

Partial molar Properties

The thermodynamic properties U, H, S, A and G named internal energy (U), enthalpy (H), entropy (S), work function A and Gibbs free energy (G) are extensive properties, its value change with change in number of moles.

$$\text{Let } X = f(T, P, n_1, n_2, \dots, n_i, \dots) \quad \text{--- (1)}$$

$$\text{where } n_1 + n_2 + n_3 + \dots + n_i = N$$

For small change in temp, pressure and no. of moles of the Component,

$$dx = \left(\frac{\partial x}{\partial T}\right)_{P, N} dT + \left(\frac{\partial x}{\partial P}\right)_{T, N} dP + \left(\frac{\partial x}{\partial n_1}\right)_{P, T, n_2, n_3, \dots, n_i} dn_1 + \dots \quad \text{--- (2)}$$

The quantity $\left(\frac{\partial x}{\partial n_1}\right)_{T, P, n_2, n_3, \dots, n_i}$ is called the partial molar properties of 1st Component and represented by \bar{X}_1

Similarly for the i th Component: -

$$\left(\frac{\partial x}{\partial n_i}\right)_{T, P, n_1, n_2, n_3, \dots} = \bar{X}_i = \text{Partial molar Properties}$$

$$\left(\frac{\partial U}{\partial n_i}\right)_{T, P, n_1, n_2, \dots} = \bar{U}_i = \text{Partial molar internal energy}$$

$$\left(\frac{\partial H}{\partial n_i}\right)_{T, P, n_1, n_2, \dots} = \bar{H}_i = \text{Partial molar enthalpy}$$

$$\left(\frac{\partial S}{\partial n_i}\right)_{T, P, n_1, n_2, n_3, \dots} = \bar{S}_i = \text{Partial molar entropy}$$

$$\left(\frac{\partial V}{\partial n_i}\right)_{T, P, n_1, n_2, \dots} = \bar{V}_i = \text{Partial molar Volume}$$

Chemical Potential: - The partial molar free energy is designated as chemical potential and represented by symbol μ .

$$\left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_1, n_2, n_3, \dots} = \bar{G}_i = \mu_i \quad \text{--- (3)}$$

For infinitesimal change in free energy, we can write the following equation.

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, N} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, \dots, n_i, \dots} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_2, n_3, \dots, n_i, \dots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T, P, n_1, n_3, \dots, n_i, \dots} dn_2 + \dots$$

$$\text{or, } dG = \left(\frac{\partial G}{\partial T}\right)_{P, N} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, \dots, n_i, \dots} dP + \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_i dn_i \quad \text{--- (4)}$$

where $\mu_1, \mu_2, \mu_3, \dots, \mu_i$ are chemical potential of 1, 2, 3, 4, ... i th Component respectively.

$$\text{If } T \text{ and } P \text{ remains constant then } (dG)_{T, P} = \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_i dn_i \quad \text{--- (5)}$$

If a system has a definite composition having $n_1, n_2, n_3, \dots, n_i$ moles of constituents 1, 2, 3, ... i th respectively, then integrating eqn (5) we have

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

For one mole of pure substance $G = \mu$

i.e free energy is identical with chemical potential.

Chemical Potential of an ideal gas Mixture.

The variation of chemical potential of any component 'i' of the gaseous system with Pressure is represented as follows

$$\frac{\partial G}{\partial P} (\partial n_i) = \left(\frac{\partial \mu_i}{\partial P} \right)_{T,N} \quad \text{--- (1)}$$

$$\text{and } \frac{\partial^2 G}{(\partial n_i)(\partial P)} = \left(\frac{\partial v}{\partial n_i} \right)_{T,P,n_1,n_2,\dots} \quad \text{--- (2)}$$

From equation (1) and (2)

$$\left(\frac{\partial \mu_i}{\partial P} \right)_{T,N} = \bar{v}_i \quad \text{--- (3)}$$

Let us consider a system consisting of a number of ideal gases having number of moles n_1, n_2, \dots, n_i respectively in the mixture.

$$\text{From ideal gas eqn, } V = \frac{nRT}{P} = (n_1 + n_2 + \dots + n_i) \frac{RT}{P} \quad \text{--- (4)}$$

On differentiating eqn (4) w.r.t. to n_i at constant Temperature and Pressure.

$$\text{We have, } \left(\frac{\partial V}{\partial n_i} \right)_{T,P,n_1,n_2,n_3,\dots} = \bar{v}_i = \frac{RT}{P} \quad \text{--- (5)}$$

$$\text{From eqn (3) and (5) } \left(\frac{\partial \mu_i}{\partial P} \right)_{T,N} = \frac{RT}{P} \quad \text{--- (6)}$$

For constant composition and const temp. eqn (6) may be expressed as,

$$d\mu_i = RT \cdot \frac{dP}{P} = RT d(\ln P) \quad \text{--- (7)}$$

Let P_i be the Partial Pressure of constituent 'i' present in the mixture, since each constituent behaves as an ideal gas.

$$\text{therefore, } P_i V = n_i RT \text{ or } P_i = \left(\frac{n_i}{n} \right) \cdot P \quad \text{--- (8)}$$

Since n_i and n are constants, therefore, on taking log and differentiating we have

$$d(\ln P_i) = d(\ln P) \quad \text{--- (9)}$$

On substituting the value of $d(\ln P)$ in eqn (7) we have

$$d\mu_i = RT d(\ln P_i) \quad \text{--- (10)}$$

On integrating equation (10) we have

$$\mu_i = \mu_{i,P}^{\circ} + RT \ln P_i \quad \text{--- (11)}$$

where $\mu_{i,P}^{\circ}$ is the integration constant. Its value depends on Temperature and the nature of the gas.

At constant temperature the partial pressure of the constituent 'i' is unity, i.e. $P_i = 1$

$$\text{then } \mu_i = \mu_{i,P}^{\circ} \quad \text{--- (12)}$$

where $\mu_{i,P}^{\circ}$ is the chemical potential of ith constituent when Partial Pressure is unity, and temperature is constant

$$\text{Now from eqn (8) } P_i = \left(\frac{n_i}{V} \right) RT \quad \text{--- (13)}$$

if $\left(\frac{n_i}{V} \right)$ represents the molar concentration of constituent 'i' in the mixture.

$$\text{then } P_i = C_i RT \quad \text{--- (14)}$$

Now from eqn (11) and (14)

$$\text{on integrating the above eqn. we have, } \mu_i = \mu_{i,P}^{\circ} + RT \ln(C_i RT)$$

$$\mu_i = \mu_{i,P}^{\circ} + RT \ln C_i + RT \ln RT$$

$$\text{or } \mu_i = \mu_{i,C}^{\circ} + RT \ln C_i \quad \text{--- (15)}$$

where $\left(\mu_{i,C}^{\circ} = \mu_{i,P}^{\circ} + RT \ln RT \right)$ $\mu_{i,C}^{\circ}$ is a const. depending upon temp & nature of gas.

If $(i = 1)$ then $\mu_i = \mu_{i,c}^0$

Thus $\mu_{i,c}^0$ represents the Chemical Potential of the Constituent i when the concentration of the constituent i in the mixture is unity, and $(\frac{\partial \mu_i}{\partial n_i})$ represents the mole fraction (x_i) of constituent i in the mixture, then equation (8) can be represented as

$$P_i = x_i P \quad \text{--- (16)}$$

Substituting the value of P_i in the equation (11) at const. Pressure

$$\mu_i = \mu_{i,p}^0 + RT \ln x_i P$$

$$\mu_i = \mu_{i,p}^0 + RT \ln x_i + RT \ln P$$

$$\therefore \mu_i = \mu_{i(x)}^0 + RT \ln x_i$$

$$\text{where } \left[\mu_{i(x)}^0 = \mu_{i,p}^0 + RT \ln P \right]$$

So, $\mu_{i(x)}^0$ represents the Chemical Potential of the Constituent i when mole fraction is unity at constant Temperature and Pressure.

Gibbs-Duhem Equation

The free energy equation, $(G)_{T,P,N} = n_1 \mu_1 + n_2 \mu_2 + n_3 \mu_3 + \dots + n_i \mu_i$ shows that the free energy of a system at constant temperature and pressure can be expressed as a sum of $n_i \mu_i$ terms for the individual components of the system.

The total differential of 'G', written as

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

$$dG = (\mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_i dn_i) + (n_1 d\mu_1 + n_2 d\mu_2 + \dots + n_i d\mu_i) \quad \text{--- (1)}$$

We know that $(dG)_{T,P} = (\mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_i dn_i) \quad \text{--- (2)}$

From eq (1) and (2) at const. Temp & Pressure for a system of definite composition

$$dG = dG + (n_1 d\mu_1 + n_2 d\mu_2 + \dots + n_i d\mu_i)$$

$$\text{or, } n_1 d\mu_1 + n_2 d\mu_2 + \dots + n_i d\mu_i = 0$$

$$\therefore \sum n_i d\mu_i = 0$$

This relation is called Gibbs-Duhem equation.

For a system having two components

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

$$\text{or, } d\mu_1 = \left(\frac{n_2}{n_1} \right) \cdot d\mu_2$$

It shows the variation in chemical potential of one component affects the value for the other component.

If μ_1 increases, then μ_2 must decrease and vice versa.

