Thermodynamic Derivation of Law of Mass action.

Let us consider a reversible reaction of ideal gas

$$aA + bB \rightleftharpoons mM + nN \qquad \text{--- (1)}$$

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,

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

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

Similarly for the product

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

Now the difference between free energy is as follows

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

Or

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

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

SO, the above eqn Can be Written as.

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

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

The chemical Potential of the ith species in a gaseous State is given as, $\mu_i = \mu_i^0 + RT \ln P_i$ --- ④

Where P_i is the partial pressure of the ith component. and μ_i^0 is its standard chemical Potential.

On the basis of eqn (4)

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

$$\& \ \mu_B = \mu_B^0 + RT \ln P_B \ \ldots\ldots$$

Now substituting this Value in eqn ③ we have

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

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

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

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

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

Since ΔG^0 depends only on temp. and R is a gas constant so, $e^{-\frac{(\Delta G^0)_{reaction}}{RT}} = \text{Const.}$

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

The above equation defines law of mass action.

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

$$G_i = G_i^0 + RT \ln X_i \quad \text{—— ⑧}$$

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)

then $$G_i = G_i^0 + RT \ln C_i \quad \text{—— (10)}$$

from which we obtained the following expression like.

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

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

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)is 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)is are the fugacities,

For a mixture of real gases

$\gamma_i = f_i / P_i$ or $f_i = \gamma_i P_i$ (Where γ_is are activity-coefficients)

Hence $$K_f = \frac{\gamma_M^m \gamma_N^n}{\gamma_A^a \gamma_B^b} \times \frac{P_M^m P_N^n}{P_A^a \cdot P_B^b} = K_\gamma K_p$$