LECTURE-19

PARTIAL AND INTEGRAL MOLAR QUANTITIES:

For a closed system, where there is no possibility of mass and concentration change, change of the components present in the system and the Thermodynamic properties mainly depends on P, V and T, where as in case of open system Thermodynamic properties essentially depends on P, V, T and mass of the system.

Let X be the Thermodynamic property

Case-1 (In case of closed system):

$$K_1' = f(P,V); K_2' = f(T,V) \quad (154)$$

$$K_3' = f(P,T) \quad (155)$$

Case-II (In case of Open system):

Open system in which and chemical composition may change, the extensive properties i. e. U, G, S, V, H etc. must depends on the amount of composition present in the system.

Continued…

So any extensive properties

$$K' = f(P, T, n_1, n_2, \dots, n_i) \qquad (156)$$

Where $n_1, n_2, \dots, n_i$ are number of moles of the 1st, 2nd, … , ith component in the system present as gm/mol.

Let us consider, there is a very small change in all the variables in the systems.

$$K' = \left(\frac{\partial K}{\partial \mathrm{P}}\right)_{\mathrm{T,n_1,n_2,\dots,n_i}} \partial \mathrm{P} + \left(\frac{\partial K}{\partial \mathrm{T}}\right)_{\mathrm{P,n_1,n_2,\dots,n_i}} \partial \mathrm{T} + \left(\frac{\partial K}{\partial \mathrm{n_1}}\right)_{\mathrm{P,T,n_2,\dots,n_i}} \partial \mathrm{n_1} +$$

$$\left(\frac{\partial K}{\partial \mathrm{n_2}}\right)_{\mathrm{P,T,n_1,..,n_i}} \partial \mathrm{n_2} + \cdots + \left(\frac{\partial K}{\partial \mathrm{n_i}}\right)_{\mathrm{P,T,n_1,..,n_{i-1}}} \partial \mathrm{n_i} \qquad (157)$$

Continued…

From the above relation, we have

$$\left.\begin{aligned}\overline{K_1} &= \left(\frac{\partial K}{\partial n_1}\right)_{P,T,n_2,\dots,n_i}\\ \overline{K_2} &= \left(\frac{\partial K}{\partial n_2}\right)_{P,T,n_1,\dots,n_i}\\ &.\\ &.\\ \overline{K_i} &= \left(\frac{\partial K}{\partial n_1}\right)_{P,T,n_1,\dots,n_{i-1}}\end{aligned}\right\} \qquad (158)$$

Rate of change of Thermodynamic properties on addition of 1 mole of the component when all other variables are unchanged. So we have at constant P, T equation (158) becomes

$$dK' = \overline{K_1}dn_1 + \overline{K_2}dn_2 + \cdots + \overline{K_i}dn_i = \sum_i \overline{K_i}dn_i \qquad (159)$$

Continued…

Now if K mean to molar properties of a solution. Then K′ i. e. the value of quantity K for the entire solution given by

$$K' = n_T K \Rightarrow dK' = n_T dK \qquad (160)$$

[Where $n_T = \sum_i n_i = n_1 + n_2 + \cdots + n_i$

K– Integral molar value of X in the solution]

Now from equation (159) and (160), we will have

$$\sum_i \overline{K_i}\, dn_i = n_T dK \qquad (161)$$

$$dK = \sum_i \overline{K_i} \frac{dn_i}{n_T} = \sum_i \overline{K_i}\, dX_i \qquad (162)$$

[Where $dX_i = \frac{dn_i}{n_T}$ = Mole fraction of component i in the solution

dK – Integral molar value of the solution

$\overline{K_i}$ – Partial molar value of X′ of component i in the solution]

Continued…

CHEMICAL POTENTIAL: Thermodynamic equilibrium requires attainment of physic-chemical equilibrium, besides mechanical & thermal equilibrium. This means chemical potential should be uniform in the entire system in addition to uniformity of pressure & temperature.

There is a difference between the molar quantity (Q) & the same for system as whole (Q') as

$$Q' = n_T Q \qquad (163)$$

[Where, $n_T = Total\ number\ of\ moles = n_1 + n_2 + \dots\dots\dots + n_i$]

By adopting the convention, let us consider a system with variable composition. Then the auxiliary relation becomes

$$dU' = TdS' - PdV' + \left(\frac{\partial U'}{\partial n_1}\right)_{S',V',n_2,..,except n_1} dn_1 + \cdots + \left(\frac{\partial U'}{\partial n_i}\right)_{S',V',n_1,..,except n_i} dn_i \qquad (164)$$

$$\Rightarrow dU' = TdS' - PdV' + \sum_i \left(\frac{\partial U'}{\partial n_i}\right) dn_i \qquad (165)$$

$$\Rightarrow dU' = TdS' - PdV' + \sum_i \mu_i \, dn_i \qquad (166)$$

Continued…

[Where, μ_i = Chemical potential for ith component for equation (167)

$$= \left(\frac{\partial U'}{\partial n_i}\right) s', v', n_1, \text{except } n_i$$

Similarly, we have

$$dH' = TdS' + VdP' + \left(\frac{\partial H'}{\partial n_1}\right)_{S',P',n_2,..,except n_1} dn_1 + \cdots + \left(\frac{\partial H'}{\partial n_i}\right)_{S',P',n_1,..,except n_i} dn_i \quad (167)$$

$$\Rightarrow dH' = TdS' + VdP' + \sum_i \mu_i \, dn_i \quad (168)$$

$$dA' = -S'dT - PdV' + \left(\frac{\partial A'}{\partial n_1}\right)_{T',V',n_2,..,except n_1} dn_1 + \cdots + \left(\frac{\partial A'}{\partial n_i}\right)_{T',V',n_1,..,except n_i} dn_i$$

(169)

Continued…

$$\Rightarrow dA' = -S'dT - PdV' + \sum_i \mu_i \, dn_i \qquad (170)$$

$$dG' = -S'dT + V'dP + \left(\frac{\partial G'}{\partial n_1}\right)_{T,P,n_2,..,except n_1} dn_1 + \cdots + \left(\frac{\partial G'}{\partial n_i}\right)_{T,P,n_1,..,except n_i} dn_i \qquad (171)$$

$$\Rightarrow dG' = -S'dT + V'dP + \sum_i \mu_i \, dn_i \qquad (172)$$

So, chemical potential for equation (168), (170) & (172) respectively are

$$\mu_i = \left(\frac{\partial H'}{\partial n_i}\right)_{S',P',n_1,..,except n_i} \qquad (173)$$

$$\mu_i = \left(\frac{\partial A'}{\partial n_i}\right)_{T',V',n_1,..,except n_i} \qquad (174)$$

$$\mu_i = \left(\frac{\partial G'}{\partial n_i}\right)_{T,P,n_1,..,except n_i} \qquad (175)$$

So, μ_i is same as the partial molar extensive properties of component i in a solution.

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Application of Chemical Potential:

- Studies of phase equilibria
- In multi-component system, if we are interested in one component only. Then easily can be obtained by considering the chemical potential of that component.
- Allows easily visualization as to which way a species (element or compound) would tend to get transferred

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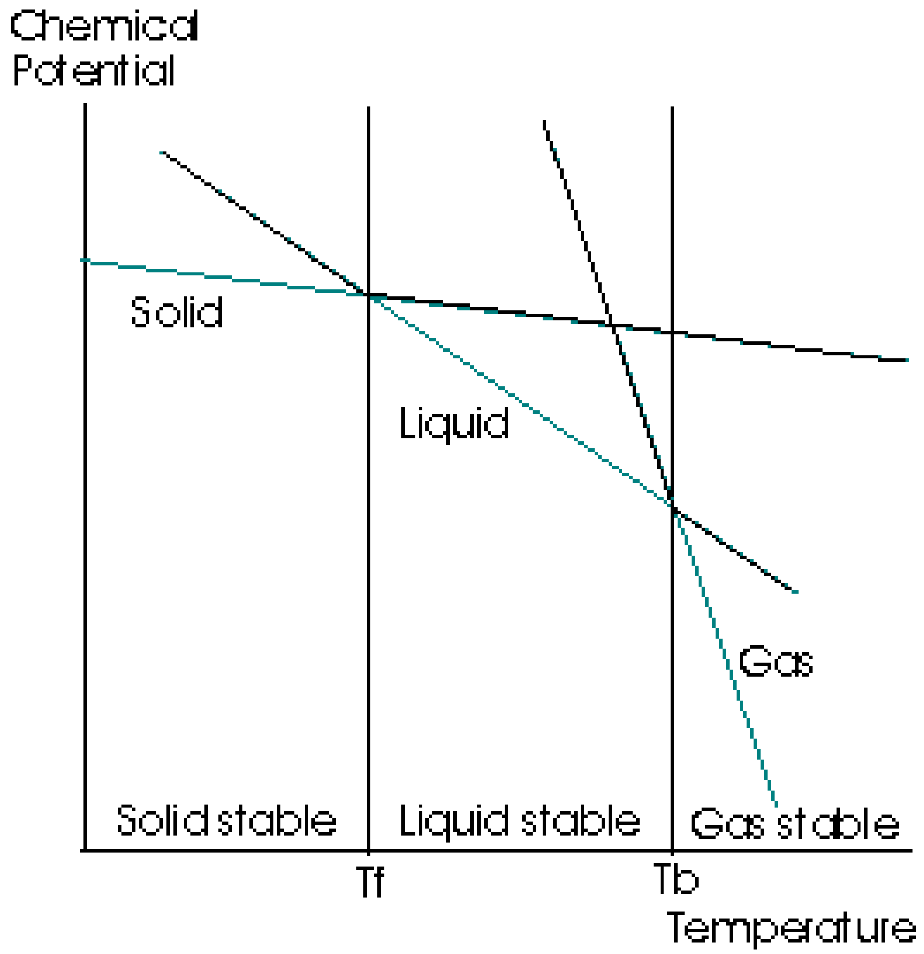

- **Chemical potential change for different phases followed the order**

  Solid<Liquid<Gas

Chemical potential used in phase transitions

Ref-https://socratic.org/questions/how-do-colligative-properties-affect-freezing-point