M. Sc (II Semester)
Unit III
Classical thermodynamics

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## Gibb's Duhem Equation for Binary system:

For a solution having two Components in equilibrium with their vapours at constant temperature and pressure, we have

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad \text{- - (1)}$$

Where $n_1$ and $n_2$ are number of moles of two Components and $\mu_1$ and $\mu_2$ are the chemical potential respectively.

Dividing eqn(1) by $(n_1+n_2)$ we have

$$\frac{n_1}{n_1+n_2} d\mu_1 + \frac{n_2}{n_1+n_2} d\mu_2 = 0 \quad \text{- - (2)}$$

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \quad \text{- - (3)}$$

Where $x_1$ is the mole fraction of the Constituent 1 and $x_2$ is the mole fraction of the Constituent 2.

Equation (3) can be put in the following forms

$$x_1 \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} dx_1 + x_2 \left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P} dx_2 = 0 \quad \text{- - (4)}$$

We also know that

$$x_1 + x_2 = 0 \quad \text{. - (5)}$$

then Differentiate we get

$$dx_1 + dx_2 = 0 \quad \text{- - - (6)}$$

$$dx_1 = -dx_2 \quad \cdots (7)$$

From equation (6) and (7) we get

$$x_1\left(\frac{\partial\mu_1}{\partial x_1}\right)_{T,P} dx_1 - x_2\left(\frac{\partial\mu_2}{\partial x_2}\right) dx_1 = 0$$

$$\left(\frac{\partial\mu_1}{\frac{1}{x_1}\partial x_1}\right)_{T,P} dx_1 = \left(\frac{\partial\mu_2}{\frac{1}{x_2}\partial x_2}\right)_{T,P} dx_1$$

Both side $dx_1$ cancelled out, then we get

$$\left(\frac{\partial\mu_1}{\partial \ln x_1}\right)_{T,P} = \left(\frac{\partial\mu_2}{\partial \ln x_2}\right)_{T,P}$$

$$\boxed{\left(\frac{\partial\mu_1}{\partial \ln x_1}\right)_{T,P} - \left(\frac{\partial\mu_2}{\partial \ln x_2}\right)_{T,P} = 0}$$

This equation finds usefuls applications particularly in gas liquids equilibria involved in distillation.

## Variation of Chemical Potential with Temperature and Pressure.

### (A) Variation with Temperature :

For a closed system, i.e $dn_1 = 0, dn_2 = 0$, we have

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP \quad \cdots (1)$$

We know that

$$dG = VdP - SdT \quad \text{- - (2)}$$

Comparing equation (1) and (2)

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V \quad \text{- - - (3)}$$

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \quad \text{- - - (4)}$$

Differentiating equation (4) with respect to $n_i$, we get

$$\frac{\partial}{\partial n_i}\left[\frac{\partial G}{\partial T}\right]_{P,n_1,n_2 ..} = -\left[\frac{\partial S}{\partial n_i}\right]_{T,P,n_1,n_2,...} \quad \text{- - - (5)}$$

$$\frac{\partial^2 G}{\partial T \partial n_i} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_1,n_2,..} = -\overline{S}_i \quad \text{- - (6)}$$

Where $\overline{S}_i$ is partial molar entropy.

We know that

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1,n_2,...} = \mu_i = \overline{G}_i \quad \text{- - (7)}$$

Differentiate equation (7) with respect to temperature We get

$$\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1,n_2,..} = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_1,n_2,..}$$

$$\frac{\partial^2 G}{\partial T \partial n_i} = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_1,n_2 ...} \quad \text{- - - (8)}$$

Equation (6) and (8) we get

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P, n_1, n_2, \ldots} = \overline{S_i} \quad \cdots (9)$$

Equation (9) gives the variation of chemical potential with temperature.

(B) Variation of chemical potential with pressure ;

For the definition of chemical potential, we know that

$$\left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_1, n_2, \ldots} = \mu_i \quad \cdots \cdots (1)$$

Differentiating equation (1) with respect to pressure, we get

$$\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_1, n_2, \ldots} = \frac{\partial}{\partial P}(\mu_i)$$

$$\left(\frac{\partial^2 G}{\partial P . \partial n_i}\right)_{T, P, n_1, n_2, \ldots} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_1, n_2, \ldots} \cdots (2)$$

We also know that

$$\left(\frac{\partial G}{\partial P}\right)_{T, N} = V \quad \cdots \cdots (3)$$

Differentiating equation(3) withrespect to $n_i$

$$\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial P}\right)_{T,N} = \frac{\partial}{\partial n_i}(V)$$

$$\frac{\partial^2 G}{\partial P.\partial n_i} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_1,n_2,\ldots} = \overline{V}_i \quad \text{--(4)}$$

Where $\overline{V}_i$ = partial molar Volume of $i^{th}$ Component.

Comparing the equation (2) and (4) We get

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_1,n_2,\ldots} = \overline{V}_i \quad \text{--(5)}$$

Equation (5) represents the variation of Chemical potential with pressure. This Shows that the rate of change of chemical potential with pressure of a particular Constituents of the system, at Constant temperature is equal to the partial molar volume of the constituents.

## Another form of Gibb's Helmoltz equation;

Again, We know that

$$G = H - TS$$

Differentiating both sides with respect to $n_i$ at Constant T, P and $n_1, n_2 - - -$ We get

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1,n_2 \cdots} = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_1,n_2 \cdots} - T\left(\frac{\partial S}{\partial n_i}\right)_{P,T,n_1,n_2 \cdots}$$

We also know that

$$\mu_i = \bar{G}_i = \bar{H}_i - T\,\bar{S}_i \quad - - (1)$$

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

Where $\bar{H}_i$ = Partial molar enthalpy of component 'i'

$\bar{S}_i$ = Partial molar entropy of component 'i'

We know that $\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = -\left(\frac{\partial S}{\partial n_i}\right)_{P,T,n_1,n_2 \cdots} = -\bar{S}_i - (1)$

From equation (1), We have

$$\mu_i = \bar{H}_i + T\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N}$$

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

Dividing both sides by $(-T^2)$, We get

$$\frac{\mu_i - T\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N}}{-T^2} = -\frac{\bar{H}_i}{T^2}$$

$$\mu\left(\frac{-1}{T^2}\right) + \frac{1}{T}\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = -\frac{\bar{H}_i}{T^2} \quad - - (A)$$

We know that differentation of two function

$$\frac{d}{dx}(x_1 \cdot x_2) = x_1 \frac{d}{dx}(x_2) + x_2 \frac{d}{dx}(x_1)$$

When we consider the two function $(\mu_i \cdot \frac{1}{T})$, then differentiate according to — the above equation, we get

$$\frac{\partial}{\partial T}\left\{\mu_i \cdot \frac{1}{T}\right\} = \mu_i \frac{\partial}{\partial T}\left(\frac{1}{T}\right) + \frac{1}{T}\frac{\partial}{\partial T}(\mu_i)$$

$$= \mu_i\left(-\frac{1}{T^2}\right) + \frac{1}{T}\left(\frac{\partial \mu_i}{\partial T}\right) \quad -(B)$$

Equation (A) can be writterns as according to equation (B) we get

$$\left[\frac{\partial}{\partial T}\left(\frac{\mu_i}{T}\right)\right]_{P,N} = -\frac{\overline{H}_i}{T^2} \quad -(C)$$

Equation 'C' gives the variation of Chemical potential with Temperature.

Physical Significance of Chemical potential :-

(i) It is small amount $dn_i$ moles of the Component i is added to the system (keeping T, P and moles of the other components constant), the increase in free energy per mole of Component 'i' added is given by

$$(dG)_{P,T,n,n_i-} = \mu_i dn_i$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_1,n_2,\ldots}$$

It is evident from the above equation that chemical potential of any component 'i' is the increase in the Gibb's free energy of the system which occurs due to the addition of one mole of component 'i' at constant temperature and pressure when other component remain unchanged.

(ii) Chemical potential is independent of the mass but is not independent of the composition of the system. Hence chemical potential is an intensive property and it must have the same value everywhere within the system in equilibrium.

(iii) Matter flows spontaneously from a region of high chemical potential to a region of low chemical potential.

(iv) Another name of chemical potential is the escaping tendency. Thus if '$\mu_i$' is high then component 'i' has large escaping tendency and vice-versa.

## Partial molar properties:

The thermodynamic properties G, H, S, A, E etc. changes with the change in mass (in the number of moles) of the system because they are extensive properties. For closed system (i.e. a system in which mass and composition do not vary) these properties depend upon P, V and T. But for an open system (i.e. a system in which mass and composition may changed), leads to introducing a thermodynamic property say 'X', which was called partial molar property. This property must be a function of temperature, pressure and the number of moles of various components present in the system.

In an open system any thermodynamic property 'X' may be defined as follows:

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

Where $n_1, n_2, \ldots n_i$ are the number of moles of components 1, 2, 3, ... i in the system.

Partial differential of the above is given by

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

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

The term $\left(\frac{\partial X}{\partial n_1}\right)_{P,T,n_2,n_3 \cdots}$ is called Partial molar quantity or property of Component 1 . This is presented by putting a bar over the symbol of thermodynamic property. Hence

$$\bar{X}_1 = \left(\frac{\partial X}{\partial n_1}\right)_{P,T,n_2,n_3,\cdots} \quad \cdots (1)$$

$$\bar{X}_2 = \left(\frac{\partial X}{\partial n_2}\right)_{P,T,n_1,n_3,\cdots} \quad \cdots (2)$$

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$$\bar{X}_i = \left(\frac{\partial X}{\partial n_i}\right)_{P,T,n_1,n_2,n_3,\cdots} \quad \cdots (3)$$

where $\bar{X}_1, \bar{X}_2 \cdots \bar{X}_i$ are the partial molar properties for the Components 1,2,....i respectively.

From equation (1, 2 and 3) it can be concluded that partial molar properties for a given system is the increase in extensive property of it due to addition of one mole of the given component at constant temperature, pressure and moles of other components remaining constant to such a large amount of the system that there occurs no appreciable change in the concentration.

If the system undergoes a change only increase of its components at constant temperature (dT=0) and at constant pressure (dP=0), we can write

$$(dX)_{T,P} = \bar{X}_1 dn_1 + \bar{X}_2 dn_2 - - - - + \bar{X}_i dn_i \quad (4)$$

On the basis of equation (4) at constant P and T, the change in entropy may be written as follows;

$$dS = \bar{S}_1 dn_1 + \bar{S}_2 dn_2 - - - - + \bar{S}_i dn_i$$

where $\bar{S}_1$ = Partial molar entropy of component '1'

$\bar{S}_2$ = Partial molar entropy of component '2'

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$\bar{S}_i$ = Partial molar entropy of component 'i'

Similary for $i^{th}$ component in a system

Partial molar internal energy $\overline{E}_i = \left(\frac{\partial E}{\partial n_i}\right)_{P,T,n_1,n_2 \ldots}$

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

Partial molar Gibb's potential $\overline{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_1,n_2 \ldots}$

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

## Physical significance of partial molar properties:

(1) Partial molar quantities are related to each other in the same way as the total quantities. For example

$$H = E + PV$$

Differentiating it with respect to '$n_i$' keeping $P, T, n_1, n_2, \ldots$ constant, we get

$$\left(\frac{\partial H}{\partial n_i}\right)_{P,T,n_1,n_2 \ldots} = \left(\frac{\partial E}{\partial n_i}\right)_{P,T,n_1,n_2 \ldots} + P\left(\frac{\partial V}{\partial n_i}\right)_{P,T,n_1,n_2 \ldots}$$

$$\overline{H}_i = \overline{E}_i + P\overline{V}_i$$

Similarly we can show that

$$\bar{G}_i = \bar{H}_i - T\bar{S}_i$$

$$\bar{A}_i = \bar{E}_i - T\bar{S}_i$$

The symbol 'μ' is generally used for partial molal free energy ($\bar{G}_i$). It is called chemical potential. Hence we can write

$$\mu_i = \bar{G}_i = \bar{H}_i - T\bar{S}_i$$

(ii) We know that for a given extensive property 'X' at constant P and T

$$(dX)_{P,T} = \bar{X}_1 dn_1 + \bar{X}_2 dn_2 + \dots + \bar{X}_i dn_i$$

Integrating it, we get

$$(X)_{P,T} = \bar{X}_1 n_1 + \bar{X}_2 n_2 + \dots + \bar{X}_i n_i$$

$$= \sum_{i=1}^{i=i} n_i \bar{X}_i$$

Hence, $E = \sum n_i \bar{E}_i$, $H = \sum n_i \bar{H}_i$,

$S = \sum n_i \bar{S}_i$, $A = \sum n_i \bar{A}_i$, etc.

If the system contains only one component (say i) then

$$(X)_{P,T} = \bar{X}_i n_i$$

$$\bar{X}_i = \frac{(X)_{P,T}}{n_i}$$

Hence $\bar{E}_i = \frac{E}{n_i}$, $\bar{H}_i = \frac{H}{n_i}$, $\bar{S}_i = \frac{S}{n_i}$

$\bar{A}_i = \frac{A}{n_i}$ etc.

i.e the partial molar quantities are identical with the molar quantities.

(iii) Partial molar quantities are intensive properties and these are independent of the size of the system.

## Determination of Partial Molar properties:

1. **Direct method**: Partial molar quantity may be defined as follows:

$$X_i = \left(\frac{\partial X}{\partial n_i}\right)_{P, T, n_1, n_2, \ldots} \quad \text{- - - - (1)}$$

In order to determine partial molar property, a graph is plotted between the extensive property X at constant temperature and pressure for a number of binary mixtures against the number of moles e.g '$n_2$' of one of them keeping '$n_1$' constant. Now a tangent is drawn to the curve. The slope of the curve at any particular composition gives the value of $\bar{X}_2$ as shown in figure 1.

Now the value of $\bar{X}_1$ can be determined by equation(2.)

$$X = n_1\bar{X}_1 + n_2\bar{X}_2$$

$$\bar{X}_1 = \frac{(X - n_2\bar{X}_2)}{n_1} \quad \cdots (2)$$

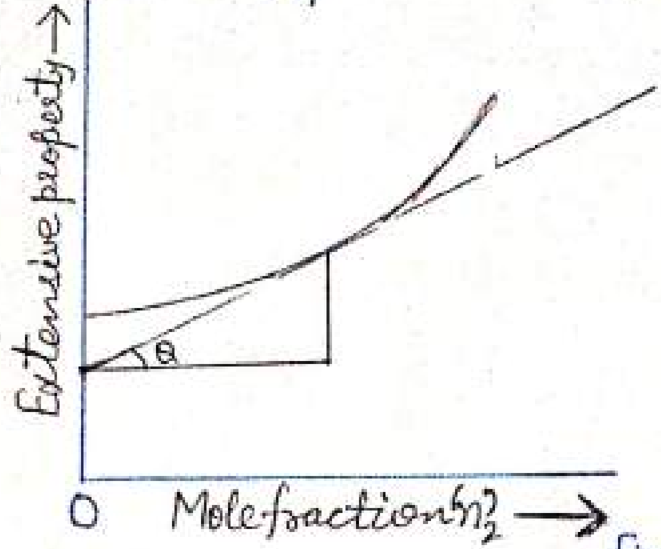

Figure 1

Limitations: This method does not give very accurate result because the exact slope of the curve can not be determined very accurately.

2. Method of Intercepts: This method is very useful for the determination of partial molar properties. Suppose 'X' is the mean value of a particular extensive property per mole of mixture. Then the observed value of the property 'X' for the system is given by

$$X = (n_1 + n_2)x \quad --- (3)$$

Differentiating equation (3) with respect to $n_2$ at constant '$n_1$' constant temperature and pressure. We get

$$\bar{X}_2 = \left(\frac{\partial X}{\partial n_2}\right)_{n_1} = x + (n_1+n_2)\left(\frac{\partial X}{\partial n_2}\right)_{n_1} \quad --(4)$$

The mole fraction $N_1$ of the component 1 is given by

$$N_1 = \frac{n_1}{n_1+n_2} \quad --- \quad (5)$$

Differentiating the above equation at constant $n_1$, We get

$$dN_1 = \frac{-n_1 dn_2}{(n_1+n_2)^2} = -\frac{n_1}{(n_1+n_2)} \cdot \frac{dn_2}{(n_1+n_2)}$$

From equation (5)

$$dN_1 = -N_1 \cdot \frac{dn_2}{n_1+n_2}$$

$$\frac{n_1+n_2}{dn_2} = -\frac{N_1}{dN_1}$$

Multiplying the above equation by '$dX$', We have

$$(n_1+n_2)\left(\frac{\partial X}{\partial n_2}\right)_{n_1} = -N_1\left(\frac{\partial X}{\partial N_1}\right)_{n_1}$$

Substituting the above equation in equation (4)

$$\bar{X}_2 = x - N_1\left(\frac{\partial X}{\partial N_1}\right)_{n_1} \quad --(6)$$

Now the values of the mean molar property $(x)$ for mixture of different Compositions are plotted against mole fraction $N_1$ as shown in figure (2). Suppose we have to determine partial molar property Corresponding to point $\underline{O}$. We draw a tangent $\underline{CD}$ at point $\underline{O}$ and the horizontal line $\underline{EF}$ parallel to the base line $\underline{AB}$. Then

$$\text{Slope } \underline{CD} = \frac{dx}{dN_1}$$

$$\text{Intercept } \underline{CE} = N_1 \frac{dx}{dN_1} \text{ at } \underline{O}$$

The value of $\underline{AE}$ is equal to the value of '$\underline{x}$' at point $\underline{O}$. It is evident from equation (6) that the distance AC gives the partial molar property $\overline{X}_2$. It Can also be Shown that the distance BD gives the value of $\overline{X}_1$ for the mixture whose composition is represented by the point O. Thus $\overline{X}_1$ and $\overline{X}_2$ are determined at the same time.