Fugacity and activity-

An ideal gas, an ideal gas mixture and an ideal solution are defined as the ones following the relationships :

Ideal gas :

$$\mu = \mu^{\circ} + RT\ln (P / P^{\circ}) \quad -(1)$$

Ideal gas mixture:

$$\mu_i = \mu_i^{\circ} + RT\ln p_i \quad -(2)$$

Ideal solution :

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

where

P = pressure of the gas (pure)

P° = Pressure of the gas at standard conditions; generally $P^{\circ} = 1$ atm

p_i = Partial pressure of the ith component of a gas mixture

x_i = mole fraction of the ith component of a liquid solution.

μ_i° and μ° are assumed to be functions of temperature only. μ_i^{*} is a function of both temperature as well as pressure.

A pure ideal gas :

Considering the standard state $P^\circ = 1$ atm, we have for a pure ideal gas,

$$\mu = \mu^\circ + RT\ln P$$

$$\Rightarrow \left(\frac{\partial \mu}{\partial P}\right)_T = \left(\frac{\partial \mu^\circ}{\partial P}\right)_T + RT\left(\frac{\partial \ln P}{\partial P}\right)_T$$

$$\Rightarrow \left(\frac{\partial \mu}{\partial P}\right)_T = \frac{RT}{P} \qquad -(4)$$

For a pure component system

$$G = n\mu$$

Further,

$$dG = -SdT + VdP + \mu dn$$

$$\Rightarrow \left(\frac{\partial G}{\partial P}\right)_{T,n} = V$$

$$\Rightarrow \left(\frac{\partial (n\mu)}{\partial P}\right)_{T,n} = V$$

$$\Rightarrow \left(\frac{\partial \mu}{\partial P}\right)_{T,n} = \frac{V}{n} \qquad -(5)$$

From Eqⁿs (4) and (5), we get

$$PV = nRT \qquad \text{-ideal gas equation}$$

Therefore, the ideal gas equation can be recovered using the expression for chemical potential given by Eqⁿ (1). Now we differentiate Eqⁿ (1) with respect to T at constant P.

$$\left(\frac{\partial \mu}{\partial T}\right)_P = \left(\frac{\partial \mu^\circ}{\partial T}\right)_P + R\ln P \qquad -(6)$$

Again, $\left(\frac{\partial G}{\partial T}\right)_{P,n} = -S$

$$\Rightarrow \left(\frac{\partial \mu}{\partial T}\right)_{P,n} = -\frac{S}{n}$$

$$\Rightarrow S = -n\left\{\left(\frac{\partial \mu^\circ}{\partial T}\right)_{P,n} + R\ln P\right\} \qquad -(7)$$

We use Eqⁿ (7) to determine the enthalpy of an ideal gas.

$$H = G + TS$$

$$\Rightarrow h = \mu + Ts$$

$$\Rightarrow h = \mu^\circ + RT\ln P - \left(\frac{\partial \mu^\circ}{\partial T}\right)_{P,n} T - RT\ln P$$

$$\Rightarrow h = \mu^\circ - \left(\frac{\partial \mu^\circ}{\partial T}\right) T \qquad -(8)$$

In Eqⁿ (8), μ° is a function of T only. Hence, h is a function of T only. Further,

$$U = H - PV$$

$$\Rightarrow u = h - Pv$$

$$\Rightarrow u = h - RT$$

∴ For an ideal gas, internal energy and enthalpy are independent of the volume of the gas and the pressure of the gas. These quantities depend upon temperature only.

Eq^n (1) is valid only for an ideal gas. Suppose we need to deal with a non-ideal gas and wish to have an "analogous" equation for chemical potential then the pressure in the equation creates a problem. We need to change pressure as pressure for an ideal gas differs from pressure for a non-ideal gas.

To keep the form of Eq^n (1) intact, we need to introduce a new quantity to account for the non-ideal gas pressure. Consider the following equation.

$$\mu = \mu^0 + RT \ln f \quad - (9)$$

'f' in Eq^n (9) is called fugacity and Eq^n (9) is applicable to non-ideal gases. Since the form of Eq^n (1) and Eq^n (9) is the same, we must have

$$\lim_{P \to 0} f/P = 1$$

From the above condition, it can be stated that fugacity equals the pressure of the gas under conditions where it obeys the ideal gas equation. Since the term pressure is already available for an ideal gas, the use of the term fugacity is limited for non-ideal gas. f/P shows the non-ideality in the system and is called the fugacity coefficient.

Mixture of ideal gases :

An ideal gas mixture is defined by the equation

$$\mu_i = \mu_i^\circ + RT\ln p_i \; ; \; \mu_i^\circ = \mu_i^\circ(T)$$

The partial pressure of i^{th} component at a total pressure of P equals $p_i = y_i P$ where y_i is the mole fraction.

$$\Rightarrow \mu_i = \mu_i^\circ + RT\ln(y_i P)$$

$$\Rightarrow \mu_i = \mu_i^\circ + RT\ln y_i + RT\ln P$$

$$\Rightarrow \left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_1, \ldots n_N} = \frac{RT}{P} \quad - (10)$$

Now consider the following equation.

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, p, n_i^*}$$

$$\Rightarrow \left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_1, \ldots, n_N} = \frac{\partial}{\partial P}\left\{\left(\frac{\partial G}{\partial n_i}\right)_{T, p, n_i^*}\right\}_{T, n_1, \ldots n_N}$$

$$= \frac{\partial}{\partial n_i}\left\{\left(\frac{\partial G}{\partial P}\right)_{T, n_1, \ldots, n_N}\right\}_{T, p, n_i^*}$$

$$= \left(\frac{\partial V}{\partial n_i}\right)_{T, p, n_i^*}$$

$$\Rightarrow \left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_1, n_2, \ldots, n_N} = \bar{V}_i \quad - (11)$$

From Eq^n_s (10) and (11)

$$\bar{V}_i = \frac{RT}{P}$$

But $$v = \sum_{i=1}^{N} n_i \bar{v}_i$$

$$\Rightarrow v = \sum_{i=1}^{N} n_i \left(\frac{RT}{P}\right)$$

$$\Rightarrow PV = RT \sum_{i=1}^{N} n_i$$

$$\Rightarrow PV = n_T R T$$

The appear of the ideal gas equation in this form for a mixture clearly indicates that the volume change on mixing is zero for an ideal gas mixture. Now consider the derivative of the chemical potential with respect to T.

$$\mu_i = \mu_i^\circ + RT\ln P + RT\ln y_i$$

$$\Rightarrow \frac{\mu_i}{T} = \frac{\mu_i^\circ}{T} + R\ln P + R\ln y_i$$

$$\Rightarrow \frac{\partial}{\partial T}\left(\frac{\mu_i}{T}\right)_{P,n_1,\dots,n_N} = \frac{d}{dT}\left(\frac{\mu_i^\circ}{T}\right)$$

Like the previous derivation, it can be easily shown that

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_1,\dots n_N} = -\bar{S}_i$$

But

$$\bar{G}_i = \bar{H}_i - T\bar{S}_i$$

$$\Rightarrow \mu_i = \bar{H}_i - T\bar{S}_i$$

$$\Rightarrow \bar{H}_i = \mu_i + T\bar{S}_i$$

$$\Rightarrow \frac{\bar{H}_i}{T^2} = \frac{\mu_i}{T^2} + \frac{\bar{S}_i}{T}$$

$$\Rightarrow \frac{\bar{H}_i}{T^2} = \frac{\mu_i}{T^2} - \frac{1}{T}\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_1,\ldots n_N}$$

$$\Rightarrow \frac{\bar{H}_i}{T^2} = -\frac{\partial}{\partial T}\left\{(\mu_i/T)\right\}_{P,n_1,\ldots,n_N}$$

$$\Rightarrow \frac{\bar{H}_i}{T^2} = -\frac{d}{dT}\left(\frac{\mu_i^\circ}{T}\right)$$

$$\Rightarrow \bar{H}_i = -T^2\frac{d}{dT}\left(\frac{d\mu_i^\circ}{dT}\right) \quad -(12)$$

It can be seen from Eq^n (12) that the partial molar enthalpy of an ideal gas mixture is independent of the composition. As the composition is changed, $\bar{H}_i$ remains constant. This implies that this quantity will remain unchanged as the mole fraction of any one of the components, y_i, approaches unity. That means the partial molar enthalpy of pure component is the same as the enthalpy of the pure component i.e. enthalpy of mixing of an ideal gas mixture is zero.

The total Gibbs free energy of the mixture

$$G_M = \sum_{i=1}^{N} n_i\mu_i$$

$$\Rightarrow G_M = \sum_{i=1}^{N} n_i\mu_i^\circ + \sum_{i=1}^{N} RT(n_i \ln p_i) \quad -(13)$$

Before mixing, the gases were present at pressures $P_1, P_2 \ldots P_N$. The temperature of each gas was T. Therefore, the total Gibbs free energy before mixing

$$\sum_{i=1}^{N} G_i = \sum_{i=1}^{N} (n_i \mu_i^{\circ} + RT n_i \ln P_i) \qquad - (14)$$

From Eq^{n}s (13) and (14), the Gibbs free energy of mixing

$$\Delta G = RT \sum_{i=1}^{N} n_i \ln (p_i / P_i) \qquad - (15)$$

Further,

$$\Delta G = \Delta H - T\Delta S$$

$$\Rightarrow \Delta S = -\frac{1}{T} \Delta G$$

$$\Rightarrow \Delta S = -R \sum_{i=1}^{N} n_i \ln (p_i / P_i) \qquad - (16)$$

When the partial pressures in the mixture are equal to pressures before mixing,

$$\Delta G = \Delta S = 0$$

Lewis - Randall rule:

For an ideal gas mixture, we have the chemical potential as

$$\mu_i = \mu_i^{0} + RT \ln P + RT \ln y_i$$

μ_i^{0} is a function of T only. We can include the first two terms on RHS to define a new quantity $\mu_i^{*} = \mu_i^{0} + RT \ln P$ such that $\mu_i^{*} = \mu_i^{*}(T, P)$.

$$\mu_i = \mu_i^{*} + RT \ln y_i \qquad - (17)$$

$$\Rightarrow \left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_1, \dots n_N} = \left(\frac{\partial \mu_i^*}{\partial P}\right)_{T, n_1, \dots n_N}$$

It was shown previously that

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_1, \dots n_N} = \bar{V}_i$$

$$\Rightarrow \left(\frac{\partial \mu_i^*}{\partial P}\right)_{T, n_1, \dots n_N} = \bar{V}_i$$

Further

$$\mu_i = \mu_i^\circ + RT\ln f_i$$

$$\mu_i = \mu_i^* + RT\ln y_i$$

$$\Rightarrow \mu_i^* - \mu_i^\circ = RT\ln(f_i/y_i) \quad - (18)$$

LHS of Eq^n (18) is independent of mixture composition. To have this f_i/y_i must also be independent of mixture composition. This means that f_i/y_i will remain invarient as one reaches pure component.

$$\Rightarrow f_i/y_i = f_i'$$

$$\text{or } f_i = f_i' y_i \quad - (19)$$

where f_i' is the pure component fugacity. Eq^n (19) is referred to as the Lewis-Randall rule.

Activity and activity coefficient :

We defined fugacity for a non-ideal gas to replace pressure in chemical potential expression keeping the form intact. The same can be done to liquids. For an ideal liquid solution,

$$\mu_i = \mu_i^* + RT\ln x_i$$

and for a non-ideal liquid solution,

$$\mu_i = \mu_i^* + RT\ln a_i \qquad -(20)$$

where a_i is called the activity of the i^{th} component.

$$\mu_i = f(T, P, x_1, x_2 \dots x_N)$$
$$\mu_i^* = f(T, P^*, x_1^*, x_2^* \dots x_N^*)$$

We revert back to the original definition of fugacity.

$$\mu_i = \mu_i^\circ + RT\ln f_i$$
$$\mu_i^* = \mu_i^\circ + RT\ln f_i^*$$
$$\Rightarrow \mu_i - \mu_i^* = RT\ln(f_i/f_i^*)$$
$$\Rightarrow \mu_i = \mu_i^* + RT\ln(f_i/f_i^*) \qquad -(21)$$

Comparison of Eq^n (20) and (22) gives

$$a_i = f_i/f_i^* \qquad -(22)$$

Hence, activity is the ratio of fugacity of the i^{th} component to the fugacity of that component at standard state and same temperature.

Similar to the fugacity coefficient, activity coefficient can be defined which indicates the deviation from non-ideality. Activity coefficient γ_i

$$\gamma_i = a_i/x_i \qquad -(23)$$

Determination of fugacity

We have the following two relationships

$$\mu_i = \mu_i^\circ + RT\ln f_i \quad -(1)$$

$$\bar{V}_i = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n} \quad -(2)$$

$$\Rightarrow d\mu_i\Big|_{T,n} = \bar{V}_i\, dP\Big|_{T,n}$$

$$\Rightarrow d(\mu^\circ + RT\ln f_i)\Big|_{T,n} = \bar{V}_i\, dP\Big|_{T,n}$$

$$\Rightarrow RT\, d\ln f_i\Big|_{T,n} = \bar{V}_i\, dP\Big|_{T,n}$$

$$\Rightarrow RT\, d\ln f_i - RT\, d\ln p_i\Big|_{T,n} = \bar{V}_i - RT\, d\ln p_i\Big|_{T,n}$$

$$\Rightarrow RT\, d\ln(f_i/p_i)\Big|_{T,n} = \left(\bar{V}_i - \frac{RT}{P}\right)dP$$

$$\Rightarrow RT\, d\ln(f_i/y_iP)\Big|_{T,n} = \left(\bar{V}_i - \frac{RT}{P}\right)dP$$

$$\Rightarrow RT\ln(f_i/y_iP) = \int_0^P \left(\bar{V}_i - \frac{RT}{P}\right)dP \quad -(3)$$

For a pure substance $\bar{V}_i = V/n$

$$RT\ln(f/P) = \int_0^P \left(\frac{V}{n} - \frac{RT}{P}\right)dP \quad -(4)$$

Hence the fugacity of the i^{th} component can be obtained by determining the molar volume of the i^{th} component at temperature T by tabulation of the properties from P = 0 to measurement pressure.

In case of an ideal gas,

$$V = \frac{(n_1+n_2+\cdots n_N)\,RT}{P}$$

and $\bar{V_i} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_i^*} = \frac{RT}{P}$

We substitute the above in Eq^n (3).

$$RT\ln(f_i/y_iP) = \int_0^P\left(\frac{RT}{P} - \frac{RT}{P}\right)dP$$

$$\Rightarrow \quad f_i = y_iP = p_i$$

Hence, for an ideal gas, fugacity of ith component equals its partial pressure.

When the gas follows Amagat's law,

$$V = \sum_{i=1}^{N} n_i v_i$$

where v_i is the molar volume of pure ith component.

$$\Rightarrow \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_i^*} = \frac{\partial}{\partial n_i}\left(\sum_{i=1}^{N} n_i v_i\right)$$

$$\Rightarrow \quad \bar{V_i} = v_i \qquad -(5)$$

$$\Rightarrow \quad RT\ln(f_i/y_iP) = \int_0^P\left(v_i - \frac{RT}{P}\right)dP \qquad -(6)$$

A comparison of Eq^n (4) and (6) yields

$$\frac{f_i}{y_i} = f_i^{Pure}$$

or

$$f_i = y_i f_i^{Pure} \qquad -(7)$$

Eq^n (7) is known as the Lewis rule.

Lewis rule derived before was applicable to a mixture of gases which behaves ideally. Now we extend our analysis. Consider the following equation of state.

$$Pv = RT + \left(b - \frac{a}{RT}\right)P \qquad -(8)$$

v is the above equation is the molar volume. In order to calculate the fugacity of ith component using Eqn (3), we require $\overline{V}_i$. Let us consider a binary gas mixture.

$$\overline{V}_i = \left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_2}$$

$$v = \frac{RT}{P} + b - \frac{a}{RT}$$

$$\Rightarrow V = \frac{n_T RT}{P} + n_T b - \frac{n_T a}{RT}$$

The mixing rules are given as follows:

$$a = y_1^2 a_1 + 2 y_1 y_2 \sqrt{a_1 a_2} + y_2^2 a_2$$

$$b = y_1 b_1 + y_2 b_2$$

$$\Rightarrow n_T a = n_1^2 a + 2 n_1 n_2 \sqrt{a_1 a_2} + n_2^2 a_2$$

$$\text{and } n_T b = n_1 b_1 + n_2 b_2$$

$$\Rightarrow V = \frac{(n_1 + n_2)RT}{P} + (n_1 b_1 + n_2 b_2)$$

$$-\left(n_1^2 a + 2 n_1 n_2 \sqrt{a_1 a_2} + n_2^2 a_2\right)$$

$$\Rightarrow \bar{V}_1 = \frac{RT}{P} + b_1 - \frac{1}{RT}\left\{\frac{n_T(2n_1a_1 + 2n_2\sqrt{a_1a_2} - n_T^2 a}{n_T^2}\right\}$$

Substitution of the above equation in Eqⁿ (3) yields

$$\frac{f_1}{y_1 P} = \exp\left\{\left(b_1 - \frac{a_1}{RT}\right)\frac{P}{RT}\right\} \exp\left\{\frac{(a_1^{1/2} - a_2^{1/2})^2 y_2^2 P}{(RT)^2}\right\}$$

As $y_2 \to 0$, only component 1 is present. Thus $f_1 \to f_1^{pure}$.

$$\Rightarrow f_1^{pure} = P\exp\left\{\left(b_1 - \frac{a_1}{RT}\right)\frac{P}{RT}\right\}$$

$$\Rightarrow f_1 = y_1 f_1^{pure} \exp\left\{\frac{(a_1^{1/2} - a_2^{1/2})^2 y_2^2 P}{(RT)^2}\right\} \quad -(9)$$

The second term exponential indicates a correction factor for the Lewis rule.

Using Eqⁿ (4) the fugacity was obtained by integration over P. Now consider the following

$$\ln\phi = \int_0^P \left(\frac{v}{n} - \frac{RT}{P}\right) dP$$

$$\Rightarrow \ln\phi = \int_0^P \frac{\left(\frac{Pv}{nRT} - 1\right)}{P} dP$$

$$\Rightarrow \ln\phi = \int_0^P \left(\frac{Z-1}{P}\right) dP \quad -(10)$$

where Z is the compressibility factor

$$Z = \frac{Pv}{nRT}$$

Activity and excess property

Excess property is defined as the difference between the property in the non-ideal state and the property of the ideal solution state at the same temperature, pressure and composition as the original mixture. Excess properties give an indication of the deviation of the mixture from ideality. For any general property B the excess function is defined as

$$B^{Ex} = B - B^{Id} \quad -(1)$$

The superscript 'Ex' signifies excess property and the superscript 'Id' signifies ideal solution state. Further,

$$B = \sum_{i=1}^{N} n_i \overline{B_i}$$

$$B^{Id} = \sum_{i=1}^{N} n_i \overline{B_i}^{Id}$$

$$\Rightarrow B - B^{Id} = \sum_{i=1}^{N} n_i (\overline{B_i} - \overline{B_i}^{Id})$$

$$\Rightarrow \quad B^{Ex} = \sum_{i=1}^{N} n_i \overline{B_i}^{Ex} \quad -(2)$$

From the above equation, it can be seen that B^{Ex} and $\overline{B_i}^{Ex}$ are analogous to any other thermodynamic properties B and $\overline{B_i}$. Hence, any excess property can be calculated using the thermodynamic framework developed for other thermodynamic properties.

For any non-ideal solution,

$$\mu_i = \mu_i^* + RT\ln(\gamma_i x_i)$$

$$\Rightarrow \mu_i - \mu_i^* = RT\ln(\gamma_i x_i)$$

$$\Rightarrow \overline{\Delta G_i} = RT\ln(\gamma_i x_i)$$

$$\Rightarrow \overline{\Delta G_i}^{Id} + \overline{\Delta G_i}^{Ex} = RT\ln(\gamma_i x_i)$$

$$\Rightarrow \overline{\Delta G_i}^{Ex} = RT\ln(\gamma_i x_i) - \overline{\Delta G_i}^{Id} \qquad - (3)$$

But $\overline{\Delta G_i}^{Id} = \mu_i^{Id} - \mu_i^{Id*} = RT\ln x_i$

$$\Rightarrow \overline{\Delta G_i}^{Ex} = RT\ln \gamma_i \qquad - (4)$$

For any thermodynamic property B,

$$\overline{\Delta B_i} = \overline{B_i} - \overline{B_i}^*$$

$$\overline{\Delta B_i}^{Id} = \overline{B_i}^{Id} - \overline{B_i}^*$$

$$\Rightarrow \overline{\Delta B_i} - \overline{\Delta B_i}^{Id} = \overline{B_i} - \overline{B_i}^{Id}$$

$$\Rightarrow \overline{\Delta B_i}^{Ex} = \overline{B_i}^{Ex} \qquad - (5)$$

$$\Rightarrow \overline{\Delta G_i}^{Ex} = \overline{G_i}^{Ex} = \mu_i^{Ex} \qquad - (6)$$

From Eq^n (4) and (6),

$$\mu_i^{Ex} = RT\ln \gamma_i \qquad - (7)$$

It can be seen from Eq^n (7) that the activity coefficient of the ith component can be obtained by the calculation of excess chemical potential of the ith component in the solution. We now discuss various models developed to calculate the activity coefficients.

Consider a liquid - liquid solution of two components A and B. The Gibbs free energy of the pure components and on mixing is given as follows:

Gibbs free energy of pure A $= n_A \mu_A^{Pure}$

Gibbs free energy of pure B $= n_B \mu_B^{Pure}$

Gibbs free energy of the solution

$$= n_A \mu_A^{Sol} + n_B \mu_B^{Sol}$$

$$\left.\begin{aligned} \mu_A^{Sol} &= \mu_A^{Pure} + RT \ln x_A \\ \mu_B^{Sol} &= \mu_B^{Pure} + RT \ln x_B \end{aligned}\right\} \text{ideal solution}$$

Gibbs free energy of mixing when the solution behaves ideally

$$\Delta G^{Mix} = n_A \mu_A^{Sol} + n_B \mu_B^{Sol} - n_A \mu_A - n_B \mu_B$$

$$\Rightarrow \Delta G^{Mix} = RT\,(n_A \ln x_A + n_B \ln x_B)$$

$$\Rightarrow \frac{\Delta G^{Mix}}{RT} = n_A \ln x_A + n_B \ln x_B \quad -(8)$$

Since x_A and x_B are always lesser than unity, ΔG^{Mix} is always lesser than zero. This shows that an ideal solution will always be formed spontaneously. Now we calulate the change in entropy of the system on the formation of an ideal solution.

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

$$\Rightarrow \Delta S^{Mix} = -\left(\frac{\partial \Delta G^{Mix}}{\partial T}\right)_{P, n_A, n_B}$$

$$\Rightarrow \Delta S^{Mix} = -R(n_A \ln x_A + n_B \ln x_B) \quad -(9)$$

Eqⁿ (9) shows that $\Delta S^{Mix} > 0$ since x_A, $x_B < 0$. This means that entropy always increases when ideal solutions are formed. Similarly,

$$\Delta V^{Mix} = \left(\frac{\partial \Delta G^{Mix}}{\partial p}\right)_{T, n_A, n_B}$$

$$\Rightarrow \Delta V^{Mix} = 0 \quad -(10)$$

Therefore there does not occur any change in the volume of the system on formation of ideal solutions. Further

$$\Delta H^{Mix} = \Delta G^{Mix} + T\Delta S^{Mix}$$

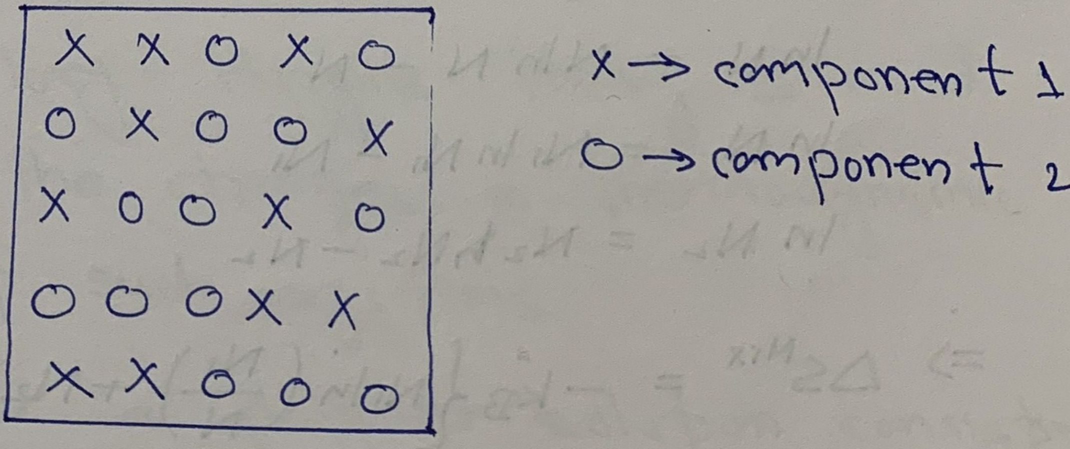
$$= RT(n_A \ln x_A + n_B \ln x_B) + T\{-R(n_A \ln x_A + n_B \ln x_B)\}$$

$$\Rightarrow \Delta H^{Mix} = 0 \quad -(11)$$

Therefore there does not occur any chang in the enthalpy of the system on form ation of ideal solutions.

The lattice model for solutions :

The solutions dealt till now have been assumed to be such that the system is perfectly homogeneous i.e. there are no local variations in the mole fractions of the different components. The solution behaves significantly from ideality when this does not hold true. To understand this, we use the lattice model for a solution. In this model, the solution is assumed to be formed by distributing the pure components on the sites of a regular lattice. The molecules are assumed to be indistinguishable with same size and identical energies of interaction.



X → component 1

O → component 2

Let there be N_1 molecules of type 1 and N_2 molecules of type 2. Total number of molecules in the system is $N = N_1 + N_2$.

Total number of different ways of arranging molecules of type 1 and 2 on the lattice $= \Omega = \dfrac{N!}{N_1!\,N_2!}$

The entropy of the system $S = k_B \ln \Omega$.
This is equal to entropy change of mixing as before mixing, there is only one way of arranging the molecules on the lattice resulting in zero entropy.

$$\Delta S^{Mix} = k_B \ln \Omega$$
$$= k_B \ln \left(\frac{N!}{N_1!\,N_2!} \right)$$
$$= k_B (\ln N! - \ln N_1! - \ln N_2!)$$

Using Stirling approximation, we have

$$\ln N = N \ln N - N$$
$$\ln N_1 = N_1 \ln N_1 - N_1$$
$$\ln N_2 = N_2 \ln N_2 - N_2$$

$$\Rightarrow \Delta S^{Mix} = -k_B \left\{ N_1 \ln\left(\frac{N_1}{N}\right) + N_2 \ln\left(\frac{N_2}{N}\right) \right\}$$

For all practical purposes $N \approx N_A$, the avogadro number. Therefore

$$\Rightarrow \Delta S^{Mix} = -k_B N_A \left\{ \frac{N_1}{N_A} \ln\left(\frac{N_1}{N_A}\right) + \frac{N_2}{N_A} \ln\left(\frac{N_2}{N_A}\right) \right\}$$

$$\Rightarrow \Delta S^{Mix} = (-k_B N_A)(x_A \ln x_A + x_B \ln x_B)$$

In general for an N-component mixing

$$\Delta S^{Mix} = -R \sum_{i=1}^{N} x_i \ln x_i \quad -(12)$$

$$\Rightarrow \Delta G^{Mix} = -RT \sum_{i=1}^{N} x_i \ln x_i \quad -(13)$$

$$\text{and} \quad \Delta V^{Mix} = \Delta H^{Mix} = 0 \quad -(14)$$

Again, perfect homogeneity of the system was assumed in the lattice model. When this is not the case and there are local variations in the mole fractions, then x_i's in Eq^n (13) and (14) need correction. Consider a solution of a polymer in a solvent. The system is non-ideal and this correction is important. Flory-Huggins theory is used to explain the changes in thermodynamic properties of such systems.

Consider a polymer solution consisting of N_1 solvent molecules, each occupying a single lattice site and N_2 polymermolecules, each occupying n lattice sites.

$$N_1 + n N_2 = N \qquad -(15)$$

If 'i' polymer molecules are initially placed on an empty lattice we need to determine the number of ways $(i+1)^{st}$ molecule can be placed.

Number of ways of adding the first segment of $(i+1)^{st}$ molecule = number of unoccupied sites $= N - ni$

If z is the coordination number of the lattice then number of ways of adding second segment of $(i+1)^{st}$ molecule

$$= \underbrace{z}_{\text{Number of sites adjacent to first segment}} \underbrace{\left(\frac{N-ni}{N}\right)}_{\text{Average fraction of vacant sites on the lattice as a whole}}$$

Now that one site in the coordination sphere is occupied by segment number 2, number of ways of adding the third segment

$$= \left(\frac{N-ni}{N}\right)(z-1)$$

and so on.

Therefore on a lattice already containing i polymer molecules $(i+1)^{st}$ polymer molecule can be placed in w_{i+1} ways where

$$w_{i+1} = (N - ni) z \left(\frac{N-Ni}{N}\right)\left\{(z-1)\left(\frac{N-ni}{N}\right)\right\}^{n-2}$$

$$\Rightarrow w_{i+1} = z(z-1)^{n-2} N \left(\frac{N-ni}{N}\right)^{n} \quad -(16)$$

$$\Rightarrow w_i = z(z-1)^{n-2} N \left\{\frac{N-n(i-1)}{N}\right\}^{n} \quad -(17)$$

Total number of ways of placing N_2 polymer molecules on the lattice:

$$\Omega = \frac{w_1 w_2 \dots w_i \dots w_{N_2}}{N_2!} = \frac{1}{N_2!}\left(\prod_{i=1}^{N_2} w_i\right) - (18)$$

$$\Rightarrow S^{Mix} = k_B \ln \Omega$$

$$= k_B \ln\left\{\frac{1}{N_2!}\left(\prod_{i=1}^{N} w_i\right)\right\}$$

$$\Omega \doteq \frac{z^{N_2}(z-1)^{N_2(n-2)}}{N_2!\, N^{N_2(n-1)}} \prod_{i=1}^{N_2}\left\{N - n(i-1)\right\}^{n}$$

$$\prod_{i=1}^{N_2}\left\{N - n(i-1)\right\}^{n} = n^{nN_2}\prod_{i=1}^{N_2}\left(\frac{N}{n}+1-i\right)^{n}$$

$$\prod_{i=1}^{N_2}\left(\frac{N}{n}+1-i\right)^{n} = \left(\frac{N}{n}+1-1\right)^{n}\left(\frac{N}{n}+1-2\right)^{n}\dots\left(\frac{N}{n}+1-N_2\right)^{n}$$

We observe that

$$\frac{\left(\frac{N}{n}\right)!}{\left(\frac{N}{n}-N_2\right)!} = \frac{1\cdot 2\cdot 3\cdot\ldots\cdot\left(\frac{N}{n}-N_2\right)\left(\frac{N}{n}-N_2+1\right)\ldots\left(\frac{N}{n}\right)}{1\cdot 2\cdot 3\ldots\left(\frac{N}{n}-N_2\right)}$$

$$\Rightarrow \prod_{i=1}^{N_2}\left(\frac{N}{n}+1-i\right)^n = \left\{\frac{\left(\frac{N}{n}\right)!}{\left(\frac{N}{n}-N_2\right)!}\right\}^n$$

$$\Rightarrow \Omega = \frac{Z^{N_2}(Z-1)^{N_2(n-2)}\, n^{nN_2}}{N_2!\, N^{N_2(n-1)}}\left\{\frac{\left(\frac{N}{n}\right)!}{\left(\frac{N}{n}-N_2\right)!}\right\}$$

$$\Rightarrow \frac{S^{Mix}}{k_B} = -N_2\ln\left(\frac{nN_2}{N}\right) - N_1\ln\left(\frac{N_1}{N}\right) + N_2\left\{\ln Z + (n-2)\ln(Z-1) + (1-n) + \ln n\right\}$$

Pure solvent case $N_2 = 0$, $S_1 = 0$

Pure polymer case $N_1 = 0$

$$\Rightarrow S_2 = k_B N_2\left\{\ln Z + (n-2)\ln(Z-1) + (1-n) + \ln n\right\}$$

$$\Rightarrow \frac{\Delta S^{Mix}}{k_B} = -\left\{N_1\ln\left(\frac{N_1}{N}\right) + N_2\ln\left(\frac{nN_2}{N}\right)\right\} \qquad - (19)$$

Now the assumption of homogeneity may not hold true. The following quantities signifying local fractions can be defined.

$$\frac{N_1}{N} = \Phi_1$$

$$\frac{nN_2}{N} = \Phi_2$$

$$\Rightarrow \frac{\Delta S^{Mix}}{R} = -(x_1 \ln \Phi_1 + x_2 \ln \Phi_2) \quad -(20)$$

$$\Rightarrow \frac{\Delta G^{Mix}}{RT} = -(x_1 \ln \Phi_1 + x_2 \ln \Phi_2) \quad -(21)$$

The solution is said to exhibit "athermal" behaviour if the above hold true and further to it $\Delta H^{Mix} = 0$. Now

$$\frac{\Phi_2}{\Phi_1} = \frac{nN_2}{N_1}$$

$$x_2 = \frac{N_2}{N_1 + N_2} = \frac{(N_2/N_1)}{1 + (N_2/N_1)}$$

$$\Rightarrow x_2 = \frac{\frac{1}{n}\left(\frac{\Phi_2}{\Phi_1}\right)}{1 + \frac{1}{n}\left(\frac{\Phi_2}{\Phi_1}\right)}$$

$$x_1 + x_2 = 1$$

and $\Phi_1 + \Phi_2 = 1$

$$\Rightarrow \quad x_2 = \frac{\left(\frac{1}{n}\right)\left(\frac{\Phi_2}{1-\Phi_2}\right)}{1+\left(\frac{1}{n}\right)\left(\frac{\Phi_2}{1-\Phi_2}\right)}$$

$$\Rightarrow \quad \Phi_2 = \frac{x_2}{\left(\frac{1}{n}\right) + x_2\left\{1-\left(\frac{1}{n}\right)\right\}} \qquad -(22)$$

We previously made a mention of athermal solution behaviour. We discuss shortly here. If the components of the mixture have similar intermolecular intermolecular interactions and do not differ significantly in size then the solution can be approximated as an ideal solution and all the relations for ideal solutions apply. Such a behaviour is called ideal solution behaviour. Systems in which strong associative forces like hydrogen bonds are absent a behaviour called regular solution behaviour is encountered. Such a behaviour is defined when partial molar excess entropy is zero for all the components.

$$\overline{\Delta S_i}^{Ex} = 0 \quad \forall i$$

$$\Rightarrow \quad \overline{G_i}^{Ex} = \overline{H_i}^{Ex} = \overline{\Delta H_i}^{Ex}$$

Thus, a knowledge of enthalpy of mixing gives a complete information about excess Gibbs free energy. Alternatively, there can be systems for which $\overline{H_i}^{Ex} = 0$.

$$\Rightarrow \quad \overline{G_i}^{Ex} = -T\overline{S_i}^{Ex}$$

Hence, the excess Gibbs free energy is governed by excess entropy of mixing.

Guggenheim quasi-chemical equation

As before, we can imagine a liquid to consist of a 3-D lattice. The volume in the immidiate visinity of a site is referred to as a "cell". One can divide the molecule in the liquid into segments and each segment is assumed to occupy one cell.

The configurational partition for such a system can be written as

$$Z = Z_{\text{lattice}} \, Z_{\text{cell}} \qquad -(1)-$$

where Z_{lattice} refers to the situation where the centre of every segment is coincident with a lattice site and Z_{cell} gives the contributions to Z which are caused by motion of a segment about this central position.

In non-electrolytic solutions, when mixing takes place at constant temperature and pressure, volume change is small at conditions far from critical conditions. Hence, it is possible to substitute ΔG^{Ex} by ΔA^{Ex}. For a binary mixture of components 1 and 2,

$$\Delta A = -k_B T \ln \left\{ \frac{Z_{\text{lattice}}(N_1, N_2)}{Z_{\text{lattice}}(N_1, 0)\, Z_{\text{lattice}}(0, N_2)} \right\}$$

$$-\ (2)$$

The molar excess Gibbs free energy can be approximated as

$$\frac{G^{Ex}}{n_1+n_2} \approx \frac{A^{Ex}}{n_1+n_2} = \frac{\Delta A}{n_1+n_2} - RT\left(x_1 \ln x_1 + x_2 \ln x_2\right) \quad -(3)$$

Guggenheim postulated that the lattice partition function is given as

$$Z_{lattice} = \sum_{\theta} \omega(\theta) \exp\left\{-U_0(\theta) / k_B T\right\} \quad -(4)$$

The factor ω is called the combinatorial factor giving the number of ways the molecules can be arranged in space.

U_0 = potential energy of the lattice
= energy required to remove all the molecules from the lattice.

θ is the molecular configuration variable. For spherical molecules, it is obtained from the coordination number.

Every molecule can be identified as a collection of bonded segments. The "external contact" area of different segments may differ. For example, in neo-pentane the methyl group are having external contact while the central C-at does not.

If 'q_i' is defined as a parameter proportional to the external contact area of the molecule and the coordination number is z then the number of external nearest neighbours of ith component will be zq_i.

θ_{21} = local area fraction

= fraction of external sites around molecule 1 occupied by segments of molecule 2.

θ_{11} = fraction of external sites around molecule 1 occupied by segments of molecule 1.

θ_{12} and θ_{22} can be defined in an analogous manner. In a binary mixture, the following balances are valid.

$$\theta_{11} + \theta_{21} = 1 \quad -(5)$$

$$\theta_{12} + \theta_{22} = 1 \quad -(6)-$$

The lattice energy U_0 is assumed to arise from pair-wise non-bonded segments.

$$-U_0 = \left(\frac{z}{2}\right) q_1 N_1 (\theta_{11} U_{11} + \theta_{21} U_{21}) + \left(\frac{z}{2}\right) q_2 N_2 (\theta_{22} U_{22} + \theta_{12} U_{12}) \quad -(7)$$

where U_{ij} is the interaction energy of i and j. Denoting $u_{ij} = \left(\frac{z}{2}\right) U_{ij}$,

$$-U_0 = q_1 N_1 (\theta_{11} u_{11} + \theta_{21} u_{21}) + q_2 N_2 (\theta_{22} u_{22} + \theta_{12} u_{12}) \quad -(8)$$

The negative sign in the above equation arises form the fact that the interaction energy at infinite separation is zero.

For every local area fraction, it is possible to calculate the microstates with N_1 molecules of the component 1 and N_2 molecules of the component 2.

The combinatorial factor ω can be written as

$$\omega = \omega_1 \omega_2 h(N_1, N_2) \quad -(9)$$

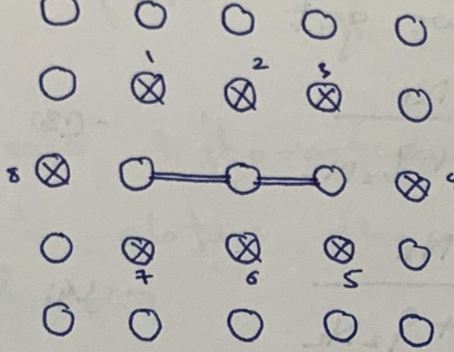
where ω_i = number of configurations associated with a site occupied by a segment of the molecule i. The function h has been assumed to be dependent only upon N_1 and N_2. Further,

$$\omega_1 = \frac{[(q_1 N_1 \theta_{11}) + (q_2 N_2 \theta_{12})]!}{(q_1 N_1 \theta_{11})!\,(q_1 N_1 \theta_{21})!} \quad -(10)-$$

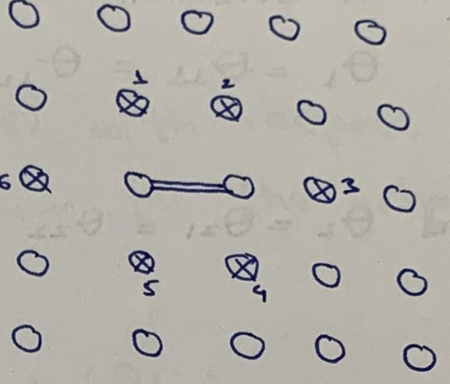
$$\omega_2 = \frac{[(q_2 N_2 \theta_{22}) + (q_1 N_1 \theta_{21})]!}{(q_2 N_2 \theta_{22})!\,(q_2 N_2 \theta_{12})!} \quad -(11)$$

$h(N_1, N_2)$ remains undetermined. For athermal solutions, $U_0 = 0$.

Now consider a binary system with molecule types 1 and 2. Type 1 molecules occupy 3 sites and type 2 molecules occupy 2 lattice sites. Therefore, the external contact of each molecule type can be determined as follows:



$z q_1 = 8$



$z q_2 = 6$

If r_i is the number of cells occupied by one molecule of ith type then $r_1 = 3$ and $r_2 = 2$.

The average segment fraction is calculated as

$$\phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} = \frac{1/2 \times 3}{1/2 \times 3 + 1/2 \times 2} = \frac{3}{5}$$

$$\phi_2 = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2} = \frac{2}{5}$$

Average segment fraction is calculated as

$$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} = \frac{x_1 q_1 z}{x_1 q_1 z + x_2 q_2 z} \quad -(12)$$

$$\Rightarrow \theta_1 = \frac{1/2 \times 8}{1/2 \times 8 + 1/2 \times 6} = \frac{4}{7}$$

$$\theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2} = \frac{3}{7}$$

Eqⁿ (12) can be re-written as

$$\theta_1 = \frac{q_1 N_1}{q_1 N_1 + q_2 N_2}$$

$$\theta_2 = \frac{q_2 N_2}{q_1 N_1 + q_2 N_2}$$

For a thermal mixtures, we get

$$\theta_1 = \theta_{11} = \theta_{12} = \frac{q_1 N_1}{q_1 N_1 + q_2 N_2} \quad -(13)$$

and

$$\theta_2 = \theta_{21} = \theta_{22} = \frac{q_2 N_2}{q_1 N_1 + q_2 N_2} \quad -(14)$$

Using Eqⁿs (10), (11), (13) and (14) we get from Eqⁿ (9)

$$h(N_1, N_2) = \frac{\omega\,(q_1 N_1 \theta_{11})!\,(q_1 N_1 \theta_{21})!\,(q_2 N_2 \theta_{22})!\,(q_2 N_2 \theta_{12})!}{(q_1 N_1 \theta_{11} + q_2 N_2 \theta_{12})!\,(q_2 N_2 \theta_{22} + q_1 N_1 \theta_{21})!} \quad -(15)$$

Now we have different quantities for substitution in Eqⁿ (3). G^{Ex} can be identified as

$$\left(\frac{G^{Ex}}{n_1 + n_2}\right)\frac{1}{RT} = x_1 \ln(\Phi_1/x_1) + x_2 \ln(\Phi_2/x_2) + \left(\frac{Z}{2}\right)\left(q_1 x_1 \ln\frac{\Phi_1}{x_1} + q_2 x_2 \ln\frac{\Phi_2}{x_2}\right) - q_1 x_1 \ln(\theta_1 + \theta_2 \tau_{21}) - q_2 x_2 \ln(\theta_2 + \theta_1 \tau_{12}) \quad -(15)$$

where

$$\tau_{21} = \exp\left\{-\left(\frac{u_{21} - u_{11}}{RT}\right)\right\}$$

and

$$\tau_{12} = \exp\left\{-\left(\frac{u_{12} - u_{22}}{RT}\right)\right\}$$

Now $\mu_i = \mu_i^* + RT \ln a_i$

$$\Rightarrow \mu_i = \mu_i^* + RT \ln x_i + RT \ln \gamma_i$$

$$\Rightarrow \mu_i = \mu_i^{Id} + RT \ln \gamma_i$$

$$\Rightarrow \mu_i - \mu_i^{Id} = RT \ln \gamma_i$$

$$\Rightarrow \left(\frac{\partial}{\partial n_i} (G^{Ex}) \right)_{T,P,n_i*} = RT \ln \gamma_i \quad - (16)$$

We can differentiate Eq^n (15) with respect to n_i to obtain the expression for the activity coefficient.

$$\Rightarrow \ln \gamma_1 = \ln \left(\frac{\Phi_1}{x_1} \right) + \left(\frac{z}{2} \right) q_1 \ln \left(\frac{\theta_1}{\Phi_1} \right) + \Phi_2 \left(l_1 - \frac{r_1}{r_2} l_2 \right) - q_1 \ln (\theta_1 + \theta_2 \tau_{21}) + \theta_2 q_1 \left(\frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} - \frac{\tau_{12}}{\theta_2 + \theta_1 \tau_{12}} \right) \quad - (17) -$$

where $l_1 = \left(\frac{z}{2} \right) (r_1 - q_1) - (r_1 - 1)$

and $l_2 = \left(\frac{z}{2} \right) (r_2 - q_2) - (r_2 - 1)$

Similar expression can be obtained for the activity coefficients of other components. Eq^n (17) is refered to as the UNIQUAC (universal quasi-chemical) equation for the activity coefficient.

UNIQUAC equations have been successfully demonstrated to describe vapour-liquid equilibria of a range of systems. τ_{12} and τ_{21} are the adjustable parameters in the equation and they are obtained by curve-fitting of the equilibrium data.

Apart from UNIQUAC equation, there are several other models used to describe VLE and LLE and determine activity coefficients. A unique quality of UNIQUAC is that under various assumptions, it gets reduced to one of the following:

Flory-Huggins, two-parameter Wilson, three-parameter Wilsen, Non Random Two Liquid model, van Laar equation, Margules equation etc.