Thermodynamic Derivation of Law of Mass action:

Lee us consider a reversible reaction of ideal gas

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

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

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

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

So, the above eqn can be written as.

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

or

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

The chemical Potential of the ith 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 ith component and μ_i° is its standard chemical Potential.

On the basis of eqn (4)

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

& $\mu_B = \mu_B^\circ + RT \ln P_B$ ......

Now substituting this Value in eqn ③ we have

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

or,

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

or,

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

$$= -[G_{Product}^\circ - G_{Reactant}^\circ] = -(\Delta G^\circ)_{Reaction} \quad \text{---} ⑤$$

or

$$RT \ln \frac{P_M^m P_N^n}{P_A^a \cdot P_B^b}$$

or

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

Since ΔG^0 depends only on temp. and R is a gas constant so,

$$e^{\frac{-(\Delta G^0)_{reaction}}{RT}} = \text{Const.}$$

Hence

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

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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

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

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

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 $(a)_i$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

$$\gamma_i = f_i / P_i \quad \text{or} \quad f_i = \gamma_i P_i$$ (Where γ_is are activity-Coefficients

Hence

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