

Partial molar Properties

The thermodynamic properties U, H, S, A and G named internal energy (U), enthalpy (H), entropy (S), Work function A and Gibbs free energy (G) are extensive properties, its value change with change in number of moles.

$$\text{Let } X = f(T, P, n_1, n_2, \dots, n_i, \dots, n_j) \quad \text{--- (1)}$$

$$\text{where } n_1 + n_2 + n_3 + \dots + n_j = N \quad (i \neq j)$$

For small change in temp, pressure and no. of moles of the Component,

$$dX = \left(\frac{\partial X}{\partial T}\right)_{P, N} dT + \left(\frac{\partial X}{\partial P}\right)_{T, N} dP + \left(\frac{\partial X}{\partial n_1}\right)_{P, T, n_2, n_3, \dots, n_j} dn_1 + \dots \quad \text{--- (2)}$$

The quantity $\left(\frac{\partial X}{\partial n_1}\right)_{P, T, n_2, n_3, \dots, n_j}$ is called the partial molar properties of

1st Component and represented by \bar{X}_1

Similarly for the i th Component: -

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

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

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

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

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

Chemical Potential: - The partial molar free energy is designated as chemical potential and represented by symbol μ .

$$\left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_1, n_2, n_3, \dots} = \bar{G}_i = \mu_i \quad \text{--- (3)}$$

For infinitesimal change in free energy, we can write the following equation.

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

$$\text{or, } dG = \left(\frac{\partial G}{\partial T}\right)_{P, N} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, \dots, n_i, \dots} dP + \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_i dn_i \quad \text{--- (4)}$$

where $\mu_1, \mu_2, \mu_3, \dots, \mu_i$ are chemical potential of 1, 2, 3, 4, ... i th Component respectively.

$$\text{If } T \text{ and } P \text{ remains constant then } (dG)_{T, P} = \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_i dn_i \quad \text{--- (5)}$$

If a system has a definite composition having $n_1, n_2, n_3, \dots, n_i$ moles of constituents 1, 2, 3, ... i respectively, then integrating eqn (5) we have

$$(G)_{T, P, N} = n_1 \mu_1 + n_2 \mu_2 + \dots + n_i \mu_i \quad \text{--- (6)}$$

For one mole of pure substance $G = \mu$

i.e free energy is identical with chemical potential.

Chemical Potential in an ideal gas Mixture.

The variation of chemical potential of any component 'i' of the gaseous system with Pressure is represented as follows

$$\frac{\partial^2 G}{(\partial P)(\partial n_i)} = \left(\frac{\partial \mu_i}{\partial P} \right)_{T,N} \quad \text{--- (1)}$$

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

From equation (1) and (2)

$$\left(\frac{\partial \mu_i}{\partial P} \right)_{T,N} = \bar{v}_i \quad \text{--- (3)}$$

Let us consider a system consisting of a number of ideal gases having number of moles n_1, n_2, \dots, n_i respectively in the mixture.

From ideal gas eqⁿ,
$$V = \frac{nRT}{P} = (n_1 + n_2 + \dots + n_i) \frac{RT}{P} \quad \text{--- (4)}$$

On differentiating eqⁿ (4) w.r.t. n_i at constant Temperature and Pressure.

We have,
$$\left(\frac{\partial V}{\partial n_i} \right)_{T,P,n_1,n_2,n_3,\dots} = \bar{v}_i = \frac{RT}{P} \quad \text{--- (5)}$$

From eqⁿ (3) and (5)

$$\left(\frac{\partial \mu_i}{\partial P} \right)_{T,N} = \frac{RT}{P} \quad \text{--- (6)}$$

For constant composition and const temp. eqⁿ (6) may be expressed as,

$$d\mu_i = RT \cdot \frac{dP}{P} = RT d \ln P \quad \text{--- (7)}$$

Let P_i be the Partial Pressure of constituent 'i' present in the mixture, since each constituent behaves as an ideal gas.

therefore,
$$P_i V = n_i RT \quad \text{or} \quad P_i = \left(\frac{n_i}{n} \right) \cdot P \quad \text{--- (8)}$$

Since n_i and n are constants, therefore, on taking log and differentiating we have

$$d \ln P_i = d \ln P \quad \text{--- (9)}$$

On substituting the value of $d \ln P$ in eqⁿ (7) we have

$$d\mu_i = RT d \ln P_i \quad \text{--- (10)}$$

On integrating equation (10) we have

$$\mu_i = \mu_{i,P}^{\circ} + RT \ln P_i \quad \text{--- (11)}$$

where $\mu_{i,P}^{\circ}$ is the integration constant. Its value depends on Temperature and the nature of the gas.

At constant temperature the partial pressure of the constituent 'i' is unity, i.e. $P_i = 1$

then
$$\mu_i = \mu_{i,P}^{\circ} \quad \text{--- (12)}$$

where $\mu_{i,P}^{\circ}$ is the chemical potential of ith constituent when Partial Pressure is unity, and temperature is constant

Now from eqⁿ (8)
$$P_i = \left(\frac{n_i}{V} \right) RT \quad \text{--- (13)}$$

If $\left(\frac{n_i}{V} \right)$ represents the molar concentration of constituent 'i' in the mixture.

then
$$P_i = C_i RT \quad \text{--- (14)}$$

Now from eqⁿ (11) and (14)

on integrating the above eqⁿ. we have,
$$\mu_i = \mu_{i,P}^{\circ} + RT \ln(C_i RT)$$

$$\mu_i = \mu_{i,P}^{\circ} + RT \ln C_i + RT \ln RT$$

$$\text{or} \quad \mu_i = \mu_{i,c}^{\circ} + RT \ln C_i \quad \text{--- (15)}$$

where $\mu_{i,c}^{\circ} = \mu_{i,P}^{\circ} + RT \ln RT$ $\mu_{i,c}^{\circ}$ is a const. depending upon temp & nature of gas.

If $C_i = 1$ then $\mu_i = \mu_{i,c}^0$

Thus $\mu_{i,c}^0$ represents the Chemical Potential of the Constituent i when the concentration of the constituent i in the mixture is unity, and $\left(\frac{\partial \mu_i}{\partial n_i}\right)$ represents the mole fraction (X_i) of constituent i in the mixture, then equation (8) can be represented as

$$P_i = X_i P \quad \text{--- (16)}$$

Substituting the value of P_i in the equation (11) at const. Pressure

$$\mu_i = \mu_{i,p}^0 + RT \ln X_i P$$

$$\mu_i = \mu_{i,p}^0 + RT \ln X_i + RT \ln P$$

or $\mu_i = \mu_{i(x)}^0 + RT \ln X_i$

where $\left[\mu_{i(x)}^0 = \mu_{i,p}^0 + RT \ln P \right]$

So, $\mu_{i(x)}^0$ represents the Chemical Potential of the Constituent i when mole fraction is unity at constant temperature and pressure.

Gibbs-Duhem Equation

The free energy equation, $(G)_{T,P,N} = n_1 \mu_1 + n_2 \mu_2 + n_3 \mu_3 + \dots + n_i \mu_i$ shows that the free energy of a system at constant temperature and pressure can be expressed as a sum of $n_i \mu_i$ terms for the individual components of the system.

The total differential of G , written as

$$dG = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 + \dots + \mu_i dn_i + n_i d\mu_i$$

$$dG = (\mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_i dn_i) + \underbrace{(n_1 d\mu_1 + n_2 d\mu_2 + \dots + n_i d\mu_i)}_{(1)}$$

We know that $(dG)_{T,P} = (\mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_i dn_i)$ — (2)

From eqn (1) and (2) at const. Temp & Pressure for a system of definite composition

$$dG = dG + (n_1 d\mu_1 + n_2 d\mu_2 + \dots + n_i d\mu_i)$$

$$\text{or, } n_1 d\mu_1 + n_2 d\mu_2 + \dots + n_i d\mu_i = 0$$

$$\text{or } \sum n_i d\mu_i = 0$$

This relation is called Gibbs-Duhem equation.

For a system having two components

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

$$\text{or, } d\mu_1 = -\left(\frac{n_2}{n_1}\right) \cdot d\mu_2$$

It shows the variation in chemical potential of one component affects the value for the other component.

If μ_1 increases, then μ_2 must decrease and vice versa.



Variation of Chemical Potential with Temperature and Pressure

Variation of chemical potential with temperature: -

Let us consider a i th component in a multicomponent system

$$\text{The chemical potential } \mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_1, \dots, n_j} \quad \text{--- (1)}$$

On differentiating eqⁿ (1) w.r. to temp. keeping pressure and composition of the system constant.

$$\text{We have, } \frac{\partial^2 G}{\partial T \partial n_i} = \left(\frac{\partial \mu_i}{\partial T} \right)_{P, N} \quad \text{--- (2)}$$

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

On differentiating eqⁿ (3) w.r. to n_i , we have

$$\frac{\partial^2 G}{\partial n_i \partial T} = - \left(\frac{\partial S}{\partial n_i} \right)_{T, P, N} = -\bar{S}_i \quad \text{--- (4)}$$

Since G is a perfect differential,

$$\frac{\partial^2 G}{\partial T \partial n_i} = \frac{\partial^2 G}{\partial n_i \partial T}$$

Hence from eqⁿ (2) & (4) we have

$$\left(\frac{\partial \mu_i}{\partial T} \right)_{P, N} = -\bar{S}_i \quad (\text{Partial molar entropy}) \quad \text{--- (5)}$$

It is the eqⁿ of variation of chemical potential with temperature. Since entropy is always +ve, so the chemical potential decrease with increase in temperature.

Variation of Chemical Potential with Pressure: -

$$\text{We know } \left(\frac{\partial G}{\partial n_i} \right)_{T, P, N} = \mu_i \quad \text{--- (1)}$$

Differentiating eqⁿ (1) w.r. to Pressure at constant temp and N , composition of the system.

$$\text{We have, } \left(\frac{\partial^2 G}{\partial n_i \partial P} \right) = \left(\frac{\partial \mu_i}{\partial P} \right)_{T, N} \quad \text{--- (2)}$$

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

On differentiating eqⁿ (3) w.r. to n_i , we get

$$\frac{\partial^2 G}{\partial P \partial n_i} = \left(\frac{\partial V}{\partial n_i} \right)_{T, P, N} = \bar{V}_i \quad \text{--- (4)}$$

Since G is perfect differential

$$\frac{\partial^2 G}{\partial n_i \partial P} = \frac{\partial^2 G}{\partial P \partial n_i}$$

Now from eqⁿ (2) and (4), we get

$$\left(\frac{\partial \mu_i}{\partial P} \right)_{T, N} = \bar{V}_i \quad \text{--- (5)}$$

Since volume of substance is positive so chemical potential with increase in pressure.

Chemical Potential and its relation with Internal Energy (U) and Enthalpy (H).

Relation between Chemical Potential and Internal energy

As we know

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

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

$$\text{or, } dG = VdP - SdT + \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_i dn_i$$

$$\text{or, } dG = VdP - SdT + \sum_i \mu_i dn_i \quad \text{--- (1)}$$

$$\text{Now, } G = U + PV - TS$$

$$U = G - PV + TS$$

$$dU = dG - PdV - VdP + Tds + SdT$$

$$= Tds - PdV + \sum_i \mu_i dn_i$$

$$\text{or, } (\partial U)_{V, S} = \sum_i \mu_i dn_i$$

$$\text{or, } \mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{V, S, \dots, n_j} \quad (j \neq i)$$

Relation between Chemical Potential and Enthalpy:

$$\text{We know, } G = H - TS$$

$$H = G + TS$$

$$dH = dG + Tds + SdT \quad \text{--- (2)}$$

$$\text{and we know } dG = VdP - SdT + \sum_i \mu_i dn_i$$

$$\therefore dH = VdP - SdT + \sum_i \mu_i dn_i + Tds + SdT$$

$$= VdP + Tds + \sum_i \mu_i dn_i$$

$$\text{or } (dH)_{P, S} = \sum_i \mu_i dn_i$$

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

$$\therefore \mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{P, S, n_1, n_2, \dots}$$

Standard States Or Reference States

There is no means of finding absolute value of free-energy (G) or Chemical Potential (μ) of any substance.

It is necessary, therefore, to make such measurements with reference to the value obtained for some convenient though arbitrary reference state called Standard State.

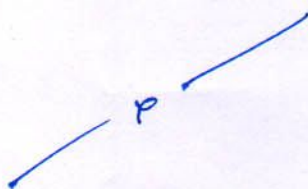
The standard state for a gas at any given temperature is defined as that state in which the fugacity of the gas is equal to unity.

Since $a = \frac{f}{f^0}$, it follows that if $f^0 = 1$, $a = f$.
The standard state for a gaseous component is such that
 $f_i = a_i = 1$

The standard state for a liquid is the pure state of the liquid at one atmosphere pressure at any given temperature. In this state of the liquid, $f = f^0$ and $a = 1$.
The standard state for a liquid component i in a liquid solution is the pure state of the component such that $a_i = 1$.

The standard state for a solid is the pure state of the solid at one atmosphere pressure at any given temperature.

In this state, its activity $a = 1$.



Fugacity :-

An American chemist, G.N. Lewis introduced the concept of fugacity for representing the actual behaviour of real gases which is different from the behaviour of ideal gases.

Variation of free energy with Pressure at Constant temperature is given by the following equation

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{--- (1)}$$

This equation is applicable to all gases whether ideal or non ideal. If one mole of gas is under consideration, then V refers to Molar Volume.

For ideal gas the above equation may be written as

$$\left(\frac{dG}{dP}\right)_T = RT \frac{dP}{P} \quad \text{--- (2)}$$

$$\text{For } n \text{ moles, } \left(\frac{dG}{dP}\right)_T = nRT \frac{dP}{P} = nRT d(\ln P) \quad \text{--- (3)}$$

On integrating the above eqn we have

$$G = G^* + nRT \ln P \quad \text{--- (4)}$$

Where G^* is the integration constant. It defines the free energy of n moles of the ideal gas at temperature T , when the pressure P is unity. and this eqn gives the free energy of ideal gas at Temp. T and pressure P .

On integrating eqn (2) between pressure P_1 and P_2 at const. T .

$$\Delta G = \int_{P_1}^{P_2} nRT \frac{dP}{P} = nRT \ln \frac{P_2}{P_1} \quad \text{--- (5)}$$

$$\text{For 1 mole, } \Delta G = RT \ln \frac{P_2}{P_1} \quad \text{--- (6)}$$

The equation (4) and (6) are not valid for real gases since volume V is not exactly equal to $\frac{RT}{P}$.

In order to make these simple equations applicable to real gases, Lewis introduced a few functions 'f', called fugacity function. It takes the place of P in eqn (3).

For real gases it may be expressed as

$$\left(\frac{dG}{dP}\right)_T = nRT d(\ln f) \quad \text{--- (7)}$$

and eqn (4) may be represented as,

$$G = G^* + nRT \ln f \quad \text{--- (8)}$$

where G^* is the free energy of n moles of a real gas when its fugacity happens to be 1.

The equation (8) gives the free energy of a real gas at temp. T and pressure P at which its fugacity can be taken as 'f'. On integrating eqn (7) $\left(\frac{dG}{dP}\right)_T = nRT d(\ln f)$ between fugacity f_1 and f_2 at constant temp. T . we have

$$\Delta G = nRT \ln \frac{f_2}{f_1} \quad \text{--- (9)}$$

for 1 mole of Gas

$$\Delta G = RT \ln \frac{f_2}{f_1} \quad \text{--- (10)}$$

Fugacity is a sort of fictitious pressure which is used in order to retain for real gases simple forms of equations which are applicable

to ideal gas only. The eqn (9) & (10) are applicable to real gases.

Fugacity Co-efficient and Physical Significance of fugacity

Fugacity Co-efficient \rightarrow At low Pressure, the real gases behave ideally and hence Pressure P tends to zero, f becomes equal to P

$$\text{i.e. } \lim_{P \rightarrow 0} \frac{f}{P} = 1$$

When the Pressure is high, real gases deviate from ideal behavior. So, at high Pressure, $f \neq P$

$$\text{or } \frac{f}{P} \neq 1$$

The ratio f/P is called fugacity Coefficient of the real gas and it is denoted by γ thus $\gamma = \frac{f}{P}$

As the real gas attains ideality

$$f \rightarrow P$$
$$\text{and } \gamma \rightarrow 1$$

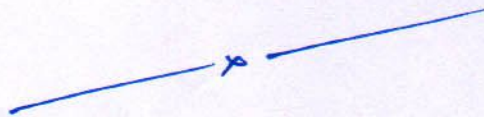
Thus fugacity Co-efficient is a measure of non-ideal character in a real gas.

Physical Significance of fugacity: - Fugacity is a measure of escaping tendency of the substance. To understand Physical Significance of it, let us consider a system consisting of liquid water in contact with its vapour.

Water molecules in the liquid phase will have a tendency to escape into the vapour phase by evaporation, while those in vapour phase will have a tendency to escape into the liquid phase by condensation.

At equilibrium the two escaping tendencies will be equal. So each substance in a given state has a tendency to escape from that state.

This escaping tendency was termed by G.N. Lewis as Fugacity.



Variation of Fugacity with Temperature and Pressure.

Variation of fugacity with Pressure:-

We know

$$\mu = \mu^0 + RT \ln f$$

$$\text{or } d\mu = RT d(\ln f) \quad \text{--- (1)}$$

Again $d\mu = V dp$ ($V = \text{molar volume}$)

Putting $d\mu = V dp$ in equation (1) we have

$$V dp = RT d \ln f$$

$$\text{or, } \left(\frac{\partial \ln f}{\partial P} \right) = \frac{V}{RT} \quad \text{--- (2)}$$

The equation (2) gives the variation of fugacity with change in pressure at constant temperature.

For a mixture of real gases,

$$\left(\frac{\partial \ln f_i}{\partial P} \right)_T = \frac{\bar{V}_i}{RT} \quad \text{--- (3)}$$

Where $f_i = \text{fugacity of } i\text{th component}$ & $\bar{V}_i = \text{Partial molar volume of } i\text{th component}$

Variation of fugacity with Temperature:-

We know,

$$\mu = \mu^0 + RT \ln f$$

$$\text{or, } \mu - \mu^0 = RT \ln f$$

$$\text{or, } \ln f = \frac{\mu - \mu^0}{RT} = \frac{\mu}{RT} - \frac{\mu^0}{RT}$$

$$\therefore \left(\frac{\partial \ln f}{\partial T} \right)_P = \frac{1}{R} \left[\frac{1}{T} \left(\frac{\partial \mu}{\partial T} \right)_P - \frac{\mu}{T^2} \right] - \frac{1}{R} \left[\frac{1}{T} \left(\frac{\partial \mu^0}{\partial T} \right)_P - \frac{\mu^0}{T^2} \right]$$

$$= \frac{T \left(\frac{\partial \mu}{\partial T} \right)_P - \mu}{RT^2} - \frac{T \left(\frac{\partial \mu^0}{\partial T} \right)_P - \mu^0}{RT^2} \quad \text{--- (4)}$$

We know, $G = H + T \left(\frac{\partial G}{\partial T} \right)_P$

So, we can write the above eqn in the form of corresponding Partial-molar Properties.

$$\therefore \bar{G} = \bar{H} + T \left(\frac{\partial \bar{G}}{\partial T} \right)_P$$

$$\text{or, } \mu = \bar{H} + T \left(\frac{\partial \mu}{\partial T} \right)_P$$

$$\text{or, } T \left(\frac{\partial \mu}{\partial T} \right)_P - \mu = -\bar{H} \quad \text{--- (5)}$$

From equation (4) and (5) we get

$$\begin{aligned} \left(\frac{\partial \ln f}{\partial T} \right)_P &= -\frac{\bar{H}}{RT^2} - \left(-\frac{\bar{H}^0}{RT^2} \right) \\ &= \frac{\bar{H}^0 - \bar{H}}{RT^2} \end{aligned} \quad \text{--- (6)}$$

The above equation (6) gives the variation of fugacity with temperature at constant pressure.

Now for a gaseous mixture

$$\left(\frac{\partial \ln f_i}{\partial T} \right)_P = \frac{\bar{H}_i^0 - \bar{H}_i}{RT^2} \quad (7)$$

where f_i = Fugacity of the i^{th} component

\bar{H}_i^0 = Standard Partial molar Enthalpy of i^{th} component

\bar{H}_i = Partial molar Enthalpy of i^{th} component

Activity and Activity Co-efficient

Activity:— We know the equation,

Since absolute value of μ_i is not known, it is not possible to evaluate μ_i^* for a substance. This difficulty has been overcome by referring all chemical potential measurements for any given substance to a standard reference point.

Let μ_i^0 be the chemical potential of a substance i in pure state and f_i^0 be its fugacity in that state.

Now equation (1) may be written as

$$\mu_i^0 = \mu_i^* + RT \ln f_i^0 \quad \text{--- (2)}$$

Let μ_i be the chemical potential of the substance in some other state with f_i as its fugacity.

Now,

$$\mu_i = \mu_i^* + RT \ln f_i \quad \text{--- (3)}$$

On subtracting equation (2) from equation (3), we have

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

or,

$$\mu_i = \mu_i^0 + RT \ln \frac{f_i}{f_i^0} \quad \text{--- (4)}$$

The ratio $\frac{f_i}{f_i^0}$ is defined as the activity of the substance and it is denoted by symbol 'a'.

Thus Activity 'a' = $\frac{f}{f^0}$

For the i th component

$$a_i = \frac{f_i}{f_i^0}$$

So, activity of a substance in any state, may be defined as the ratio of fugacity of the substance in that state to the fugacity of the same substance in the pure state or reference state.

Now equation (4) can be written as

$$\mu_i = \mu_i^0 + RT \ln a \quad \text{--- (5)}$$

If μ_1 and μ_2 are chemical potential in two different states 1 and 2 their activity is a_1 and a_2 .

$$\Delta\mu = \mu_2 - \mu_1 = (\mu^0 + RT \ln a_2) - (\mu^0 + RT \ln a_1)$$

$$\Delta\mu = RT \ln \left(\frac{a_2}{a_1} \right) = \Delta G \quad \text{--- (6)}$$

Comparing the above equation with that for an ideal gas.

$$\Delta G = \Delta\mu = RT \ln \left(\frac{P_2}{P_1} \right)$$

Thus, activity of a gas like fugacity, serves as a thermodynamic counterpart of gas pressure.

Activity Co-efficient: -

For a real gas, Activity is proportional to Pressure,

i.e. $a \propto P$

or $a = \gamma P$, where γ is known as the Activity Coefficient

or $\gamma = \frac{a}{P}$

At low Pressure, a real gas approaches ideal behaviour.

So, $\lim_{P \rightarrow 0} \frac{a}{P} = \gamma = 1$

Duhem - Margules Equation

For two Component System, the Gibbs-Duhem equation is written as,

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

Dividing equation (1) by $(n_1 + n_2)$, we have

$$\frac{n_1}{(n_1 + n_2)} \cdot d\mu_1 + \frac{n_2}{(n_1 + n_2)} d\mu_2 = 0$$

$$\text{or } x_1 d\mu_1 + x_2 d\mu_2 = 0 \quad \text{--- (2)}$$

Where x_1 and x_2 are mole fraction of component 1, and 2 respectively,

$$\text{We know, } \mu = \mu^0 + RT \ln f \quad \text{--- (3)}$$

Differentiating equation (3) at constant temperature, we have

$$d\mu = RT d \ln f$$

$$\text{or, } d\mu_i = RT d \ln f_i \quad \text{--- (4)}$$

From equation (2) and (4) we get,

$$x_1 RT d \ln f_1 + x_2 RT d \ln f_2 = 0$$

$$\text{or } \frac{x_1}{dx_1} RT d \ln f_1 + \frac{x_2}{dx_2} RT d \ln f_2 = 0$$

Since, $dx_1 = -dx_2$, then

$$\text{We have, } \frac{x_1}{dx_1} RT d \ln f_1 - \frac{x_2}{dx_2} RT d \ln f_2 = 0$$

$$\frac{x_1}{dx_1} RT d \ln f_1 = \frac{x_2}{dx_2} RT d \ln f_2$$

$$\text{or, } \frac{x_1}{dx_1} RT d \ln f_1 = \frac{x_2}{dx_2} RT d \ln f_2$$

$$\text{or } \frac{d \ln f_1}{\frac{dx_1}{x_1}} = \frac{d \ln f_2}{\frac{dx_2}{x_2}}$$

$$\text{or } \frac{d \ln f_1}{d \ln x_1} = \frac{d \ln f_2}{d \ln x_2} \quad \text{--- (5)}$$

The above equation is valid whether the vapour phase behaves ideally or non ideally. If the vapour phase behaves ideally, the fugacity can be replaced by pressure term and equation (5) may be written as

$$\frac{d \ln P_1}{d \ln x_1} = \frac{d \ln P_2}{d \ln x_2} \quad \text{--- (6)}$$

Now the eqⁿ (6) is known as **Duhem - Margules Equation**.