

## B.Sc. 2nd Sem (H) Thermodynamic derivation of the Law of Chemical Equilibrium

Let us consider a general reaction,



The chemical potential of a substance in a mixture is related to its activity by the expression

$$\mu = \mu^\circ + RT \ln a \quad \text{--- (1)}$$

where,  $\mu^\circ$  is the chemical potential of pure substance in standard state of unit activity,  $R$  is the gas constant and  $T$  is the absolute temperature.

For a mole of the substance A we can write using the equation (1) —

$$a\mu_A = a(\mu^\circ + RT \ln a_A)$$

Similarly,  $b\mu_B = b(\mu^\circ + RT \ln a_B)$

$$c\mu_C = c(\mu^\circ + RT \ln a_C)$$

$$d\mu_D = d(\mu^\circ + RT \ln a_D)$$

The change in free energy for the reaction is given by —  $\Delta G = G_{\text{products}} - G_{\text{reactants}}$

On substitution, we get —

$$\begin{aligned} \Delta G &= (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B) \\ &= (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B) \\ &= c(\mu^\circ + RT \ln a_C) + d(\mu^\circ + RT \ln a_D) - (a(\mu^\circ + RT \ln a_A) + b(\mu^\circ + RT \ln a_B)) \end{aligned}$$

$$= c[\mu_C^\circ + RT \ln a_C] + d[\mu_D^\circ + RT \ln a_D] - [a(\mu_A^\circ + RT \ln a_A) + b(\mu_B^\circ + RT \ln a_B)]$$

$$= [\{c\mu_C^\circ + d\mu_D^\circ\} - \{a\mu_A^\circ + b\mu_B^\circ\}] + RT \ln \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b}$$

$$\Rightarrow \Delta G = \Delta G^\circ + RT \ln \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b} \quad \text{--- (2)}$$

Where,  $\Delta G^\circ$  is the difference in free energy of the reaction when all reactants and products are in their standard state. It is given by —

$$\Delta G^\circ = \{c\mu_C^\circ + d\mu_D^\circ\} - \{a\mu_A^\circ + b\mu_B^\circ\}$$

In equation (2), the factor J is given by —

$$= \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b} \quad \text{stands for the reaction}$$

quotient of activities of products and reactants. It may be denoted by 'J'. So, eqn (2) becomes —

$$\Delta G = \Delta G^\circ + RT \ln J \quad \text{--- (3)}$$

The eqn (3) is called Van't Hoff reaction isotherm. For the reaction at eqm,  $\Delta G = 0$

$$\text{Therefore, } \Delta G^\circ = -RT \ln J$$

or we can write  $J = K$ ,  $K = \text{eqm constant}$

$$\Delta G^\circ = -RT \ln K \quad \text{--- (4)}$$

$$\text{or } \Delta G^\circ = -2.303 RT \log K \quad \text{--- (5)}$$

This eqn is also called Van't Hoff isotherm.



\* The sign of  $\Delta G^\circ$  indicates whether the forward or reverse reaction is spontaneous.

Considering the eqn (4), we can have three possibilities depending on the sign of  $\Delta G^\circ$  for the reaction.

(1) If  $\Delta G^\circ$  is negative,  $\log K$  must be positive and the reaction proceeds spontaneously in the forward reaction -

(2) If  $\Delta G^\circ$  is positive,  $\log K$  must be negative and  $K$  is less than one. The reverse reaction is then spontaneous.

(3) If  $\Delta G^\circ = 0$ ,  $\log K = 0$  and  $K = 1$ , the reaction is at equilibrium.