

Thermodynamics of Open System: Partial Molar Properties

So, far, closed systems are measured in terms of systems physical variables, like pressure, temperature and volume and the like.

for a closed system, thermodynamic property, Y

$$Y = f(P, T)$$

But in chemical reactions, substances change their chemical form. As a chemical reaction proceeds, the composition of system and the thermodynamic properties change. The composition of the system change by adding substances to the system or by taking them out from the system or by a chemical reaction. Consequently, we must introduce the dependence on composition into the thermodynamic equations.

It has been assumed that the number of moles, n of a substance has remained constant in all of the changes considered so far. In open system no. of moles and hence mole fractions of the components constituting the system changes.

$$Y = f(T, P, n_1, n_2, \dots, n_n)$$

where, $n_1, n_2, n_3, \dots$ are the no. of moles of component 1, 2, 3, etc. respectively.

Y is the thermodynamic extensive property.

T and P be the temperature and pressure respectively

where $n_1 + n_2 + n_3 + \dots + n_n = \text{Total number of moles} = N$

For a small change in temperature, pressure and the number of moles of the component, the change in the property dY will be given by the expression.

$$dY = \left(\frac{\partial Y}{\partial T}\right)_{P, N} dT + \left(\frac{\partial Y}{\partial P}\right)_{T, N} dP + \left(\frac{\partial Y}{\partial n_1}\right)_{T, P, n_2, \dots, n_n} dn_1 + \left(\frac{\partial Y}{\partial n_2}\right)_{T, P, n_1, \dots, n_n} dn_2 + \left(\frac{\partial Y}{\partial n_i}\right)_{T, P, n_1, n_2, \dots, n_{j \neq i}} dn_i + \left(\frac{\partial Y}{\partial n_j}\right)_{T, P, n_1, n_2, \dots, n_{i \neq j}} dn_j \quad \text{--- (1)}$$

The quantity $\left(\frac{\partial y}{\partial n_i}\right)_{T, P, n_1, n_2, \dots, n_j \neq i}$ is called partial molar property of the i th component. This represent as $\bar{y}_i$

In equation (1), If the temp, and pressure of the system are kept constant, then $dT=0$ and $dP=0$.

So that the equⁿ (1) becomes

$$dy_{T, P} = \left(\frac{\partial y}{\partial n_1}\right)_{T, P, n_2, n_3, \dots} dn_1 + \left(\frac{\partial y}{\partial n_2}\right)_{T, P, n_1, n_3, \dots} dn_2 + \dots \quad (2)$$

Thus for the i th component in a system

$$\text{Partial molar internal energy} = \left(\frac{\partial U}{\partial n_i}\right)_{T, P, n_1, n_2, n_3, \dots} = \bar{U}_i$$

$$\text{Partial molar enthalpy} = \left(\frac{\partial H}{\partial n_i}\right)_{T, P, n_1, n_2, n_3, \dots} = \bar{H}_i$$

$$\text{Partial molar entropy} = \left(\frac{\partial S}{\partial n_i}\right)_{T, P, n_1, n_2, n_3, \dots} = \bar{S}_i$$

$$\text{Partial molar volume} = \left(\frac{\partial V}{\partial n_i}\right)_{T, P, n_1, n_2, n_3, \dots} = \bar{V}_i$$

Characteristics of partial molar quantities

A partial molar quantity must obey the following ~~four~~ criteria

- 1) To be a partial molar quantity pressure and temperature must be always constant.
- 2) Partial molar property is not the property of the whole system. It is the property of a particular component of the system.
- 3) Every partial molar property is an intensive property. Because these are expressed in terms of per mole and hence these will be nation in terms of two extensive properties.

Chemical potential

In case of a open system if the system consists of n constituent the amounts of which present in the system are $n_1, n_2, n_3, \dots$ moles, then Gibbs free energy G of the system is a function not only the temp and pressure but the amount of different constituents as well, Thus

$$G = f(T, P, n_1, n_2, n_3, \dots) \quad \text{--- (1)}$$

Now if there is a small change in the temp, pressure and the amount of the constituents, then the change in the property G is given by

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2, \dots} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, \dots} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_2, \dots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T, P, n_3, \dots} dn_2 \quad \text{--- (2)}$$

$$dG_{T, P} = \left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_2, n_3, \dots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T, P, n_1, n_3, \dots} dn_2 + \dots \quad \text{--- (3)}$$

Each derivatives of R.H.S is called partial molar property and is represented by putting a bar over the symbol.

$$\left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_2, n_3} = \left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_j \neq 1} = \bar{G}_1$$

$$\left(\frac{\partial G}{\partial n_2}\right)_{T, P, n_1, n_3, \dots} = \left(\frac{\partial G}{\partial n_2}\right)_{T, P, n_j \neq 2} = \bar{G}_2$$

general for any component i

$$\left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq i} = \bar{G}_i$$

This quantity is called partial molar free energy or chemical potential and is usually represent by the symbol μ .

$$\text{Thus } \mu_i = \bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq i}$$

$$\text{if } dn_i = 1 \text{ mole, then } \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq i}$$

The chemical potential of a given substance is, evidently, the change in free energy of the system that results on the addition of one mole of that ~~particular~~ particular substance at a constant temp^r and pressure, to such a large quantity of the system that there is no appreciable change in the overall composition of the system.

$$(dG)_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_j dn_j \quad \text{--- (4)}$$

If the system has a definite composition having $n_1, n_2, \dots, n_j$ moles of constituents 1, 2, ..., j respectively, then on integrating eqnⁿ (4) we have.

$$G_{T,P,N} = n_1 \mu_1 + n_2 \mu_2 + \dots + n_j \mu_j$$

Eqnⁿ (4), chemical potential may be defined as the contribution per mole of each particular constituent of the mixture to the total free energy of the system under conditions of constant temp^r and pressure. It readily follows that for a total ~~of~~ of one mole of a pure substance, $G = \mu$ i.e. free energy is identical with chemical potential.

As chemical potential (μ) is a ratio of two extensive properties Gibbs free energy (G) and no of moles (n_i), chemical potential is an intensive property.

For open system

$$G = f(P, T, n_1, n_2, \dots)$$

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

Now, $dG = VdP - SdT$

$$dG = VdP - SdT$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

So, eqn ① becomes

$$dG = VdP - SdT + \sum \mu_i \cdot dn_i$$

$$G = H - TS$$

$$dA = -PdV - SdT + \sum \mu_i dn_i$$

$$dH = VdP + TdS + \sum \mu_i \cdot dn_i$$

$$dU = TdS - PdV + \sum \mu_i \cdot dn_i$$

Gibbs - Duhem Equation :-

For a multicomponent open system, in which the quantity of the component may also vary, the free energy will depend on the amount of the components. In such case containing J-component

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

where, n_1 is the no of moles of component 1, n_2 is the no of moles of component 2 and so on.

Its differentiation is given by

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \sum \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j \neq i} dn_i \quad \text{--- ①}$$

$$= -SdT + VdP + \sum \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j \neq i} dn_i$$

$$= -SdT + VdP + \sum \mu_i \cdot dn_i$$

$$dG_{T,P} = \sum \mu_i \cdot dn_i = \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \dots \quad \text{--- ②}$$

Integrating the eqn ② we get

$$G_{T,P} = \sum \mu_i \cdot n_i = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \dots \quad \text{③}$$

Complete differentiation of the eqnⁿ ③ gives

$$dG_{P,T} = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 + \mu_3 dn_3 + n_3 d\mu_3 + \dots$$

$$dG_{P,T} = (\mu_1 dn_1 + \mu_2 dn_2 + \dots) + (n_1 d\mu_1 + n_2 d\mu_2 + \dots) \\ = \sum \mu_i \cdot dn_i + \sum n_i \cdot d\mu_i \quad \text{--- (4)}$$

Now subtracting the eqnⁿ ② from the eqnⁿ ④, we can readily get

$$\boxed{\sum n_i \cdot d\mu_i = 0} \quad \text{--- (5)}$$

Thus the above results can be summarised as

$$\left. \begin{array}{l} \text{i)} \quad dG_{P,T} = \mu_1 dn_1 + \mu_2 dn_2 + \dots = \sum \mu_i \cdot dn_i \\ \text{ii)} \quad G_{P,T} = \mu_1 n_1 + \mu_2 n_2 + \dots = \sum \mu_i n_i \\ \text{iii)} \quad \sum n_i \cdot d\mu_i = n_1 d\mu_1 + n_2 d\mu_2 + \dots = 0 \end{array} \right\}$$

The above relation, especially the equation ⑤ i.e. the third relation is commonly known as Gibbs Duhem equation.

Application:-

1) $dG_{P,T} < 0$ indicates spontaneity, $dG_{P,T} = 0$ is the equilibrium condition of any process.

2) Since $dG_{P,T} = \sum \mu_i \cdot dn_i$
 $\sum \mu_i \cdot dn_i < 0$ spontaneity
 $\sum \mu_i \cdot dn_i = 0$ equilibrium.

We have, $dG = VdP - SdT + \sum \mu_i \cdot dn_i$

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

$$\left(\frac{\partial \mu}{\partial n_i} \right)_{S,V, n_j \neq i} = \mu_i$$

$$dA = -PdV - SdT + \sum \mu_i \cdot dn_i$$

$$\left(\frac{\partial A}{\partial n_i} \right)_{V,T, n_j \neq i} = \mu_i$$

$$\left(\frac{\partial H}{\partial n_i} \right)_{S,P, n_j \neq i} = \mu_i$$



Free energy depends on pressure (P) for an ideal gas at a fixed temp (T) is

Let us consider that in the standard state of an ideal gas the fixed temp = T

Standard state pressure = $P_0 = 1 \text{ atm}$

Standard state molar free energy = $\bar{G}_0$

Now let the gas transfer from state i to state f.

$$dG = VdP - SdT$$

$$dG_T = VdP$$

for ideal gas

$$dG = \frac{nRT}{P} \cdot dP$$

$$\int_{G_1}^{G_2} dG = nRT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$G_2 - G_1 = nRT \ln \frac{P_2}{P_1}$$

$$\frac{G_2}{n} - \frac{G_1}{n} = RT \ln \frac{P_2}{P_1}$$

$$\bar{G}_2 - \bar{G}_1 = RT \ln \frac{P_2}{P_1}$$

at pressure $P_0 = 1 \text{ atm}$, and at pressure P_{atm} .
molar free energy changes from $\bar{G}_0$ to $\bar{G}$

$$\bar{G} - \bar{G}_0 = RT \ln \frac{P_{\text{atm}}}{1 \text{ atm}}$$

$$\text{or } \bar{G} = \bar{G}_0 + RT \ln P$$

Variation of chemical potential with temp:-

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

Differentiating this equation w.r.t temp.

$$\begin{aligned} \left(\frac{\partial \mu_i}{\partial T} \right)_{P, N} &= \left[\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j \neq i} \right]_{P, N} \\ &= \left[\frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial T} \right)_{P, N} \right]_{T, P, n_j \neq i} \\ &= - \left(\frac{\partial S}{\partial n_i} \right)_{T, P, n_j \neq i} \\ &= - \bar{S}_i \end{aligned}$$

Variation of chemical potential with pressure:-

By definition

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

differentiation w.r.t pressure.

$$\begin{aligned} \left(\frac{\partial \mu_i}{\partial P} \right)_{T, N} &= \left[\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j \neq i} \right]_{T, N} \\ &= \left[\frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial P} \right)_{T, N} \right]_{T, P, n_j \neq i} \\ &= \left(\frac{\partial V}{\partial n_i} \right)_{T, P, n_j \neq i} \\ &= \bar{V}_i \end{aligned}$$

Variation of chemical potential with partial pressure:-

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

$$\left(\frac{\partial \mu_i}{\partial P} \right)_{T, N} = \left(\frac{\partial V}{\partial n_i} \right)_{T, P, n_j \neq i}$$



$$\begin{aligned}\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} &= \frac{\partial}{\partial n_i} \left[\frac{(n_1 + n_2 + \dots) RT}{P} \right]_{P,T, n_j \neq i} \\ &= \frac{RT}{P} \left[\frac{\partial}{\partial n_i} (n_1 + n_2 + \dots) \right]_{P,T, n_j \neq i} \\ &= \frac{RT}{P}\end{aligned}$$

$$d\mu_i = \frac{RT}{P} \cdot dP$$

$$d\mu_i = RT \ln P \text{ at fixed temp } T$$

If the partial pressure of component $i = P_i$

we know $P_i = x_i P$ x_i = mole fraction of component i

$$\ln P_i = \ln (x_i P)$$

$$\ln P_i = \ln x_i + \ln P$$

Composition is fixed, so x_i constant

$$d \ln P_i = d \ln P$$

Thus equⁿ ①

$$d\mu_i = RT \ln d \ln P_i$$

Integrating

$$\int_{\mu_i^0}^{\mu_i} d\mu_i = RT \int_{P_0}^P d \ln P_i$$

$$\mu_i - \mu_i^0 = RT \ln \frac{P_i}{P_0}$$

$$\boxed{\mu_i = \mu_i^0 + RT \ln \frac{P_i}{P_0}}$$

$\mu_i \Rightarrow$ Chemical of component i , Partial pressure P_i , μ_i^0 standard state chemical potential, P_0 (1 atm). standard state is at fixed temp and a pressure at 1 atm.

Variation of chemical potential with concentration.

For component i of an ideal gas mixture,

$$P_i V = n_i RT$$

$$P_i = \frac{n_i}{V} RT$$

$$P_i = C_i RT$$

for any component i in the mixture

$$P_i = C_i RT$$

$$\mu_i = \mu_i^0(T) + RT \ln \frac{P_i}{P^0}$$

$$\mu_i = \mu_i^0(T) + RT \ln \frac{C_i RT}{P^0}$$

$$\mu_i = \mu_i^0(T) + RT \ln \left(\frac{C_i RT}{P^0} \cdot \frac{C^0}{C^0} \right)$$

$[C^0 = 1 \text{ mol/lit}]$

$$\mu_i = \mu_i^0(T) + RT \ln \left(\frac{C^0 RT}{P^0} \right) + RT \ln \frac{C_i}{C^0}$$

$$\mu_i = \mu_i^\square(T) + RT \ln \frac{C_i}{C^0}$$

$$\left[\mu_i^\square(T) = \mu_i^0(T) + RT \ln \frac{C^0 RT}{P^0} \right]$$

$\mu_i^\square(T)$ standard state chemical potential, defined as the pure state of the component i , at a fixed temp at a constant concentration of 1 mol/lit.



Variation of chemical potential with mole fraction

$$\mu_i = \mu_{oi}^0(T) + RT \ln \frac{p_i}{p^0}$$

$$\mu_i = \mu_i^0(T) + RT \ln \frac{x_i P}{p^0} \quad [P_i = x_i P]$$

$$\mu_i = \mu_i^0(T) + RT \ln \frac{P}{p^0} + RT \ln x_i$$

$$\mu_i = \mu_i^*(T, P) + RT \ln x_i$$

Thus μ_i^* is another standard state chemical potential, where standard state is defined as the pure state of the ideal gaseous component taken at a pressure and a fixed temp.

Different condition

$$\mu_i = \mu_i^* + RT \ln x_i \quad \text{at const } T, P$$

$$\mu_i = \mu_i^0 + RT \ln \frac{p_i}{p^0} \quad \text{at const } T$$

$$\mu_i = \mu_i^\square + RT \ln \frac{c_i}{c^0} \quad \text{at const } T$$