I.D.C. Part IIIrd ; Paper-Vth , Thermodynamics

Thermodynamics

Van't Hoff ~~isotherm~~ reaction isotherm —

Q Write a note on van't Hoff's reaction isotherm.

Q Derive an expression for van't Hoff's reaction isotherm

Ans. Van't Hoff's reaction isotherm involves the calculati of change in free energy when a chemical reaction i carried out at const. temp. from some arbitrary concentr of reactants to some other arbitrary concentration o others.

Let us consider a gaseous reaction.

$$A + B \rightleftharpoons C + D$$

ce energy $\underbrace{G_A \quad G_B}_{G_R} \qquad \underbrace{G_C \quad G_D}_{G_P}$

The free energy of reactants and products be given as below -

$$G_A = G_A^0 + RT \ln P_A$$

Where $G_A^0$ = standard free energy of A

and $P_A$ = Pressure of A

Similarly,

$$G_B = G_B^0 + RT \ln P_B$$

$$G_C = G_C^0 + RT \ln P_C$$

and $G_D = G_D^0 + RT \ln P_D$

so for change in free energy of the reaction is given as

$$\Delta G = G_{(products)} - G_{(reactants)}$$

$$= (G_C + G_D) - (G_A + G_B)$$

$$= (G^\circ_C + RT \ln P_C + G^\circ_D + RT \ln P_D) -$$

$$(G^\circ_A + RT \ln P_A + G^\circ_B + RT \ln P_B)$$

$$= \{(G^\circ_C + G^\circ_D) - (G^\circ_A + G^\circ_B)] +$$

$$\{(RT \ln P_C + RT \ln P_D) - (RT \ln P_A + RT \ln P$$

$$= \Delta G^\circ + RT \{(\ln P_C + \ln P_D) - (\ln P_A + \ln$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{P_C \cdot P_D}{P_A \cdot P_B} \quad -(1$$

$$= \Delta G^\circ + 2.303\, RT \log \frac{P_C \cdot P_D}{P_A \cdot P_B}$$

Where $\Delta G^\circ$ = Standard free energy change of the reaction

If the reaction is assumed to be equilibri then

$$\Delta G = 0 \; ; \; \frac{P_C \cdot P_D}{P_A \cdot P_B} = K_p$$

Hence from equation (I).

$$0 = \Delta G^0 + RT \ln K_P$$

or $$\Delta G^0 = - RT \ln K_P$$

Putting the value of $\Delta G^0$ in equation (I) we get

$$\Delta G = - RT \ln K_P + RT \ln \frac{P_C \cdot P_D}{P_A \cdot P_B} \quad \text{— (II)}$$

for a general reaction like

$$n_1 A + n_2 B \rightleftharpoons n_3 C + n_4 D$$

$$\Delta G = - RT \ln K_P + RT \ln \left( \frac{P_C^{n_3} \cdot P_D^{n_4}}{P_A^{n_1} \cdot P_B^{n_2}} \right)$$

$$- \Delta G = RT \ln K_P + RT \sum n \ln P \quad \text{— (III)}$$

Equation (III) is one form of van't Hoff's ~~equation~~ reaction isotherm.

$\because$ $P \propto C$ in terms of concentration the expression (II) may be written as.

$$- \Delta G = RT \ln K_C - RT \sum n \ln C \quad \text{— (IV}$$

Eqn. (IV) is another form of van't Hoff reaction isotherm.