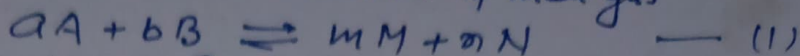


# Thermodynamic Derivation of Law of Mass action.

Let us consider a reversible reaction of ideal gas



The chemical potential or Gibbs 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  $\mu_A$  and  $\mu_B$  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.

$$0 = (m\mu_M + n\mu_N) - (a\mu_A + b\mu_B)$$

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

The chemical potential of the  $i$ th species in a gaseous state is given as,  $\mu_i = \mu_i^0 + RT \ln P_i$

where  $P_i$  is the partial pressure of the  $i$ th component and  $\mu_i^0$  is its standard chemical potential.

On the basis of eqn (4)

$$\mu_M = \mu_M^0 + RT \ln P_M, \mu_N = \mu_N^0 + RT \ln P_N, \mu_A = \mu_A^0 + RT \ln P_A, \\ \text{or } \mu_B = \mu_B^0 + RT \ln P_B \quad \dots \dots \dots$$

Now substituting this value in eqn (3) we have

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

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

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

$$\text{or } RT \ln \frac{P_M^m P_N^n}{P_A^a P_B^b} = -[G_{\text{product}}^0 - G_{\text{reactant}}^0] = -(\Delta G^0)_{\text{Reaction}} \quad \text{--- (5)}$$

$$\text{or } \frac{P_M^m P_N^n}{P_A^a P_B^b} = e^{\frac{-\Delta G^0}{RT}} \quad \text{--- (6)}$$

Since  $\Delta G^\circ$  depends only on temp. and  $R$  is a gas constant  
 so,  $-\frac{\Delta G^\circ}{RT} = \text{const.}$

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

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

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 ( $a_i$ )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 ( $f_i$ )s are the fugacities,

for a mixture of real gases

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

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