~~Thermodynamics. Paper III D2(H),~~ Dr. S. K. Jha. (Lect. 12)

Thermodynamic derivation of law of Mass action :→

Law of Mass action was given by Guldberg & Waage. Law of Mass action is linked with two terms i.e rate of reaction & active mass (Molar concentration or partial pressure of chemical species).

According to Law of mass action at constant temperature the rate of reaction is directly proportional to the active mass of reacting species, but if the no. of reacting species are two then the rate of chemical reaction at constant temperature is directly proportional to the product (Multiplication) of active mass of reacting species.

A Common reversible reaction is –

$$aA + bB \rightleftharpoons cC + dD$$

Since for the reaction in common

$$\Delta G = G_P - G_R \text{ ——— } (1)$$

(G_P = Gibb's energy of Prod. G_R = Gibb's energy of Reac.)

Now we know $G_i = \Sigma n_i \mu_i$ (μ_i = Chemical potential).

$$\text{So } \left.\begin{aligned} G_R &= a\mu_A + b\mu_B \\ G_P &= c\mu_C + d\mu_D \end{aligned}\right] \text{–(2)}$$

(for the given Common reaction)

$\Delta G = G_P - G_R$ by eqn I now we put the Value ~~of~~ of G_P & G_R from eqn 2 to Eqn I, we have:

$$\Delta G = (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B) \quad \text{——} \quad (3)$$

we know,

$$\mu = \mu^0 + RT \ln P$$ (μ = Chemical Potential, μ^0 = Standard Chemical Pot)

Here,

$$\left.\begin{aligned} \mu_A &= \mu_A^0 + RT \ln P_A \\ \mu_D &= \mu_B^0 + RT \ln P_B \\ \mu_C &= \mu_C^0 + RT \ln P_C \\ \mu_D &= \mu_D^0 + RT \ln P_D \end{aligned}\right\} \text{——} \quad (4)$$

Now we put the value of μ_A, μ_B μ_C μ_D from equation (4) to equation (3), then we have :-

or $\Delta G = C(\mu_C^0 + RT \ln P_C + d(\mu_D^0 + RT \ln P_D) - a(\mu_A^0 + RT \ln P_A + b(\mu_B^0 + RT \ln P_B)$

or $\Delta G = (c\mu_C^0 + d\mu_D^0) - (a\mu_A^0 + b\mu_B^0) + [cRT P_C + dRT \ln P_D] - [aRT \ln P_A + bRT \ln P_B]$

or a

$$\Delta G = \Delta G^0 + (cRT \ln P_C + dRT \ln P_D) - (aRT \ln P_A + bRT \ln P_B)$$

$\because \Delta G^0 = c\mu_C^0 + d\mu_D$

or $\Delta G = \Delta G^0 + (RT \ln P_C^c + RT \ln P_D^d) - (RT \ln P_A^a + RT \ln P_B^b)$

or $\Delta G = \Delta G^0 + RT(\ln P_C^c + \ln P_D^d) - (\ln P_A^a + \ln P_B^b)$

or $\Delta G =$ ~~$\Delta G^0 + RT \ln P_C^c \times P_D^d - P_A^a \times P_B^b$~~

$$\Delta G = \Delta G^{0} + RT \ln \frac{P_C^{c} \times P_D^{d}}{P_A^{a} \times P_B^{b}} \quad \text{——} \quad (5)$$

$$\text{or } \Delta G = \Delta G^{0} + RT \ln K_p \quad \text{——} \quad (6)$$

$$\text{or } \Delta G = \Delta G^{0} + 2.303\, RT \log K_p \quad \text{——} \quad (7)$$

Equation (5), (6) & (7) are the ~~derivation~~ ~~equation of~~ thermodynamic derivative equation of law of mass action.

Vant Hoff reaction Isotherm:-

$$\Delta G = \Delta G^{0} + RT \ln \frac{P_C^{c} \times P_D^{d}}{P_A^{a} \times P_B^{b}} \quad \text{——} \quad \text{I}$$

$$= \Delta G^{0} + RT \ln K_p \quad \text{——} \quad \text{II}$$

At equilibrium $\Delta G = 0$.

$$\text{So} \quad 0 = \Delta G^{0} + RT \ln K_p$$

$$\text{or} \quad \Delta G^{0} = -RT \ln K_p$$

$$\text{or} \quad \cancel{\Delta G^{0}} = -\cancel{2.303\,RT\log K_p}$$

$$\Delta G^{0} = -2.303\, RT \log_{10} K_p$$

Where it is in terms of conc^n then

$$\Delta G^{0} = -2.303\, RT \log K_c.$$

The main Vant Hoff Isotherm equation is I & II.

Vant Hoff Isochore :→

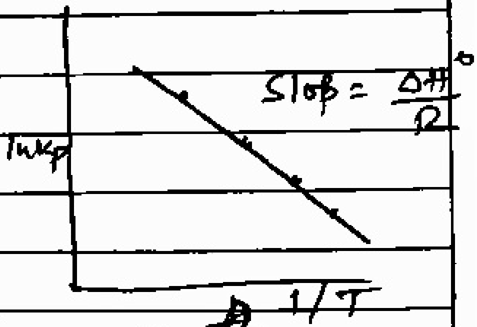
we know from Vant Hoff Isotherm,

$$\Delta G^0 = -RT \ln K_p$$

$$\ln K_p = \frac{-\Delta G^0}{T}$$

$$\ln K_p = \frac{-(\Delta H^0 - T\Delta S^0)}{RT}$$

or $$\ln K_p = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$



Assuming during study range ΔH^0 & ΔS^0 are independent. then

$$\ln K_p = \frac{\Delta H^0}{R}\left(\frac{1}{T}\right)$$

As graph shows there is linear relationship between Kp & 1/T,

Hence, $$\ln K_{p_1} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT_1} \quad \text{— I}$$

again $$\ln K_{p_2} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT_2} \quad \text{— II}$$

By eqn I & II we have:

$$\ln K_{p_2} - \ln K_{p_1} = \frac{\Delta H^0}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

So, $$\log_e \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H^0}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

or $$\boxed{\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H^0}{2.303R}\left(\frac{T_2 - T_1}{T_1 \times T_2}\right)}$$

This is Vant Hoff Isochore eqn.

Teacher's Signature :

chapter is over

CHAPTER OVER