

partial Molar properties :-

consider a thermodynamic extensive property such as volume, free energy, heat content, heat capacity, the value of which, for homogeneous system is completely determined by the state system e.g. temperature, pressure and the amount of various constituents present and may be denoted by general symbol x

thus,

$$x = f(p, T, n_1, n_2, n_3, \dots, n_i, \dots)$$

where:-

P = pressure, T = temperature and n_1, n_2, n_3, \dots are the number of moles of the constituents $1, 2, 3, \dots$ respectively and x is a thermodynamics property.

If a small change in p, T and its constituents. The change in property x is given by,

$$dx = \left(\frac{\delta x}{\delta p} \right)_{T, n_1, n_2, n_3, \dots} dp + \left(\frac{\delta x}{\delta T} \right)_{p, n_1, n_2, n_3, \dots} dt +$$

$$\left(\frac{\delta x}{\delta n_1} \right)_{P, T, n_2, n_3, \dots} dn_1 + \left(\frac{\delta x}{\delta n_2} \right)_{P, T, n_1, n_3, \dots} dn_2 \\ + \dots + \left(\frac{\delta x}{\delta n_i} \right)_{T, n_1, n_2, n_3, \dots} dn_i + \dots$$
(1)

The derivative $\left(\frac{\delta x}{\delta n_i} \right)_{P, T, n_1, n_2, n_3, \dots}$ is called

partial molar property for the constituent i , and represented by \bar{x}_i .

Therefore,

$$\left(\frac{\delta x}{\delta n_1} \right)_{P, T, n_2, n_3, \dots} = \bar{x}_1$$

$$\left(\frac{\delta x}{\delta n_2} \right)_{P, T, n_1, n_3, \dots} = \bar{x}_2$$

$$\left(\frac{\delta x}{\delta n_i} \right)_{P, T, n_1, n_2, n_3, \dots} = \bar{x}_i$$

so putting these values in eqn. ①

$$dx = \left(\frac{\delta x}{\delta P} \right)_{T, n_1, n_2, n_3} dp + \left(\frac{\delta x}{\delta T} \right)_{P, n_1, n_2, n_3, \dots} dT \\ + \bar{x}_1 dn_1 + \bar{x}_2 dn_2 + \dots + \bar{x}_i dn_i \quad \text{②}$$

At constant pressure $dp = 0$

At constant temperature $dT = 0$

so, putting these values in eqn. ②

$$dx_{P, T} = \bar{x}_1 dn_1 + \bar{x}_2 dn_2 + \dots + \bar{x}_i dn_i \quad \text{③}$$

on integration eqn. ③ for a system of definite compositions represented by $n_1, n_2, n_3, \dots, n_i$ we have:

$$x_{P, T, N} = n_1 \bar{x}_1 + n_2 \bar{x}_2 + n_3 \bar{x}_3 + \dots + n_i \bar{x}_i \\ = \sum_i^n n_i \bar{x}_i$$

on differentiating this eqn. at constant pressure and temperature but varying composition, we get :

$$dx_{PT} = (n_1 dx_1 + x_1 dn_1) + (n_2 dx_2 + x_2 dn_2) + \\ (n_3 dx_3 + x_3 dn_3) + \dots + (n_i dx_i + x_i dn_i)$$

$$dx_{PT} = (n_1 dx_1 + n_2 dx_2 + n_3 dx_3 + \dots + n_i dx_i) + \\ (\bar{x}_1 dn_1 + \bar{x}_2 dn_2 + \bar{x}_3 dn_3 + \dots + \bar{x}_i dn_i) \quad (4)$$

comparing eqn. (3) and (4) we get :

$$n_1 d\bar{x}_1 + n_2 d\bar{x}_2 + n_3 d\bar{x}_3 + \dots + n_i d\bar{x}_i = 0 \quad (5)$$

Equation (5) applies to a system of definite composition and is the basis of the Gibbs-Duhem equation first derived by Gibbs (1875) and Duhem (1886).

physical significance of partial molar quantities :

The corresponding law for some extensive thermodynamic properties are :

$$V = \sum n_i \bar{V}_i ; \quad E = \sum n_i \bar{E}_i$$

$$H = \sum n_i \bar{H}_i \quad S = \sum n_i \bar{S}_i$$

$$\bar{e}_f = \sum n_i \bar{e}_{f,i} = \sum n_i \mu_i$$

$$A = \sum n_i \bar{A}_i$$

Where,

$$\bar{E}_i = \left(\frac{\partial E}{\partial n_i} \right)_{P,T,n_1,n_2 \dots}$$

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

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

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_1,n_2 \dots}$$

$$\bar{A}_i = \left(\frac{\partial A}{\partial n_i} \right)_{P,T,n_1,n_2 \dots}$$

In a single component system, the partial molar quantities are identical with the molar quantities like:

$$\bar{E}_i = \frac{E}{\sum n_i}, \quad \bar{H}_i = \frac{H}{\sum n_i} \text{ and so on.}$$

The partial molar quantities are intensive properties and do not depend on the size of the system also. For example, if all the n 's in $H_i = \frac{H}{\sum n_i}$ get increased at constant P and T ,

The partial molar quantity \bar{H}_i will not increase but will remain constant as the total quantities ($H \dots$) increases in the same proportion.

