❖ Partial Molar Quantities (Free Energy, Volume, Heat Concept)

So far we have discussed the variation of various thermodynamic properties with respect to temperature and pressure while the composition of the system was kept constant (closed system). In 1907, G.N. Lewis started the study of open systems i.e. the variation of various thermodynamic properties with respect to the composition of one or more components. In other words, he studied the behavior of a particular thermodynamic property of the system when a component is removed from or added to the system under consideration. Now since a variation like this is observable only for an extensive property, the general definition of partial molar properties can be given as given below.

A partial molar property may simply be defined as a thermodynamic quantity which indicates how an extensive property of a solution or mixture changes with the variation in the molar composition of the mixture at constant temperature and pressure.

Basically, it is the partial derivative of the extensive property with respect to the number of moles of the component under consideration. All extensive properties of a mixture have corresponding partial molar properties. In this section, we will discuss some very important partial molar quantities like partial molar free energy ($\overline{G_i}$), partial molar volume ($\overline{V_i}$) and partial molar enthalpy ($\overline{H_i}$).

➢ ***Partial Molar Free Energy or Chemical Potential***

In order to derive the expression for partial molar free energy, consider a system that comprises of *n* types of constituents with n_1, n_2, n_3, n_4 … moles. So, being an extensive property, the partial molar free energy depends upon not only the temperature and pressure but also on the number of moles of different components. Mathematically, we can say that

$$G = f(T, P, n_1, n_2, n_3 \dots) \tag{160}$$

Now let us assume a small change in the temperature, pressure and amount of different components, this would impart a variation in partial molar free energy as given below.

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2\dots} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2\dots} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3\dots} dn_1 + \cdots \tag{161}$$

The first term on the right-hand side gives the change in the free energy with temperature at constant pressure and compositions; while the second term gives the change in the free energy with pressure at constant temperature and compositions. The terms afterward represent the variation in free energy with the amount of one component while the temperature, pressure and all other compositions are kept constant.

However, if the temperature and pressure of the system are kept constant i.e. $dT = 0$, $dP = 0$, the equation (161) takes the form

$$(dG)_{T,P} = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3\dots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,n_3\dots} dn_2 + \left(\frac{\partial G}{\partial n_3}\right)_{T,P,n_1,n_2\dots} dn_3 \dots \tag{162}$$

Every term on the right-hand side of the equation (162) is partial molar free energy and is symbolized by a "bar" over it i.e.

$$(dG)_{T,P} = \overline{G_1}\, dn_1 + \overline{G_2}\, dn_2 + \overline{G_3}\, dn_3 \dots \tag{163}$$

For the *i*th component, we can say that

$$\overline{G_i} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_2,n_3\dots} \tag{164}$$

The equation (164) gives the general expression for "partial molar free energy" or the "chemical potential" of the *i*th species.

➢ ***Partial Molar Volume***

In order to derive the expression for partial molar volume, consider a system that comprises of *n* types of constituents with n_1, n_2, n_3, n_4 … moles. So, being an extensive property, volume depends upon not only the temperature and pressure but also on the number of moles of different components. Mathematically, we can say that

$$V = f(T, P, n_1, n_2, n_3 \dots) \tag{165}$$

Now let us assume a small change in the temperature, pressure and amount of different components, this would impart a variation in partial molar volume as given below.

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P,n_1,n_2\dots} dT + \left(\frac{\partial V}{\partial P}\right)_{T,n_1,n_2\dots} dP + \left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_2,n_3\dots} dn_1 + \cdots \tag{166}$$

The first term on the right-hand side gives the change in the volume with the temperature at constant pressure and compositions; while the second term gives the change in the volume with pressure at constant temperature and compositions. The terms afterward represent the variation in volume with the amount of one component while the temperature, pressure and all other compositions are kept constant.

However, if the temperature and pressure of the system are kept constant i.e. $dT = 0$, $dP = 0$, the equation (166) takes the form

$$(dV)_{T,P} = \left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_2,n_3\dots} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_1,n_3\dots} dn_2 + \left(\frac{\partial V}{\partial n_3}\right)_{T,P,n_1,n_2\dots} dn_3 \dots \tag{167}$$

Every term on the right-hand side of the equation (167) is partial molar volume and is symbolized by a "bar" over it i.e.

$$\overline{V_1} = \left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_2,n_3\dots} \tag{168}$$

$$\overline{V_2} = \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_1,n_3\dots} \tag{169}$$

After putting the values from equations like (168 – 169) in equation (167), we get

$$(dV)_{T,P} = \overline{V_1}\, dn_1 + \overline{V_2}\, dn_2 + \overline{V_3}\, dn_3 \dots \tag{170}$$

For the *i*th component, we can say that

$$\overline{V_i} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_2,n_3\dots} \tag{171}$$

The equation (171) gives the general expression for the "partial molar volume" of the *i*th species.

➢ ***Partial Molar Enthalpy or Partial Molar Heat Content***

In order to derive the expression for partial molar enthalpy, consider a system that comprises of n types of constituents with n_1, n_2, n_3, n_4 … moles. So, being an extensive property, volume depends upon not only the temperature and pressure but also on the number of moles of different components, i.e.,

$$H = f(T, P, n_1, n_2, n_3 \dots) \tag{172}$$

Now let us assume a small change in the temperature, pressure and amount of different components, this would impart a variation in molar enthalpy as given below.

$$dH = \left(\frac{\partial H}{\partial T}\right)_{P,n_1,n_2\dots} dT + \left(\frac{\partial H}{\partial P}\right)_{T,n_1,n_2\dots} dP + \left(\frac{\partial H}{\partial n_1}\right)_{T,P,n_2,n_3\dots} dn_1 + \cdots \tag{173}$$

The first term on the right-hand side gives the change in the enthalpy with the temperature at constant pressure and compositions; while the second term gives the change in the enthalpy with pressure at constant temperature and compositions. The terms afterward represent the variation in enthalpy with the amount of one component while the temperature, pressure and all other compositions are kept constant.

However, if the temperature and pressure of the system are kept constant i.e. $dT = 0$, $dP = 0$, the equation (173) takes the form

$$(dH)_{T,P} = \left(\frac{\partial H}{\partial n_1}\right)_{T,P,n_2,n_3\dots} dn_1 + \left(\frac{\partial H}{\partial n_2}\right)_{T,P,n_1,n_3\dots} dn_2 + \left(\frac{\partial H}{\partial n_3}\right)_{T,P,n_1,n_2\dots} dn_3 \dots \tag{174}$$

Every term on the right-hand side of the equation (174) is partial molar enthalpy and is symbolized by a "bar" over it i.e.

$$\overline{H_1} = \left(\frac{\partial H}{\partial n_1}\right)_{T,P,n_2,n_3\dots} \tag{175}$$

$$\overline{H_2} = \left(\frac{\partial H}{\partial n_2}\right)_{T,P,n_1,n_3\dots} \tag{176}$$

After putting the values from equations like (175 – 176) in equation (174), we get

$$(dH)_{T,P} = \overline{H_1}\, dn_1 + \overline{H_2}\, dn_2 + \overline{H_3}\, dn_3 \dots \tag{177}$$

For the ith component, we can say that

$$\overline{H_i} = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_2,n_3\dots} \tag{178}$$

The equation (178) gives the general expression for the "partial molar enthalpy" of the ith species.

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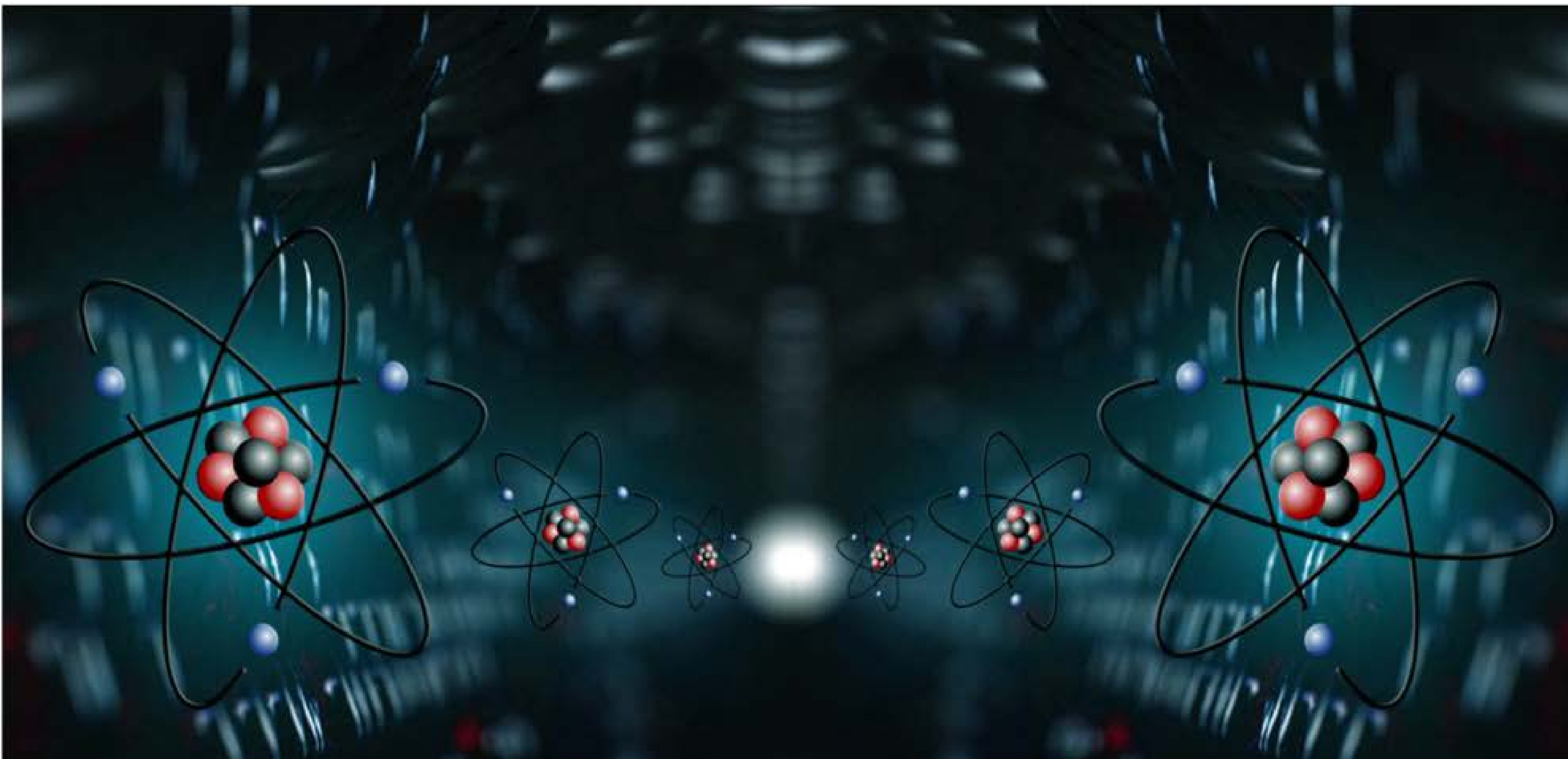

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