_A) + b(\mu_B^{\circ} + RT \ln P_B)] = 0$$

$$\text{or, } RT [\ln P_M^m P_N^n - \ln P_A^a P_B^b] = -m\mu_M^{\circ} - n\mu_N^{\circ} + a\mu_A^{\circ} + b\mu_B^{\circ}$$

$$\text{or, } RT \ln \frac{P_M^m P_N^n}{P_A^a P_B^b} = -[(m\mu_M^{\circ} + n\mu_N^{\circ}) - (a\mu_A^{\circ} + b\mu_B^{\circ})] \quad \text{--- (5)}$$

$$\text{or } RT \ln \frac{P_M^m P_N^n}{P_A^a P_B^b} = -[G_{\text{Product}}^{\circ} - G_{\text{Reactant}}^{\circ}] = -(\Delta G^{\circ})_{\text{Reaction}} \quad \text{--- (5)}$$

$$\text{or } \frac{P_M^m P_N^n}{P_A^a P_B^b} = e^{\frac{-\Delta G^{\circ}}{RT}} \quad \text{--- (6)}$$

Since ΔG° depends only on temp. and R is a gas constant

So, $-(\Delta G^\circ)_{\text{reaction}} = \text{Const.}$

$$e^{-\frac{\Delta G^\circ}{RT}}$$

$$\text{Hence } \frac{P_M^m P_N^n}{P_A^a P_B^b} = \text{Constant} = K_p \quad \text{--- (7)}$$

The above equation defines law of mass action.

Similarly, if chemical potentials of the substances evolved in reaction are expressed in terms of mole fraction (X_i) they

$$\mu_i = \mu_i^\circ + RT \ln X_i \quad \text{--- (8)}$$

then analogous to eqⁿ (7) the obtained eqⁿ is like

$$\frac{X_M^m \cdot X_N^n}{X_A^a \cdot X_B^b} = K_x \quad \text{--- (9)}$$

If on the other hand chemical potentials are expressed in terms of molar concentrations (C_i)

$$\text{then } \mu_i = \mu_i^\circ + RT \ln C_i \quad \text{--- (10)}$$

from which we obtained the following expression like

$$\frac{[M]^m [N]^n}{[A]^a [B]^b} = K_c$$

$$\text{or } \frac{C_M^m C_N^n}{C_A^a C_B^b} = K_c \quad \text{--- (11)}$$

If the reactant and products are not ideal gas, then the thermodynamic equilibrium constant K_{th} is defined as,

$$K = K_{th} = \frac{(a_M^m \cdot a_N^n)}{(a_A^a \cdot a_B^b)} \quad \text{--- (12)}$$

where (a)_s are the activities, for non ideal i.e. real gas

$$K = K_f = \frac{f_M^m f_N^n}{f_A^a f_B^b} \quad \text{--- (13)}$$

where (f)_s are the fugacities,

for a mixture of real gases

$$Y_i = \frac{f_i}{P_i} \quad \text{or } f_i = Y_i P_i \quad (\text{where } Y_i \text{ is activity-coefficients})$$

Hence

$$K_f = \frac{Y_M^m Y_N^n}{Y_A^a Y_B^b} \times \frac{P_M^m P_N^n}{P_A^a P_B^b} = K_y K_p$$