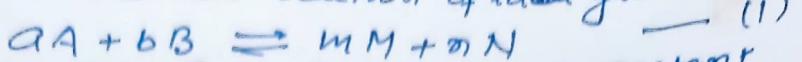


## Thermodynamic Derivation of Law of Mass action

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

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

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

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

so, the above eqn can be written as.

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

$$\text{or } (m\mu_M + n\mu_N) - (a\mu_A + b\mu_B) = 0 \quad (4)$$

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 the standard chemical potential.

On the basis of eqn (4)

$$\mu_M = \mu_M^0 + RT \ln P_M, \mu_N = \mu_N^0 + RT \ln P_N, \mu_A = \mu_A^0 + RT \ln P_A,$$

$$\text{or } \mu_B = \mu_B^0 + RT \ln P_B \dots \dots$$

Now substituting this value in eqn (3) we have

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

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

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

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

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

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

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

$$\text{Hence } \frac{P_M^u P_N^u}{P_A^a P_B^b} = \text{constant} = K_p \quad \dots \quad (7)$$

The above equation defines law of mass action.

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

$$\ell_{p_i} = \ell_i^\circ + RT \ln X_i \quad \dots \quad (8)$$

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

$$\frac{X_M^u X_N^u}{X_A^a X_B^b} = K_x \quad \dots \quad (9)$$

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

$$\text{then } \ell_{p_i} = \ell_i^\circ + RT \ln C_i \quad \dots \quad (10)$$

from which we obtained the following expression like.

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

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

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

$$K = K_{th} = \frac{(a_M^u \cdot a_N^u)}{(a_A^a \cdot a_B^b)} \quad \dots \quad (12)$$

Where ( $a$ )<sub>i</sub>s are the activities, for nonideal i.e. real gas

$$K = K_f = \frac{f_M^u f_N^u}{f_A^a f_B^b} \quad \dots \quad (13)$$

Where ( $f$ )<sub>i</sub>s are the fugacities,  
for a mixture of real gases

$$y_i = f_i / p_i \quad \text{or } f_i = y_i p_i \quad (\text{where } y_i \text{ are activity-coefficients})$$

Hence

$$K_f = \frac{y_M^u y_N^u}{y_A^a y_B^b} \times \frac{P_M^u P_N^u}{P_A^a P_B^b} = K_y K_p$$