Systems of Variable Composition :

Partial Molar Quantity :

Partial Molar Volume :

When 1 mole of H_2O is added to a huge volume of pure H_2O at 25°C, the volume increases by 18 cm^3. So, 18 cm^3 per mole is the molar volume of pure water. However, when one mole of H_2O is added to a huge volume of pure ethanol, the volume changes by only 14 cm^3. Here, so much ethanol is present that each water molecule is surrounded by ethanol molecules and the packing of the molecules result in the water molecules increasing the volume by only 14 cm^3. The quantity 14 cm^3 is the partial molar volume of water in pure ethanol.

In general, the partial molar volume of a substance 'A' in a mixture is the change in volume per mole of 'A' added to a large volume of a mixture. And the partial molar volume of a component J, at some general composition,

$$V_J = \left(\frac{\partial V}{\partial n_J}\right)_{T,P,n'} \longrightarrow (1)$$

where n' signifies the amount of all other complexes present and are constant.

When the composition of a mixture is changed by the addition of dn_A amount of A and dn_B amount of B. The total volume of the mixture changes by —

$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{T,P,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{T,P,n_A} . dn_B$$

$$\Rightarrow dV = V_A . dn_A + V_B . dn_B \longrightarrow (11)$$

$$\Rightarrow V = V_A . n_A + V_B . n_B$$

Molar volume ... is always +ve. But partial molar volume need not be. e.g. The limiting partial molar volume of $MgSO_4$ in H_2O is $-1.4\ cm^3/mol$ which means that the addition of 1 mol $MgSO_4$ to a large volume of H_2O, results in decreasing volume of $1.4\ cm^3$.

The contraction in volume occurs because the salt breaks up the open structure of H_2O as the ions become hydrated. it collapse slightly.

Chemical potential:

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

Let us consider a system at temperature T and pressure P. Let $n_1, n_2, n_3, \ldots, n_j$ be the respective no. of moles of the constituents $1, 2, 3, \ldots, j$.

$$\therefore G = f(T, P, n_1, n_2, n_3, \ldots n_j). \longrightarrow (1)$$

$$\Rightarrow dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \mu_1 dn_1 + \mu_2 dn_2 + \ldots + \mu_j dn_j$$

where, $\mu_1, \mu_2, \ldots$ and μ_j are chemical potentials of components $1, 2, \ldots$ and j, respectively.

If temperature & pressure remain constant, then.

$$(dG)_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + \ldots \mu_j dn_j \longrightarrow (11)$$

of a system has a definite composition having $n_1, n_2, \ldots n_j$ moles of constituents 1, 2, ... j respectively, then on integrating eqn (3), we get,

$$(G)_{T,P,N} = n_1\mu_1 + n_2\mu_2 + \ldots n_j\mu_j \longrightarrow (iii)$$

From eqn (iii), 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 T and P.

Gibbs - Duhem Equation :

The total Gibbs energy of a mixture is given by —

$$G = \mu_A n_A + \mu_B n_B \longrightarrow (1)$$

Now, chemical potential depends on the composition and when the composition are changed infinitesimally, we might expect 'G' of binary system to change by,

$$dG = \mu_A dn_A + n_A \cdot d\mu_A + \mu_B \cdot dn_B + n_B \cdot d\mu_B \longrightarrow (ii) .$$

At constant T and P,

$$(dG)_{T,P} = \mu_A \cdot dn_A + \mu_B \cdot dn_B \longrightarrow (III)$$

$$n_A \cdot d\mu_A + n_B \cdot d\mu_B = 0 \quad \text{and} \quad \Sigma n_j d\mu_j = 0 \longrightarrow (IV)$$

eqn (IV) is called Gibbs Duhem eqn.

Significance of Gibbs Duhem eqn is that the chemical potential of one component of a mixture can't changed independently of the chemical potential of other components in a binary mixture, if chemical potential increases for one component ~~by~~, it must decrease for other component, overall μ must not be changed.

Chemical potential of Ideal soln:

We have for pure A,

$$\mu_A^* = \mu_A^\circ + RT \ln P_A^\circ \longrightarrow (1).$$

If another substance, a solute is also present in the liquid, the chemical potential of A in liquid is μ_A and its vapour pressure is P_A. In this case,

$$\mu_A = \mu_A^\circ + RT \ln P_A \longrightarrow (II)$$

$$\Rightarrow \mu_A^\circ = \mu_A - RT \ln P_A \longrightarrow (III)$$

Substituting (III) in (1),

$$\mu_A^* = \mu_A - RT \ln P_A + RT \ln P_A^\circ .$$

$$\Rightarrow \mu_A = \mu_A^* - RT \ln \left(\frac{P_A}{P_A^\circ}\right) \longrightarrow (IV)$$

From Raoult's law, we have,

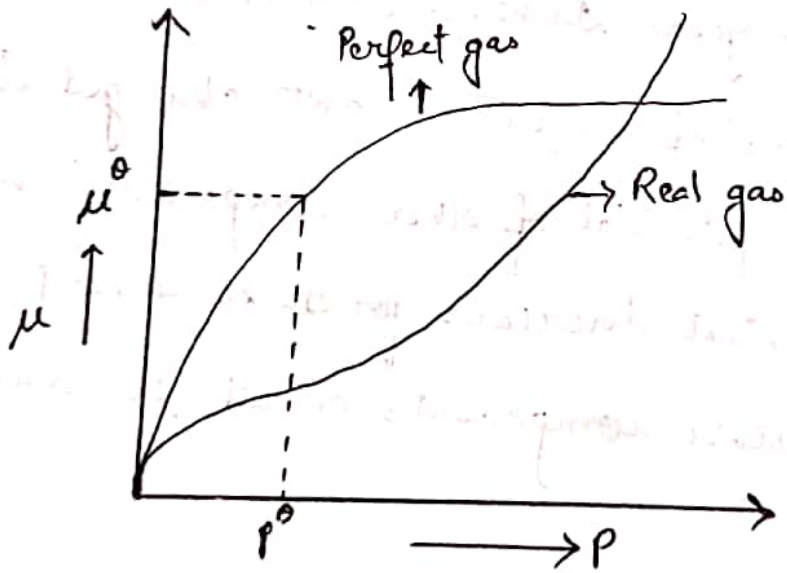
$$P_A = x_A \cdot P_A^* \longrightarrow (V)$$

$$\therefore \text{Eqn (IV)} \Rightarrow \mu_A = \mu_A^* - RT \ln \left(\frac{x_A \cdot P_A^*}{P_A^\circ}\right) \longrightarrow (VI).$$

Eqn (VI) is the definition of an ideal soln.

Fugacity (f) : Effective pressure :

The pressure dependence of a chemical potential of a real gas might resemble ~~the~~ as shown in the figure :



Thus, for real gas.

$$\mu = \mu^0 + RT\ln\left(\frac{P}{P^0}\right)$$

This changes to.

$$\mu = \mu^0 + RT\ln\left(\frac{f}{P^0}\right).$$

where the f is called the fugacity. Fugacity is a Latin word meaning effective pressure or escaping tendency. Fugacity has the same dimension as pressure.

Relation between Pressure and Fugacity:

The relation is,

$$f = \phi P$$

where ϕ is the dimensionless fugacity coefficient. In general, ϕ depends on the nature of the gas, the pressure and temperature.

$$\mu = \mu^0 + RT\ln\left(\frac{f}{P^0}\right).$$

$$\Rightarrow \mu = \mu^0 + RT\ln\left(\frac{\phi P}{P^0}\right).$$

$$\Rightarrow \mu = \mu^0 + RT\ln\left(\frac{P}{P^0}\right) + RT\ln\phi.$$

ϕ is a measure of deviation from ideality. Because, all gases become perfect as the pressure approaches zero, i.e. f tends to P, as P tends to zero. So, we have, as $P \longrightarrow 0$, $\phi \longrightarrow 1$. At low pressure, $\phi = 1$. At a general pressure P, the fugacity coefficient of a gas is given by the expression,

$$\ln \phi = \int_0^P \left(\frac{z-1}{P}\right) dP \longrightarrow (1)$$

where, $z = \frac{PVm}{RT}$, is the compressibility factor of the gas.

For most of the gases, $Z < 1$ upto moderate pressure. But at high pressure, $Z > 1$.

If $Z < 1$, the integral in equation ① is -ve. and $\phi < 1$. Thus $f < P$.

At high pressure, when $Z > 1$, $f > P$. The repulsive interactions predominates and tend to drive the particles apart. Chemical potential is now more than a perfect gas.

Thermodynamics of Mixing :

The Gibb's energy of mixing :

Let, the amount of two perfect gas in the two concentration be n_A and n_B, both are at temperature T and pressure P, then we have —

$$G_i = n_A \mu_A + n_B \mu_B \longrightarrow ①$$

$\because \quad \mu_A = \mu_A^0 + RT \ln x_A$

$\therefore$ Eqn ① $\Rightarrow G_i = n_A \left[\mu_A^0 + RT \ln x_A\right] + n_B \left[\mu_B^0 + RT \ln x_B\right]$.

$$\Rightarrow G_i = n_A \left[\mu_A^0 + RT \ln \frac{P}{P^0}\right] + n_B \left[\mu_B^0 + RT \ln \frac{P}{P^0}\right].$$

Putting, $P = P/P^0$,

$$\Rightarrow G_i = n_A \left[\mu_A^0 + RT \ln P\right] + n_B \left[\mu_B^0 + RT \ln P\right].$$

after mixing, the potential pressure of the gases P_A and P_B will be $P_A + P_B = P$. The total Gibb's energy changes to -

$$G_f = n_A\left[\mu_A^{\ominus} + RT\ln P_A\right] + n_B\left[\mu_B^{\ominus} + RT\ln P_B\right].$$

The difference, $(G_f - G_i)$ is the Gibb's energy of mixing.

$$\therefore \quad \Delta_{mix}G = G_f - G_i$$

$$\therefore \Delta_{mix}G_r = n_A\left[\mu_A^0 + RT\ln p_A/p\right] + n_B\left[\mu_B^0 + RT\ln p_B/p\right].$$

Applying Dalton's law of partial pressure ——

$$\Delta_{mix}G_r = n_A\left[\mu_A^0 + RT\ln x_A\right] + n_B\left[\mu_B^0 + RT\ln x_B\right].$$

Replacing, $n_A, n_B, n_j = x_j n$.

$$\Delta_{mix}G_r = x_A n\left[\mu_A^0 + RT\ln x_A\right] + x_B n\left[\mu_B^0 + RT\ln x_B\right].$$

$$= nRT\left[x_A \ln x_A + x_B \ln x_B\right].$$

Because, mole fractions are never greater than 1. Hence, the logarithm of the above eqn are -ve. ie. $\Delta_{mix}G_r$ of perfect gas is always -ve confirms that the process is spontaneous in all proportions. From the eqn it is seen that, $\Delta_{mix}G_r$ is directly proportional to temp^{re} and independent of pressure.

Entropy of Mixing:

$$dG_r = VdP - SdT.$$

$$\left(\frac{\partial G_r}{\partial P}\right)_P = -S.$$

$$\Delta_{mix}S = -\left(\frac{\partial \Delta_{mix}G_r}{\partial T}\right)_{P, n_A, n_B}$$

$$\Delta_{mix}G_r = -nR\left(x_A \ln x_A + x_B \ln x_B\right).$$

Since, $\ln x_A > 1$, $\Delta_{mix}S$ is always +ve. This increase in entropy is what we expect when one gas disperses into the other and becomes more disorder.