

## Thermodynamics for open system:- (1)

The thermodynamic properties  $U, H, S, A$  and  $G$  are all ~~exp~~ extensive properties as their values change with change in the mass (i.e. no. of moles) of the system.

We know,

$$dU = Tds - pdv$$

$$dH = Tds + vdp$$

$$dA = -pdv - SdT$$

$$dG = vdp - SdT$$

$$\therefore U = f(S, v)$$

$$H = f(S, p)$$

$$A = f(v, T)$$

$$G = f(p, T)$$

The above relations are valid in closed system only where no. of moles in a system is constant.

However, in case of an open system, the no. of moles is not constant.

Let us consider an open system containing two or more components. Hence, for such system there can be a change in the no. of moles of the various components as well as along with the thermodynamic variables such as  $p, T, v$ , etc.

So, for open system,

$$U = f(S, v, n_1, n_2, n_3, \dots, n_j)$$

$$H = f(S, p, n_1, n_2, n_3, \dots, n_j)$$

$$A = f(v, T, n_1, n_2, n_3, \dots, n_j)$$

$$G = f(p, T, n_1, n_2, n_3, \dots, n_j)$$

where  $n_1, n_2, n_3, \dots, n_j$  are the no. of moles of components 1, 2, 3,  $\dots, j$  present in the open system respectively.

and  $n_1 + n_2 + n_3 + \dots + n_j = \text{total no. of moles} = N$ .

Let,  $Z = f(x, y)$  where  $Z = \text{Thermodynamic Property (such as } G)$  (2)  
 $x, y \rightarrow \text{variables } (P, T)$

Then according to Euler's reciprocal theorem,

$$dZ = \left(\frac{\partial Z}{\partial x}\right)_y dx + \left(\frac{\partial Z}{\partial y}\right)_x dy.$$

Now,  $Z = f(x, y, n_1, n_2, n_3, \dots, n_j)$

$$\begin{aligned} \therefore dZ = & \left(\frac{\partial Z}{\partial x}\right)_{y, n_1, n_2, \dots, n_j} dx + \left(\frac{\partial Z}{\partial y}\right)_{x, n_1, n_2, \dots, n_j} dy \\ & + \left(\frac{\partial Z}{\partial n_1}\right)_{x, y, n_2, n_3, \dots, n_j} dn_1 + \left(\frac{\partial Z}{\partial n_2}\right)_{x, y, n_1, n_3, \dots, n_j} dn_2 \\ & + \dots + \left(\frac{\partial Z}{\partial n_i}\right)_{x, y, n_1, n_2, \dots, n_{j \neq i}} dn_i \end{aligned}$$

The quantity  $\left(\frac{\partial Z}{\partial n_i}\right)_{x, y, n_1, n_2, \dots, n_{j \neq i}}$  is called partial molar quantity of the  $i$ -th Component.

The for the  $i$ -th Component in a system,

partial molar internal energy  $= \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_1, n_2, \dots, n_j} = \bar{U}_i$

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

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

" " Gibbs free energy  $= \left(\frac{\partial G}{\partial n_i}\right)_{P, T, n_1, n_2, \dots, n_j} = \bar{G}_i = \mu_i$

Chemical Potential.



(3)

$$\text{Noco, } G = f(P, T, n_1, n_2, n_3, \dots, n_j)$$

where  $n_1, n_2, n_3, \dots, n_j$  are the no. of moles of components 1, 2, 3,  $\dots, j$  respectively present in the open system.

$$\begin{aligned} dG &= \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, \dots, n_j} dP + \left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2, \dots, n_j} dT \\ &\quad + \left(\frac{\partial G}{\partial n_1}\right)_{P, T, n_2, n_3, \dots, n_j} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{P, T, n_1, n_3, \dots, n_j} dn_2 \\ &\quad + \dots + \left(\frac{\partial G}{\partial n_i}\right)_{P, T, n_1, n_2, \dots, n_j \neq i} dn_i \\ &= \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, \dots, n_j} dP + \left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2, \dots, n_j} dT \\ &\quad + \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_i dn_i \\ &= VdP - SdT + \sum_{i=1}^j \mu_i dn_i \quad \dots \rightarrow \text{①} \end{aligned}$$

where,  $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P, T, n_1, n_2, \dots, n_j \neq i}$

Chemical potential of the  $i$ -th component of a component

So, Chemical potential may be defined as the change in Gibbs-free energy with change in no. of the moles of the component, when  $P, T$  and no. of moles of other components present <sup>in the system</sup> are constant.

$\mu_i$  :- ① It is an intensive property

② It must have the same value throughout the system at equilibrium.

③ If the chemical potential of a system is not uniform, the matter will flow spontaneously from a region of higher chemical potential to a region of lower chemical potential until its value is uniform.

throughout the system.

④

Gibbs Duhem eqn:

$$dG = Vdp - SdT + \sum_{i=1}^J \mu_i dn_i$$

$$(dG)_{T,p} = \sum_{i=1}^J \mu_i dn_i$$

$$\therefore (G)_{T,p} = \sum_{i=1}^J \mu_i n_i \quad \dots \rightarrow \textcircled{II}$$

$$= (\mu_1 n_1 + \mu_2 n_2 + \dots + \mu_J n_J)$$

$$\therefore (dG)_{T,p} = \sum \mu_i dn_i + \sum n_i d\mu_i \quad \dots \rightarrow \textcircled{III}$$

Comparing eqn ① and ③, we get.

$$\boxed{\sum n_i d\mu_i = 0} \quad \dots \rightarrow \textcircled{IV}$$

$$\therefore n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad \left[ \begin{array}{l} \text{Let a system} \\ \text{has two components} \\ \text{having no. of} \\ \text{moles } n_1 \text{ and} \\ n_2 \end{array} \right]$$

$$\Rightarrow \boxed{d\mu_2 = -\frac{n_1}{n_2} d\mu_1}$$

Thus, as the  $d\mu_1$  increases,  $d\mu_2$  decreases and vice-versa.

Eqn ④ is called Gibbs - Duhem eqn for open system.

Now, from eqn ①  ~~$dG = Vdp - SdT + \sum \mu_i dn_i$~~

$$dG = Vdp - SdT + \sum_{i=1}^J \mu_i dn_i$$

In closed system,  $n_i = \text{constant}$ .  $dn_i = 0$

$$\therefore \boxed{dG = Vdp - SdT}$$

where,  $V = \left( \frac{\partial G}{\partial p} \right)_{T, n_1, n_2, \dots, n_J}$  and

$$-S = \left( \frac{\partial G}{\partial T} \right)_{p, n_1, n_2, \dots, n_J}$$

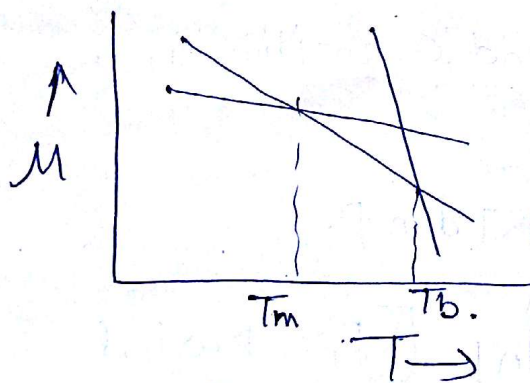
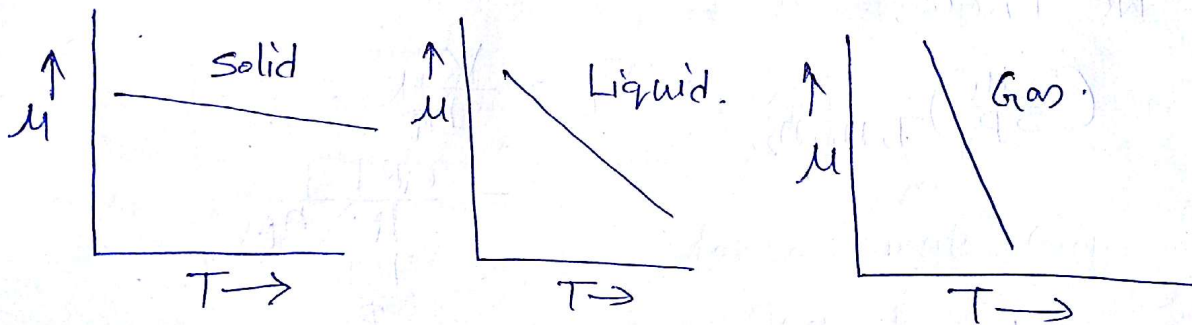


## Variation of Chemical potential with Temp. at Constant pressure and Composition:- ⑤

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

$$\begin{aligned} \therefore \left( \frac{\partial \mu_i}{\partial T} \right)_{P, n_1, n_2, n_3, \dots, n_j} &= \frac{\partial}{\partial T} \left( \frac{\partial G}{\partial n_i} \right)_{P, T, n_1, n_2, \dots, n_j \neq i} \\ &= - \frac{\partial}{\partial n_i} \left( \frac{\partial G}{\partial T} \right)_{P, n_1, n_2, \dots, n_j \neq i} \\ &= - \left( \frac{\partial S}{\partial n_i} \right)_{P, n_1, n_2, \dots, n_j} \\ &= - \bar{S}_i \rightarrow \text{partial molar entropy.} \end{aligned}$$

Since, entropy of a substance is a positive quantity. Hence, the chemical potential of a Component decreases with increasing temp. at constant pressure and composition.



At the  $T_b$  (boiling pt.),  $\mu$  of liquid and gaseous phases are same.

At  $T_m$  (melting point), chemical potential of solid and liquid phases are same.

Variation of chemical potential with Temp.

Variation of chemical potential with pressure at Constant Temp. and Composition:-

(6)

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{P, T, n_1, n_2, \dots, n_{j \neq i}}$$

$$\begin{aligned} \left( \frac{\partial \mu_i}{\partial P} \right)_{T, n_1, n_2, \dots, n_j} &= \left( \frac{\partial}{\partial P} \left( \frac{\partial G}{\partial n_i} \right) \right)_{P, T, n_1, n_2, \dots, n_{j \neq i}} \\ &= \frac{\partial}{\partial n_i} \left( \frac{\partial G}{\partial P} \right)_{T, n_1, n_2, \dots, n_j} \\ &= \left( \frac{\partial V}{\partial n_i} \right)_{T, n_1, n_2, \dots, n_{j \neq i}} \\ &= \bar{V}_i \end{aligned}$$

Since,  $\bar{V}_i$  is positive quantity, hence, chemical potential of a component increases with pressure at constant temp. and composition.

Chemical potential in a system of ideal gas

We know,

$$\begin{aligned} \left( \frac{\partial \mu_i}{\partial P} \right)_{T, n_1, n_2, \dots} &= \bar{V}_i = \frac{V}{n_i} \\ &= \frac{n_i R T}{P \cdot n_i} \\ &= \frac{R T}{P} \end{aligned}$$

$$\therefore d\mu_i = \frac{R T}{P} dP$$

Thus, at a constant Temp and Composition in case of an ideal gas,

$$d\mu_i = \frac{R T}{P} dP = R T d \ln P.$$

$$\Rightarrow \int_{\mu_i=0}^{\mu_i=\mu_i} d\mu_i = R T \int_{P=1}^{P=P_i} d \ln P \quad [P_i = \text{partial pressure of the component present in the system}]$$



$$\Rightarrow \mu_i - \mu_0 = RT \ln P_i - RT \ln 1$$

$$= RT \ln P_i$$

$$\Rightarrow \boxed{\mu_i = \mu_0 + RT \ln P_i} \quad \rightarrow \textcircled{v}$$

If partial pressure of the component 'i' is unit, then  $\boxed{\mu_i = \mu_0}$

In terms of mole-fraction

Let, ~~the~~ mole fraction of the 'i' th component is  $X_i$  and total pressure is  $p$

$$\therefore \boxed{P_i = X_i p}$$

From eqn  $\textcircled{v}$ ,

$$\mu_i = \mu_0 + RT \ln X_i p$$

$$= \mu_0 + RT \ln p + RT \ln X_i$$

$$\boxed{\mu_i = \mu_{i(pure)}^* + RT \ln X_i}$$

$X_i < 1$   $\boxed{\mu_i < \mu_{pure}}$  for a single component,  $X_i \geq 1$

In terms of Concentration,

$$P_i = C_i RT$$

$$\therefore \boxed{\mu_i = \mu_{pure}}$$

$\therefore$  From eqn  $\textcircled{v}$ ,

$$\mu_i = \mu_0 + RT \ln C_i RT$$

$$\mu_i = \mu_0 + RT \ln RT + RT \ln C_i$$

$$\boxed{\mu_i = \mu_0 + RT \ln C_i} \quad \text{at a Constant temp.}$$