SUBJECT - CHEMISTRY

CLASS - B.Sc (Hons) PART - III

PAPER - V

TOPIC - Gibbs - Duhem equation

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Q Explain the term partial molal free energy (Chemical potential) Derive the Gibbs - Duhem equation.

Ans Partial molal free energy (Chemical potential): The Thermodynamic properties Such as E, H, S, A & G are all extensive properties. Their values in a homogeneous phase depend upon the amount of the substance. If the phase is of one Component, values of extensive properties divided by total number of moles are molal properties. If the phase has many Components, the addition of one mole of the Substance in The mixture will not increase the value of extensive properties equal to molar quantity. In this Connection, the Concept of partial molal properties was introduced by G.N Lewis (1907) The partial molal quantity of a Component is the Change in extensive property of a mixture when one mole of The pure Component is added in Such a way that there is no Change in T, P and Composition. This is possible if the System Considered is very large

Thus any extensive property X may be given as -

$$X = f(P, T, n_1, n_2, n_3 \cdots n_i)$$

where P = Pressure, T = temperature and $n_1, n_2$ -- are the number of moles of the Constituents 1, 2, 3 --- respectively.

$$\therefore\ dX = \left(\frac{\partial X}{\partial P}\right)_{T, n_1, n_2} dP + \left(\frac{\partial X}{\partial T}\right)_{P, n_1, n_2 \cdots} dT + \left(\frac{\partial X}{\partial n_1}\right)_{P, T, n_2 n_3} dn_1$$

$$+\left(\frac{\partial X}{\partial n_2}\right)_{P,T,n_1,n_3} dn_2 \text{ ------ } + \left(\frac{\partial X}{\partial n_i}\right)_{P,T,n_1,n_2,n_3 \cdots} dn_i + \cdots \quad -(1)$$

The derivative $\left(\frac{\partial X}{\partial n_i}\right)_{P,T,n_1,n_2 \cdots} dn_i$ is called the partial molal property for ith component $(\bar{X}_i)$. It is shown by a bar over the symbol of the property of the ith component. Hence we have –

$$dX = \left(\frac{\partial X}{\partial P}\right)_{T,n_1,n_2} dP + \left(\frac{\partial X}{\partial T}\right)_{P,n_1,n_2 \cdots} dT + \bar{X}_1 dn_1 + \bar{X}_2 dn_2 + \cdots \bar{X}_i dn_i + \cdots \quad (2)$$

If the thermodynamic property is Gibb's free energy (G), then

$$\left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_1,n_2} = \bar{G}_i = \mu_i \quad \text{--} (3)$$

where $\bar{G}_i$ is partial molal free energy of the ith component and $\mu_i$ is the chemical potential of ith component,

And equation (2) becomes –

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2 \cdots} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2 \cdots} dT + \mu_1 dn_1 + \mu_2 dn_2 + \cdots \quad (4)$$

At constant T & P, we get

$$(dG)_{P,T} = \mu_1 dn_1 + \mu_2 dn_2 + \cdots + \mu_i dn_i + \cdots \quad (5)$$

on integration we have –

$$(G)_{P,T} = \mu_1 n_1 + \mu_2 n_2 + \cdots \mu_i n_i \cdots \quad (6)$$

Therefore the chemical potential is the contribution per mole to each particular constituent of the mixture to the total free energy of the system under conditions of constant T & P

on differentiation, the equation (6) becomes –

$$dG = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 + \cdots n_i d\mu_i + \mu_i dn_i + \cdots$$

$$dG = (\mu_1 dn_1 + \mu_2 dn_2 + \cdots + \mu_i dn_i + \cdots)$$
$$+ n_1 d\mu_1 + n_2 d\mu_2 + \cdots + n_i d\mu_i + \cdots ) \text{--} (7)$$

The 1st term on RHS of eqn (7) is $dG$ at constant T & P as per equation (6), hence at constant T & P. for a system of a definite composition –

$$dG = dG + n_1 d\mu_1 + n_2 d\mu_2 + \cdots n_j d\mu_j + \cdots$$

$$\text{or} \quad 0 = n_1 d\mu_1 + n_2 d\mu_2 + \cdots + n_j d\mu_j + \cdots$$

$$\text{or} \quad \sum n_j d\mu_j = 0 \qquad \cdots (8)$$

Eqn (8) is called Gibbs-Duhem equation. It finds useful applications particularly in gas-liquid equilibria involved in distillations.