Phase Equilibria I: Problem Formulation

So far, we have used thermodynamics to form relationships between the states of a system that undergoes certain processes. We can apply the first and second law to both reversible and irreversible processes to get information about:

(1) how much power is needed or obtained.

(2) how much heat has been absorbed or dissipated.

(3) the value of an unknown property (e.g., T) of the final (or initial) state.

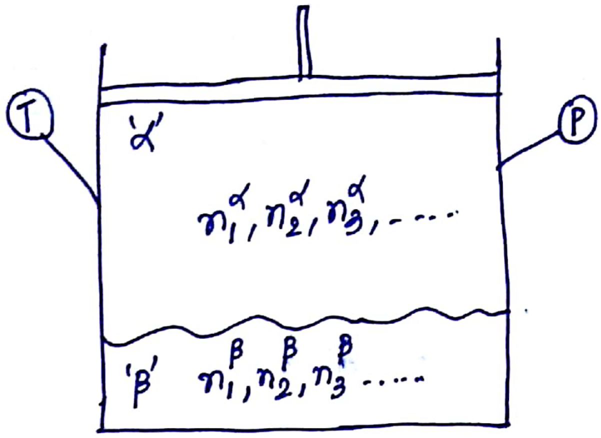
In the remaining classes, we examine another type of problem that we can also use thermodynamics to address — "the composition a mixture obtains when it reaches equilibrium between coexisting phases or in the presence of chemical reactions."

Chemical engineers routinely deal with processes through which species chemically react to form a desired product(s). This product must then be separated from the other by-products as well as any reactants that remain. Typical separation schemes involve contact or formation of different phases through which one species of a mixture preferentially segregates.

Therefore, it is desirable to be able to estimate the degree to which species will react and the degree to which a given species will transfer into a different phase as a function of process conditions.

These problems lead to the second major branch of thermodynamics, which we will now formulate. It deals only with equilibrium systems. In these problems, we wish to calculate how species distribute among phases when more than one phase is present (phase equilibria) or which type of species distributions systems obtain as they approach equilibrium when molecules in the system chemically react (chemical reaction equilibria).

We will consider phase equilibria first. These calculations are restricted to equilibrium systems; therefore, they give information on the direction of the driving force for a given system but no information on the rate at which it will reach equilibrium.



Generic phase equilibria problem.

'α' and 'β' can represent any phase: solid, liquid or vapor.

We may be interested in any of the following:

vapor – liquid
liquid – liquid
liquid – solid
gas – solid

We consider a closed system, since only closed systems can be in thermodynamic equilibrium.

For thermodynamic equilibrium:

These two criteria deal with measurable properties. →

$$\left\{\begin{array}{l} T^\alpha = T^\beta \\ P^\alpha = P^\beta \end{array}\right.$$

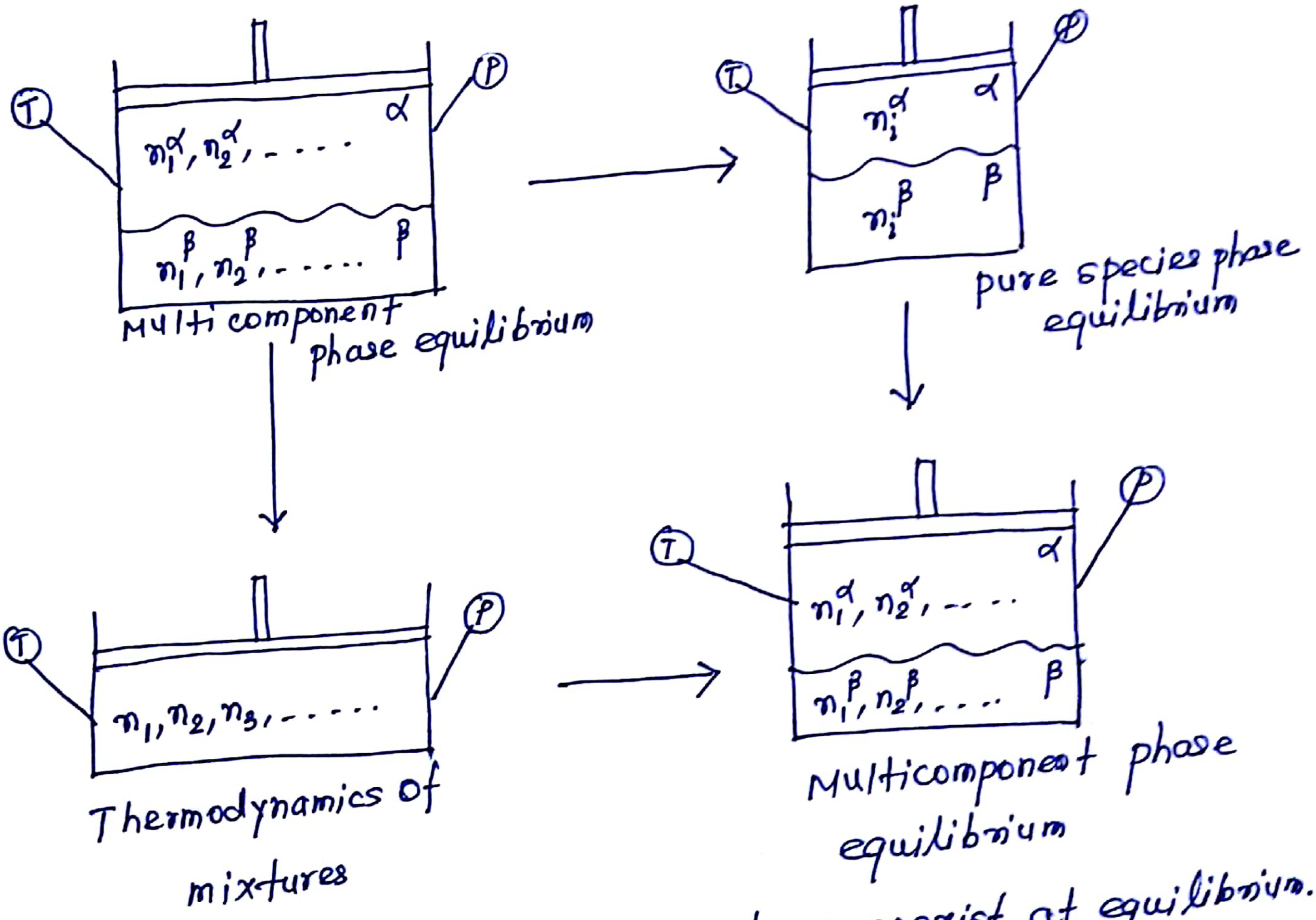
$T^\alpha = T^\beta$ Thermal equilibrium

$P^\alpha = P^\beta$ Mechanical equilibrium

$\mu_i^\alpha = \mu_i^\beta$ chemical equilibrium.

- * Neither mole fraction nor concentration, both measurable properties, represents the driving force for species transfer between phases.
- * Unfortunately, the thermodynamic property that drives a system toward chemical equilibrium is not a measurable property.

Reduction of the multicomponent phase equilibria problem



- * We will learn why two phases coexist at equilibrium.
- * We will learn how to carefully and formally describe the thermodynamics of mixtures.

Thermodynamics of Mixtures

* In this section, we explore how to formally treat thermodynamic properties of species in mixtures.

* For a pure species i, all the intermolecular interactions are identical. The resulting thermodynamic properties- such as V_i, U_i, S_i, H_i and G_i - are a manifestation of those interactions.

* Since a mixture contains more than one species, its properties are determined only in part by an average of each of the pure species (i-i) interactions. We must now also take into account how each of the species interacts with the other species in the mixture, that is, the unlike (i-j) interactions. Thus the properties of a mixture depend on the nature and amount of each of the species in the mixture. The values of the mixture's properties will be affected not only by how those species behave by themselves but also by how they interact with each other.

Consider, for example, the mixture of ethanol and water. If we mix 50 ml of ethanol with 20 ml of water at 25°C and measure the resulting volume of solution, as careful as we might be, we get 67 ml. where has the other 3 ml gone ? The solution has "shrunk" because the ethanol and water can pack together more tightly than can each species by itself. This is due to the nature of the hydrogen bonding involved in the structure of the liquid. We still have the same total mass, since mass is a conserved quantity; however, the mixture volume is different from the sum of the pure species volume. The difference in the mixture is based on the nature of the unlike ethanol-water interactions and the fact that they are different from the water-water or ethanol-ethanol pure species interactions.

This example shows that in the treatment of multi-component mixtures, it is important to realize that species in solution can behave quite differently than they do by themselves, depending on the chemical nature of their neighbors in solution. This behavior will affect all the thermodynamic properties of the solution.

When a species becomes part of a mixture, it loses its identity; yet it still contributes to the properties of the mixture, since the total solution properties of the mixture depend on the amount present of each species and its resultant interactions.

* We wish to develop a way to account for how much of a solution property (V, H, U, S, G, ...) can be assigned to each species. We do this through a new formalism: the partial molar property.

Total thermodynamic properties of a homogeneous phase are functions of T, P and the number of moles of the individual species comprise the phase. Thus, for property M:

$$nM = M(T, P, n_1, n_2, \ldots, n_i, \ldots) \longrightarrow (1)$$

The total differential of nM is:

$$d(nM) = \left[\frac{\partial(nM)}{\partial P}\right]_{T,n} dP + \left[\frac{\partial(nM)}{\partial T}\right]_{P,n} dT + \sum_i \left[\frac{\partial(nM)}{\partial n_i}\right]_{T,P,n_j} dn_i \longrightarrow (2)$$

where subscript 'n' indicates that all mole numbers are held constant and subscript 'n_j' that all mole numbers except 'n_i' are held constant.

It is convenient to define a new thermodynamic function, the partial molar property $\bar{M}_i$ of species 'i' in solution as:

$$\bar{M}_i = \left[\frac{\partial(nM)}{\partial n_i}\right]_{T,P,\underbrace{n_{j\neq i}}} \longrightarrow (3)$$

Always in terms of 'n_i' never 'x_i'

Always hold P & T constant

the number of moles of all other species except 'i' are held constant.

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* A partial molar property is always defined at constant temp. and pressure.

* partial molar properties are defined with respect to number of moles. The number of moles of all other 'j' species in the mixture are held constant; it is only the number of moles of species 'i' that is changed.

Thus from eq^n. (2) and eq^n. (3),

$$d(nM) = n\left(\frac{\partial M}{\partial P}\right)_{T,x} dp + n\left(\frac{\partial M}{\partial T}\right)_{P,x} dT + \sum_i \bar{M}_i dn_i \longrightarrow (4)$$

where subscript 'x' denotes differentiation at constant composition.

since, $n_i = x_i n$

$$dn_i = x_i dn + n dx_i$$

and $$d(nM) = n dM + M dn$$

Thus, from eq^n. (4),

$$n dM + M dn = n\left(\frac{\partial M}{\partial P}\right)_{T,x} dp + n\left(\frac{\partial M}{\partial T}\right)_{P,x} dT + \sum_i \bar{M}_i (x_i dn + n dx_i)$$

collecting terms of 'n' and 'dn':

$$\left[dM - \left(\frac{\partial M}{\partial P}\right)_{T,x} dp - \left(\frac{\partial M}{\partial T}\right)_{P,x} dT - \sum_i \bar{M}_i dx_i\right] n + \left[M - \sum_i \bar{M}_i x_i\right] dn = 0$$

Therefore,

$$dM = \left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \left(\frac{\partial M}{\partial T}\right)_{P,x} dT + \sum_i \bar{M}_i dx_i \longrightarrow (5)$$

and

$$\boxed{M = \sum_i \bar{M}_i x_i} \longrightarrow (6)$$

Multiplication of Eq^n. (6) by 'n'-

$$\boxed{nM = \sum_i \bar{M}_i n_i} \longrightarrow (7)$$

Eq^n. (6) & Eq^n. (7) are Known as "Summability relations", they allow calculation of mixture properties from partial properties.

Now, differentiation of Eq^n. (6) gives-

$$dM = \sum_i x_i d\bar{M}_i + \sum_i \bar{M}_i dx_i \longrightarrow (8)$$

Comparison of Eq^n. (5) & Eq^n. (8) gives-

$$\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \left(\frac{\partial M}{\partial T}\right)_{P,x} dT - \sum_i x_i d\bar{M}_i = 0$$

$$\longrightarrow (9)$$

Eq^n. (9) is Known as Gibbs-Duhem equation.

At constant T & P,

$$\boxed{\sum x_i d\bar{M}_i = 0} \longrightarrow (10)$$

- * Eq^{n}. (6) & Eq^{n}.(7) indicates that solution property is equal to the sum of the partial molar properties of its constituent species, each adjusted in proportion to the quantity of that species present.

- * The partial molar property can be thought of as species i's contribution to the total solution property.

- * The Gibbs-Duhem equation provides a very useful relationship between the partial molar properties of different species in a mixture. For example, in a binary mixture, if we know the partial molar property of one of the species, we can apply the Gibbs-Duhem equation to simply calculate the partial molar property values for the other species.

- * Partial properties, like solution properties, are functions of composition. In the limit as a solution becomes pure in species 'i', both M and $\overline{M}_i$ approach the pure-species property, M_i.

Mathematically,
$$\lim_{x_i \to 1} M = \lim_{x_i \to 1} \overline{M}_i = M_i$$

$$\lim_{x_i \to 0} \overline{M}_i = \overline{M}_i^{\infty}$$

$\hookrightarrow$ infinite-dilution.

The essential equations of this Section are:

Definition: $$\bar{M}_i = \left[\frac{\partial(nM)}{\partial n_i}\right]_{P,T,n_j}$$

which yields partial properties from total properties.

Summability: $$M = \sum_i x_i \bar{M}_i$$

which yields total properties from partial properties.

Gibbs/Duhem: $$\sum_i x_i \, d\bar{M}_i = \left(\frac{\partial M}{\partial P}\right)_{T,x} dp + \left(\frac{\partial M}{\partial T}\right)_{P,x} dT$$

which shows that the partial properties of species making up a solution are not independent of one another.

Partial properties in Binary solutions

For binary solution, the summability relation becomes:

$$M = x_1 \bar{M}_1 + x_2 \bar{M}_2 \longrightarrow (11)$$

$$\Rightarrow dM = x_1 d\bar{M}_1 + \bar{M}_1 dx_1 + x_2 d\bar{M}_2 + \bar{M}_2 dx_2 \longrightarrow (12)$$

Now, from Gibbs/Duhem equation at constant temp. & pressure,

$$x_1 d\bar{M}_1 + x_2 d\bar{M}_2 = 0 \longrightarrow (13)$$

Because $x_1 + x_2 = 1$

$$\Rightarrow dx_1 = -dx_2 \longrightarrow (14)$$

Using Eq^n. (14) in Eq^n. (12),

$$dM = x_1 d\bar{M}_1 + \bar{M}_1 dx_1 + x_2 d\bar{M}_2 - \bar{M}_2 dx_1$$

$$dM = \underbrace{(x_1 d\bar{M}_1 + x_2 d\bar{M}_2)}_{\downarrow \; 0 \; (\text{Eq}^n.\ 13)} + (\bar{M}_1 - \bar{M}_2) dx_1$$

$$\Rightarrow \frac{dM}{dx_1} = \bar{M}_1 - \bar{M}_2 \longrightarrow (15)$$

Now, from eq^n. (11),

$$M = x_1 \bar{M}_1 + (1 - x_1) \bar{M}_2$$

$$M = x_1 \bar{M}_1 + \bar{M}_2 - \bar{M}_2 x_1$$

$$\Rightarrow M = \bar{M}_2 + (\bar{M}_1 - \bar{M}_2) x_1 \longrightarrow (16)$$

Again from eqⁿ. (11),

$$M = (1-x_2)\bar{M}_1 + x_2 \bar{M}_2$$

$$= \bar{M}_1 - \bar{M}_1 x_2 + x_2 \bar{M}_2$$

$$M = \bar{M}_1 + (\bar{M}_2 - \bar{M}_1) x_2 \longrightarrow$$

$$M = \bar{M}_1 - (\bar{M}_1 - \bar{M}_2) x_2 \longrightarrow (17)$$

Eqⁿ. (15) & Eqⁿ. (16) gives-

$$M = \bar{M}_2 + \frac{dM}{dx_1} x_1$$

$$\Rightarrow \boxed{\bar{M}_2 = M - x_1 \frac{dM}{dx_1}} \longrightarrow (18)$$

Eqⁿ. (15) & Eqⁿ. (17) gives-

$$M = \bar{M}_1 - \frac{dM}{dx_1} x_2$$

$$\boxed{\bar{M}_1 = M + x_2 \frac{dM}{dx_1}} \longrightarrow (19)$$

* Thus for binary systems, the partial properties are readily calculated directly from an expression for the solution property as a function of composition at constant T & P.

Gibbs/Duhem equation may be written in derivative forms:

From eq^n. (12),

$$\boxed{x_1 \frac{d\bar{M}_1}{dx_1} + x_2 \frac{d\bar{M}_2}{dx_1} = 0} \longrightarrow (20)$$

or,
$$\boxed{\frac{d\bar{M}_1}{dx_1} = -\frac{x_2}{x_1}\frac{d\bar{M}_2}{dx_1}} \longrightarrow (21)$$

* Clearly, when $\bar{M}_1$ and $\bar{M}_2$ are plotted vs. x_1, the slopes must be of opposite sign.

Moreover,

$$\lim_{x_1 \to 1} \frac{d\bar{M}_1}{dx_1} = 0 \quad \left(\text{provided } \lim_{x_1 \to 1} \frac{d\bar{M}_2}{dx_1} \text{ is finite}\right)$$

Similarly,
$$\lim_{x_2 \to 1} \frac{d\bar{M}_2}{dx_1} = 0 \quad \left(\text{Provided } \lim_{x_2 \to 1} \frac{d\bar{M}_1}{dx_1} \text{ is finite}\right)$$

Thus, plots of $\bar{M}_1$ and $\bar{M}_2$ vs. x_1 become horizontal as each species approaches unity.

* Finally, given an expression for $\bar{M}_1(x_1)$, integration of Eq^n. (20) or Eq^n. (21) gives an expression for $\bar{M}_2(x_1)$ that satisfies the Gibbs/Duhem equation. This means that expressions can't be specified arbitrarily for both $\bar{M}_1(x_1)$ and $\bar{M}_2(x_1)$.

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Example 11.4

The enthalpy of a binary liquid system of species 1 and 2 at fixed T and P is represented by the equation-

$$H = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2)$$

where H is in J/mol.

Determine expressions for $\bar{H}_1$ and $\bar{H}_2$ as function of x_1, numerical values for the pure-species enthalpies H_1 and H_2, and numerical values for the partial enthalpies at infinite dilution $\bar{H}_1^\infty$ and $\bar{H}_2^\infty$.

Solution: Replacing x_2 by $(1-x_1)$,

$$H = 400x_1 + 600(1-x_1) + x_1(1-x_1)\{40x_1 + 20(1-x_1)\}$$

$$= 400x_1 + 600 - 600x_1 + (x_1 - x_1^2)(40x_1 + 20 - 20x_1)$$

$= ~~400x~~$

$$= 600 - 200x_1 + (x_1 - x_1^2)(20x_1 + 20)$$

$$= 600 - 200x_1 + \cancel{20x_1^2} + 20x_1 - 20x_1^3 - \cancel{20x_1^2}$$

$$H = 600 - 180x_1 - 20x_1^3$$

Thus, $\dfrac{dH}{dx_1} = -180 - 60x_1^2$

Therefore, from eq^n. (19), $\bar{H}_1 = H + x_2\dfrac{dH}{dx_1}$

$$= (600 - 180x_1 - 20x_1^3) + (1-x_1)(-180 - 60x_1^2)$$

$$\bar{H}_1 = (600 - 180x_1 - 20x_1^3) - (1-x_1)(180+60x_1^2)$$

$$= 600 - \cancel{180x_1} - 20x_1^3 - 180 - 60x_1^2 + \cancel{180x_1} + 60x_1^3$$

$$\boxed{\bar{H}_1 = 420 - 60x_1^2 + 40x_1^3} \longrightarrow (A)$$

From eqⁿ. (18),

$$\bar{H}_2 = H - x_1 \frac{dH}{dx_1}$$

$$= (600 - 180x_1 - 20x_1^3) - x_1(-180 - 60x_1^2)$$

$$= (600 - \cancel{180x_1} - 20x_1^3) + \cancel{180x_1} + 60x_1^3$$

$$\boxed{\bar{H}_2 = 600 + 40x_1^3} \longrightarrow (B)$$

Pure-species enthalpy, H_1:

since, $H = 600 - 180x_1 - 20x_1^3$

for pure-species 1, $x_1 = 1$

$\therefore H_1 = 600 - 180(1) - 20(1)^3 = 400$ J/mol

$$\boxed{H_1 = 400 \text{ J/mol}}$$

The same can be calculated from eqⁿ. (A)

$H_1 = 420 - 60(1)^2 + 40(1)^3$

$= 420 - 60 + 40 = 400$

$H_1 = 400$ J/mol.

Similarly, pure-species enthalpy, H_2

$$H = 600 - 180x_1 - 20x_1^3$$

For pure-species 2, $x_1 = 0$

$$\therefore \boxed{H_2 = 600 \text{ J/mol}}$$

Similarly from eqⁿ. (B),

$$H_2 = 600 \text{ J/mol.}$$

Now, partial enthalpies at infinite dilution:

From eqⁿ. (A),

$$\bar{H}_1 = 420 - 60x_1^2 + 40x_1^3$$

At infinite dilution for component 1,

$x_1 \simeq 0$

$$\therefore \boxed{\bar{H}_1^\infty = 420 \text{ J/mol}}$$

At infinite dilution for component 2,

$x_2 \simeq 0$ & $x_1 \simeq 1$

Thus, from (B),

$$\bar{H}_2^\infty = \cancel{600 \text{ J/mol}}\ 600 + 40(1)^3$$

$$\boxed{\bar{H}_2^\infty = 640 \text{ J/mol}}$$

Example: Develop expressions for the partial molar enthalpies
(a) of sulfuric acid and water in a binary mixture at 21°C. The pure species enthalpies are 1.596 KJ/mol and 1.591 KJ/mol, respectively. Calculate their values for an equimolar mixture of sulfuric acid and water. plot $\bar{H}_{H_2SO_4}$ and $\bar{H}_{H_2O}$ vs. $x_{H_2SO_4}$.

Given,
$$H = 1.596\, x_{H_2SO_4} + 1.591\, x_{H_2O} - 74.40\, x_{H_2SO_4}\, x_{H_2O}\,(1 - 0.561\, x_{H_2SO_4})$$
[KJ/mol]

Ans: $\bar{H}_{H_2SO_4} = -6.6$ KJ/mol

$\bar{H}_{H_2O} = -17.0$ KJ/mol

(b) verify that expressions developed above for the partial molar enthalpies of sulfuric acid and water in a binary mixture at 21°C satisfy the Gibbs-Duhem equation

(c) Graphically determine values for the partial molar enthalpies of sulfuric acid and water in an equimolar mixture at 21°C by plotting
$$H = 1.596\, x_{H_2SO_4} + 1.591\, x_{H_2O} - 74.40\, x_{H_2SO_4}\, x_{H_2O}\,(1 - 0.561\, x_{H_2SO_4})$$
[KJ/mol]

Example 11.2 Graphical interpretation of the following equations: (Lecture-40)

$$\bar{M}_1 = M + x_2 \frac{dM}{dx_1}$$

and,
$$\bar{M}_2 = M - x_1 \frac{dM}{dx_1}$$

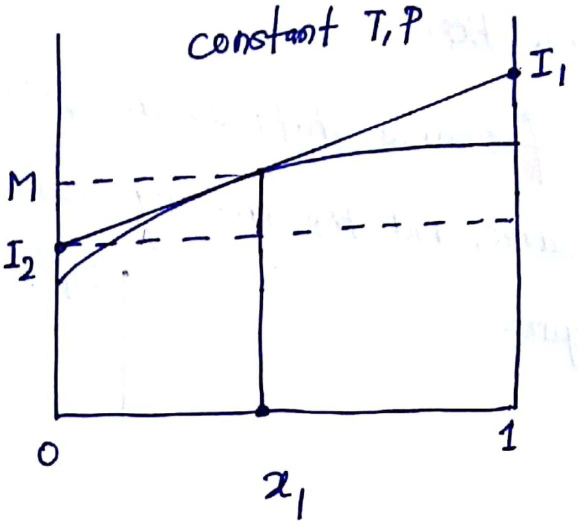

Figure shows a representative plot of 'M' vs. x_1 for a binary system. The tangent line shown extends across the figure, intersecting the edges (at $x_1 = 1$ and $x_1 = 0$) at points labeled I_1 and I_2. As is evident from the figure, two equivalent expressions can be written for the slope of this tangent line:

$$\frac{dM}{dx_1} = \frac{M - I_2}{x_1} \quad \text{and} \quad \frac{dM}{dx_1} = I_1 - I_2$$

From 1st equation:

$$M - I_2 = x_1 \frac{dM}{dx_1}$$

$$I_2 = M - x_1 \frac{dM}{dx_1}$$

using I_2 in 2nd equation:

$$I_1 = I_2 + \frac{dM}{dx_1}$$

$$= M - x_1 \frac{dM}{dx_1} + \frac{dM}{dx_1} = M + (1 - x_1)\frac{dM}{dx_1}$$

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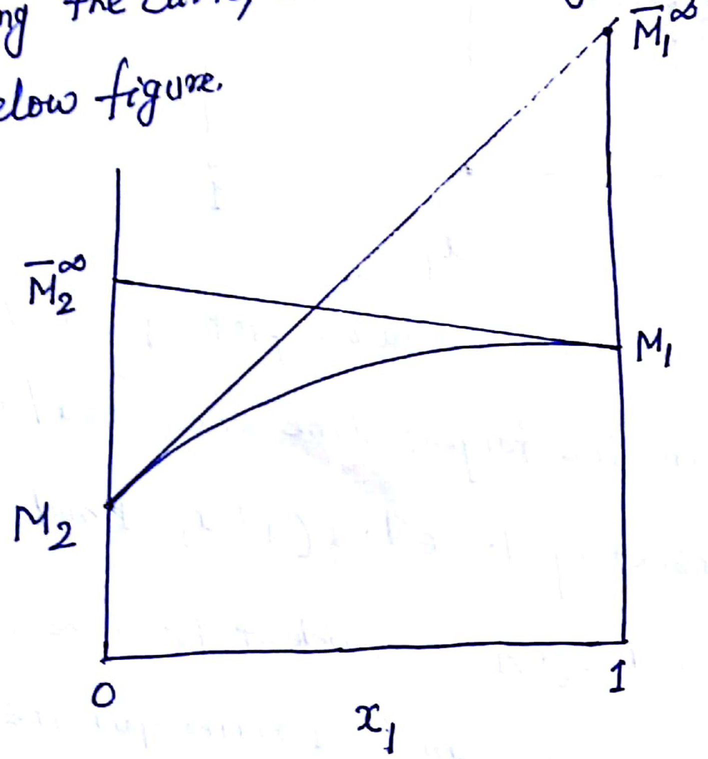
Comparisons of these expressions with the given expression, we get-

$$I_1 = \bar{M}_1 \; \{\text{Intercept at } x_1=1 \text{ gives } \bar{M}_1\}$$

$$I_2 = \bar{M}_2 \; \{\text{intercept at } x_1=0 \text{ gives } \bar{M}_2\}$$

Thus, the tangent intercepts give directly the values of the two partial properties.

These intercepts of course shift as the point of tangency moves along the curve, and the limiting values are indicated in the below figure.



For the tangent line drawn at $x_1=0$ (pure species 2),

$$\bar{M}_2 = M_2$$

and the opposite intercept, $\bar{M}_1 = \bar{M}_1^{\infty}$.

Similarly, tangent drawn at $x_1 = 1$ (pure species 1).

$$\bar{M}_1 = M_1 \text{ and } \bar{M}_2 = \bar{M}_2^{\infty}.$$

Total gibbs energy of any closed system can be written as:

$$d(nG) = (nV)dP - (nS)dT \rightarrow (22)$$

From eqn. (22),

$$\left[\frac{\partial(nG)}{\partial P}\right]_{T,n} = nV \longrightarrow (23)$$

and,

$$\left[\frac{\partial(nG)}{\partial T}\right]_{P,n} = -nS \longrightarrow (24)$$

For the general case of a single-phase,

$$nG = g(T, P, n_1, n_2, \ldots n_i, \ldots)$$

Then,

$$d(nG) = \left[\frac{\partial(nG)}{\partial P}\right]_{T,n} dP + \left[\frac{\partial(nG)}{\partial T}\right]_{P,n} dT + \sum_i \left[\frac{\partial(nG)}{\partial n_i}\right]_{T,P,n_j} dn_i \rightarrow (25)$$

Let us define, chemical potential of species 'i' in the mixture as,

$$\mu_i = \bar{G}_i = \left[\frac{\partial(nG)}{\partial n_i}\right]_{T,P,n_j} \rightarrow (26)$$

Using eqn. (23), (24) & (26) in eqn. (25), we get-

$$\boxed{d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i \, dn_i} \longrightarrow (27)$$

Eq^n. (27) is the fundamental property relation for single-phase fluid systems of variable composition.

For the special case of one mole of solution,

$$n = 1 \text{ and } n_i = x_i :$$

$$dG = V dP - S dT + \sum_i \mu_i dx_i \longrightarrow (28)$$

The chemical potential & phase equilibria

For a closed system consisting of two phases in equilibrium, each individual phase is open to the other, and mass transfer between phases may occur. Eq^n. (27) applies separately to each phase:

$$d(nG)^{\alpha} = (nV)^{\alpha} dP - (nS)^{\alpha} dT + \sum_i \mu_i^{\alpha} dn_i^{\alpha}$$

$$d(nG)^{\beta} = (nV)^{\beta} dP - (nS)^{\beta} dT + \sum_i \mu_i^{\beta} dn_i^{\beta}$$

where superscripts 'α' and 'β' identify the phases.

The change in the total Gibbs energy of the two-phase system is the sum of these equations.

$$d(nG)^{\alpha} + d(nG)^{\beta} = (nV)^{\alpha} dP + (nV)^{\beta} dP - \{(nS)^{\alpha} dT + (nS)^{\beta} dT\} + \sum_i \mu_i^{\alpha} dn_i^{\alpha} + \sum_i \mu_i^{\beta} dn_i^{\beta}$$

when each total-system property is expressed by an equation of the form,

$$nM = (nM)^{\alpha} + (nM)^{\beta}$$

Then,

$$d(nG) = (nV)dp - (nS)dT + \sum_i \mu_i^{\alpha} dn_i^{\alpha} + \sum_i \mu_i^{\beta} dn_i^{\beta}$$

Because the two-phase system is closed,

$$d(nG) = (nV)dp - (nS)dT$$

Thus,

$$\sum_i \mu_i^{\alpha} dn_i^{\alpha} + \sum_i \mu_i^{\beta} dn_i^{\beta} = 0$$

The changes dn_i^{α} and dn_i^{β} result from mass transfer between the phases; mass conservation therefore requires.

$$dn_i^{\alpha} = -dn_i^{\beta}$$

$$\Rightarrow \sum_i (\mu_i^{\alpha} - \mu_i^{\beta}) dn_i^{\alpha} = 0$$

Quantities dn_i^{α} are independent and arbitrary; therefore the only way the left side of the second equation can in general be zero if for each term in parenthese separately is zero

Hence,

$$\boxed{\mu_i^{\alpha} = \mu_i^{\beta}} \quad (i = 1, 2, \ldots N)$$

* Thus, multiple phases at the same T and P are in equilibrium when the chemical potential of each species is the same in all phases.

*
$$\mu_i = \left[\frac{\partial (nG)}{\partial n_i}\right]_{T,P,n_j}$$

For simplicity, we consider a two-component system at some temperature T and pressure P with N_A and N_B the number of molecules of components A and B, respectively.

Thus, we can write,

$$\mu_A = G(T, P, N_A+1, N_B) - G(T, P, N_A, N_B)$$

i.e. chemical potential of component 'A' is the change in the Gibbs energy caused by the addition of one 'A' molecule to the system while keeping T, P and N_B unchanged.

(Lecture-41)

Fugacity and fugacity coefficient:

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pure species

From fundamental property relation-

$$dG = Vdp - SdT$$

At constant temp., for an ideal gas-

$$dG_i^{ig} = V_i^{ig} dP = \frac{RT}{P} dp = RT d\ln P$$

On integration,

$$G_i^{ig} = \Gamma_i(T) + RT\ln P \longrightarrow (1)$$

$\downarrow$

integration constant at constant T, is a species-dependent function of temperature only.

For a real fluid, we write an analogous equation that defines 'f_i', the fugacity of pure species 'i':

$$G_i = \Gamma_i(T) + RT\ln f_i \longrightarrow (2)$$

This new property 'f_i', with units of pressure, replaces 'P' in eqn. (1).

Clearly, eqn. (1) is a special case of eqn. (2), then:

$$f_i^{ig} = P$$

i.e. the fugacity of pure species 'i' as an ideal gas is equal to its pressure.

Subtraction of eqⁿ. (1) from eqⁿ. (2), both written for the same T and P, gives-

$$G_i - G_i^{ig} = RT\ln\frac{f_i}{P} \longrightarrow (3)$$

The dimensionless ratio f_i/P has been defined as another new property, the fugacity coefficient, given by symbol ϕ_i:

$$\boxed{\phi_i = \frac{f_i}{P}} \longrightarrow (4)$$

Thus, from eqⁿ. (3),

$$\boxed{G_i - G_i^{ig} = RT\ln\phi_i} \longrightarrow (5)$$

From the definition of residual Gibbs energy,

$$G_i^R = G_i - G_i^{ig} \cancel{= RT\ln\phi_i} \longrightarrow (6)$$

Thus, from eqⁿ. (5) and eqⁿ. (6),

$$\boxed{G_i^R = RT\ln\phi_i} \longrightarrow (7)$$

* These equations apply to pure species 'i' in any phase at any condition.

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* For an ideal gas, from eq^n. (7),

$$G_i^R = 0$$

$$\Rightarrow \ln \phi_i = 0$$

$$\therefore \boxed{\phi_i = 1}$$

* $$\lim_{P \to 0} \phi_i = \lim_{P \to 0} \frac{f_i}{P} = 1.$$

* From eq^n. (7),

$$\boxed{\ln \phi_i = \frac{G_i^R}{RT} = \int_0^P (Z_i - 1)\frac{dP}{P}} \longrightarrow (8)$$

(const. T)

→ Fugacity coefficients (and therefore fugacities) for pure gases are evaluated by this equation from PVT data or from equation of state.

For example, when the compressibility factor is given by-

$$Z_i = 1 + \frac{B_{ii} P}{RT}$$

Thus,

$$\ln \phi_i = \frac{B_{ii}}{RT}\int_0^P dP = \frac{B_{ii} P}{RT}$$

Example: For H_2O at a temp. of 300°c and for pressure at 4000 kpa, calculate values of f_i and ϕ_i.
~~from data in the~~

Given, At $P = 1 kpa$; $T = 300°C$,

$$H = 3076.8 \ J/g \ ; \ S = 10.3450 \ J/g/K$$

At $P = 4000 \ kpa$; $T = 300°c$

$$H = 2962 \ J/g \ ; \ S = 6.3642 \ J/g/k.$$

Solution: Since,

$$G_i = \Gamma_i(T) + RT \ln f_i \longrightarrow (1)$$

Therefore, writing eq^n. (1) twice: first, for a state at pressure P; second, for a low-pressure reference state, denoted by *, both for temp. T:

$$G_i = \Gamma_i(T) + RT \ln f_i \quad \text{and} \quad G_i^* = \Gamma_i(T) + RT \ln f_i^*$$

Subtraction yields,

$$G_i - G_i^* = RT \ln \frac{f_i}{f_i^*}$$

$$\Rightarrow \ln\left(\frac{f_i}{f_i^*}\right) = \frac{G_i - G_i^*}{RT} = \frac{(H_i - TS_i) - (H_i^* - TS_i^*)}{RT}$$

$$= \frac{(H_i - H_i^*) - T(S_i - S_i^*)}{RT}$$

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$$\Rightarrow \ln\left(\frac{f_i}{f_i^*}\right) = \frac{1}{R}\left[\frac{H_i - H_i^*}{T} - (S_i - S_i^*)\right]$$

$$= \frac{1}{R}\left[\frac{(2962 - 3076.8)}{573.15} - (6.3642 - 10.3450)\right]\frac{J}{gK}$$

$$= \frac{1}{R}\left[(-0.2) - (-3.9808)\right]\frac{J}{gK}$$

$$= \frac{3.7808\ (J/gK)}{8.314\ J/molK} \times (18\ g/mol)$$

$$= 8.186$$

$$\Rightarrow \frac{f_i}{f_i^*} = 3611$$

$$\Rightarrow f_i = (3611)(f_i^*) = (3611)(1\ kpa) = 3611\ kpa.$$

$$f_i = 3611\ kpa.$$

Thus, the fugacity coefficient at 4000 kpa is

$$\phi_i = \frac{f_i}{P} = \frac{3611}{4000} = 0.9028$$

$$\phi_i = 0.9028.$$

Fugacity and fugacity coefficient:

Species in solution

The definition of a residual property is-

$$M^R = M - M^{ig} \longrightarrow (9)$$

Multiplying eq^n. (9) by 'n' mol,

$$nM^R = nM - nM^{ig} \longrightarrow (10)$$

Differentiating eq^n. (10) w.r.t. n_i at constant T, P and n_j, gives

$$\left[\frac{\partial(nM^R)}{\partial n_i}\right]_{P,T,n_j} = \left[\frac{\partial(nM)}{\partial n_i}\right]_{P,T,n_j} - \left[\frac{\partial(nM^{ig})}{\partial n_i}\right]_{P,T,n_j}$$

From the definition of partial Molar property, the above reduces to-

$$\bar{M}_i^R = \bar{M}_i - \bar{M}_i^{ig} \longrightarrow (11)$$

written for the Gibbs energy, eq^n. (11) becomes-

$$\bar{G}_i^R = \bar{G}_i - \bar{G}_i^{ig} \longrightarrow (12)$$

$\downarrow$

(partial residual Gibbs energy)

(Lecture-42)

Gibb's theorem:

A partial molar property (other than volume) of a constituent species in an ideal-gas mixture is equal to the corresponding molar property of the species as a pure ideal gas at the mixture temperature but at a pressure equal to its partial pressure in the mixture.

This is expressed mathematically for generic partial property $\bar{M}_i^{ig} \neq \bar{V}_i^{ig}$ by the equation:

$$\bar{M}_i^{ig}(T,P) = M_i^{ig}(T,P_i) \longrightarrow (13)$$

The enthalpy of an ideal gas is independent of pressure: therefore

$$\bar{H}_i^{ig}(T,P) = H_i^{ig}(T,P_i) = H_i^{ig}(T,P)$$

More simply,

$$\bar{H}_i^{ig} = \underset{\downarrow}{H_i^{ig}} \longrightarrow (14)$$

pure-species value at the mixture T and P.

* An analogous equation applies for U^{ig} and other properties that are independent of pressure.

For an ideal gas,

$$dS^{ig} = C_p^{ig} \frac{dT}{T} - R \frac{dP}{P} \longrightarrow (15)$$

At constant temperature,

$$dS_i^{ig} = -R\, d\ln P \qquad (\text{const } T)$$

Integration from P_i to P gives-

$$S_i^{ig}(T,P) - S_i^{ig}(T,P_i) = -R\ln \frac{P}{P_i} = -R\ln\left(\frac{P}{y_i P}\right)$$

$$S_i^{ig}(T,P) - S_i^{ig}(T,P_i) = R\ln y_i \longrightarrow (16)$$

Using equation (13) for entropy:

~~$\bar{S}_i^{ig} = S_i^{ig}$~~ $\bar{S}_i^{ig}(T,P) = S_i^{ig}(T,P_i) \longrightarrow (17)$

Using (16) & (17),

~~$\bar{S}_i^{ig} = S_i^{ig}(T,$~~

$$S_i^{ig}(T,P) - \bar{S}_i^{ig}(T,P) = R\ln y_i$$

$$\bar{S}_i^{ig}(T,P) = S_i^{ig}(T,P) - R\ln y_i \longrightarrow (18)$$

For the Gibbs energy of an ideal-gas mixture,

$G^{ig} = H^{ig} - TS^{ig}$; the parallel relation for partial properties is-

$$\bar{G}_i^{ig} = \bar{H}_i^{ig} - T\bar{S}_i^{ig} \longrightarrow (19)$$

In combination with Eqs. (14) and (18) this becomes -

$$\bar{G}_i^{ig} = H_i^{ig} - T\{S_i^{ig} - R\ln y_i\}$$

$$\mu_i^{ig} = H_i^{ig} - TS_i^{ig} + RT\ln y_i$$

$$\mu_i^{ig} = \bar{G}_i^{ig} = G_i^{ig} + RT\ln y_i \longrightarrow (20)$$

Using eq^n. (11),

$$\mu_i^{ig} = \bar{G}_i^{ig} = \Gamma_i(T) + RT\ln P + RT\ln y_i$$

$$\bar{G}_i^{ig} = \mu_i^{ig} = \Gamma_i(T) + RT\ln(y_i P) \longrightarrow (21)$$

The definition of the fugacity of a species in solution is parallel to the definition of the pure species fugacity.

For species 'i' in a mixture of real gases or in a solution of liquids, the equation analogous to eq^n. (21) is:

$$\bar{G}_i = \mu_i = \Gamma_i(T) + RT\ln\hat{f}_i \longrightarrow (22)$$

where $\hat{f}_i$ is the fugacity of species 'i' in solution, replacing the partial pressure $y_i P$.

Using eqⁿ. (21) & (22) in eqⁿ. (12),

$$\bar{G}_i^R = \bar{G}_i - \bar{G}_i^{ig} = \mu_i - \mu_i^{ig} = RT\ln\left(\frac{\hat{f}_i}{y_i P}\right)$$

$$\bar{G}_i^R = RT\ln\hat{\phi}_i \longrightarrow (23)$$

where by definition,

$$\hat{\phi}_i = \frac{\hat{f}_i}{y_i P} \longrightarrow (24)$$

The dimensionless ratio $\hat{\phi}_i$ is called the fugacity coefficient of species 'i' in solution.

* Because Eqⁿ. (21) for an ideal gas is a special case of the Eqⁿ. (22), then

$$\hat{f}_i^{ig} = y_i P \longrightarrow (25)$$

Thus the fugacity of species 'i' in an ideal-gas mixture is equal to its partial pressure.

Moreover,

$\hat{\phi}_i^{ig} = 1$ and for an ideal gas $\bar{G}_i^R = 0$.

The fundamental Residual-Property Relation

$$d\left(\frac{nG}{RT}\right) = \frac{1}{RT}d(nG) - \frac{nG}{RT^2}dT \longrightarrow (26)$$

and,

$$d(nG) = (nV)dp - (nS)dT + \sum_i \mu_i dn_i \longrightarrow (27)$$

Using eqn. (27) in eqn. (26), we get-

$$d\left(\frac{nG}{RT}\right) = \frac{1}{RT}\left\{nVdp - nSdT + \sum_i \mu_i dn_i\right\} - \frac{nG}{RT^2}dT$$

$$= \frac{nV}{RT}dp - \frac{nS}{RT}dT + \sum_i \frac{\mu_i dn_i}{RT} - \frac{nG}{RT^2}dT$$

$$= \frac{nV}{RT}dp - \frac{nS}{RT}\cancel{dT} + \sum_i \frac{\bar{G}_i}{RT}dn_i - \frac{(nH - T(nS))dT}{RT^2}$$

$$= \frac{nV}{RT}dp - \cancel{\frac{nS}{RT}dT} + \sum_i \frac{\bar{G}_i}{RT}dn_i - \frac{nH}{RT^2}dT + \cancel{\frac{T(nS)}{RT^2}dT}$$

$$\boxed{d\left(\frac{nG}{RT}\right) = \frac{nV}{RT}dP - \frac{nH}{RT^2}dT + \sum_i \frac{\bar{G}_i}{RT}dn_i} \longrightarrow (28)$$

Eqn. (28) may be written for the special case of an idealgas: ⑥

$$d\left(\frac{nG^{ig}}{RT}\right) = \frac{nV^{ig}}{RT}dp - \frac{nH^{ig}}{RT^2}dT + \sum_i \frac{\bar{G}_i^{ig}}{RT}dn_i \longrightarrow (29)$$

Eq^n. (28) − Eq^n. (29) gives -

$$d\left(\frac{nG^R}{RT}\right) = \frac{nV^R}{RT}dp - \frac{nH^R}{RT^2}dT + \sum_i \frac{\bar{G}_i^R}{RT}dn_i \xrightarrow{} (30)$$

Eq^n. (30) is the fundamental residual-property relation.

Using eq^n. (23) in eq^n. (30),

$$d\left(\frac{nG^R}{RT}\right) = \frac{nV^R}{RT}dp - \frac{nH^R}{RT^2}dT + \sum_i \ln\hat{\phi}_i dn_i \xrightarrow{} (31)$$

In addition,

$$\ln\hat{\phi}_i = \left[\frac{\partial(nG^R/RT)}{\partial n_i}\right]_{T,P,n_j} \xrightarrow{} (32)$$

Also, we have,

$$\frac{G^R}{RT} = \int_0^P (Z-1)\frac{dp}{P}$$

For 'n' mole of a constant-composition mixture,

$$\frac{nG^R}{RT} = \int_0^P (nZ-n)\frac{dp}{P}$$

Thus, from eq^n. (32),

$$\ln \hat{\phi}_i = \int_0^P \left[\frac{\partial(nZ - n)}{\partial n_i}\right]_{T, P, n_j} \frac{dP}{P}$$

$$\ln \hat{\phi}_i = \int_0^P (\bar{Z}_i - 1)\frac{dP}{P} \longrightarrow (33)$$

where, $\bar{Z}_i = \frac{\partial(nZ)}{\partial n_i}$ and $\frac{\partial n}{\partial n_i} = 1$.

(Lecture-43)

The ideal-solution Model

The chemical potential as given by the ideal-gas mixture model,

$$\mu_i^{ig} = \bar{G}_i^{ig} = G_i^{ig}(T,P) + RT \ln y_i \longrightarrow (34)$$

A natural extension of Eqⁿ. (34) replaces $G_i^{ig}(T,P)$ by $G_i(T,P)$, the Gibbs energy of pure 'i' in its real physical state of gas, liquid or even solid.
Thus, we define an ideal solution as one for which

$$\mu_i^{id} = \bar{G}_i^{id} = G_i(T,P) + RT \ln x_i \longrightarrow (35)$$

where superscript 'id' denotes an ideal-solution property.

The Lewis/Randall Rule:

We have,

$$\mu_i = \Gamma_i(T) + RT\ln \hat{f}_i \longrightarrow (36)$$

and,

$$G_i = \Gamma_i(T) + RT\ln f_i \longrightarrow (37)$$

Eqn. (36) & Eqn. (37) yields the general equation:

$$\mu_i = G_i + RT\ln\left(\frac{\hat{f}_i}{f_i}\right) \longrightarrow (38)$$

For the special case of an ideal solution,

$$\mu_i^{id} = \bar{G}_i^{id} = G_i + RT\ln\left(\frac{\hat{f}_i^{id}}{f_i}\right) \longrightarrow (39)$$

Comparing eqn. (39) and eqn. (35), gives-

$$\boxed{\hat{f}_i^{id} = x_i f_i} \longrightarrow (40)$$

This equation, known as the Lewis/Randall rule, applies to each species in an ideal solution at all conditions of temp., pressure, and composition. It shows that the fugacity of each species in an ideal solution is proportional to its mole fraction; the proportionality constant is the fugacity of pure species 'i' in the same physical state as the solution and at the same T and P.

Division of both sides of eqn. (40) by Px_i,

$$\frac{\hat{f}_i^{id}}{Px_i} = \frac{x_i f_i}{Px_i}$$

$$\Rightarrow \quad \hat{\phi}_i^{id} = \frac{f_i}{P} = \phi_i$$

$$\boxed{\hat{\phi}_i^{id} = \phi_i} \longrightarrow (41)$$

Thus, the fugacity coefficient of species 'i' in an ideal solution is equal to the fugacity coefficient of pure species 'i' in the same physical state as the solution and at the same T and P.

Excess properties

The residual Gibbs energy and the fugacity coefficient are directly related to exprimental PVT data. Where such data can be adequately correlated by equations of state, thermodynamic-property information is advantageously provided by residual properties. Indeed, if convenient treatment of all fluids by means of equations of state were possible, the thermodynamic-property relations would suffice. However, liquid solutions are often more easily ~~dealth~~ dealt with through properties that measure their departures, not from ideal-gas behavior, but from ideal-solution behavior. Thus, the mathematical formalism of excess properties is analogous to that of the residual properties.

If 'M' represents the molar value of any extensive thermodynamic property, then an excess property M^E is defined as the difference between the actual property value of a solution and the value it would have as an ideal solution at the same temp, pressure and composition Thus,

$$M^E = M - M^{id} \longrightarrow (42)$$

For example,

$$\left.\begin{aligned} G^E &= G - G^{id} \\ H^E &= H - H^{id} \\ S^E &= S - S^{id} \\ G^E &= H^E - TS^E \end{aligned}\right\} \longrightarrow (43)$$

- The definition of 'M^E' is analogous to the definition of a residual property.

- Excess properties have a simple relation to residual properties.

$$M^R = M - M^{ig}$$

$$M^E = M - M^{id}$$

Thus,

$$\begin{aligned} M^E - M^R &= (M - M^{id}) - (M - M^{ig}) \\ &= -M^{id} + M^{ig} \\ &= -(M^{id} - M^{ig}) \end{aligned}$$

- An ideal-gas mixture is an ideal solution of ideal gases.

- The partial-property relation analogous to Eq^n. (42) is

$$\bar{M}_i^E = \bar{M}_i - \bar{M}_i^{id} \longrightarrow (44)$$

where $\bar{M}_i^E$ is a partial excess property.

Analogous to Eq^n (30), [Fundamental residual-property relation], we can write-

$$d\left(\frac{nG^E}{RT}\right) = \frac{nV^E}{RT}dp - \frac{nH^E}{RT^2}dT + \sum_i \frac{\bar{G}_i^E}{RT}dn_i \longrightarrow (45)$$

This is the fundamental excess-property relation.

The Excess Gibbs Energy and the Activity coefficient

we have, $\bar{G}_i = \Gamma_i(T) + RT\ln\hat{f}_i$

For an ideal solution, this becomes-

$$\bar{G}_i^{id} = \Gamma_i(T) + RT\ln(x_i f_i)$$

By difference,

$$\underbrace{\bar{G}_i - \bar{G}_i^{id}}_{\bar{G}_i^E} = RT\ln\left(\frac{\hat{f}_i}{x_i f_i}\right) \longrightarrow \boxed{\gamma_i = \frac{\hat{f}_i}{x_i f_i}} \longrightarrow (46)$$

$\downarrow$ Partial Excess Gibbs Energy

γ_i: activity coefficient of species 'i' in solution.

Thus,

$$\boxed{\bar{G}_i^E = RT\ln\gamma_i} \longrightarrow (47)$$

For an ideal solution, $\bar{G}_i^E = 0$ &

therefore, $\gamma_i = 1$.

From eq^n. (47),

$$\bar{G}_1 - \bar{G}_i^{id} = RT\ln\gamma_i$$

Using eq^n. (35),

$$\bar{G}_i - G_i(T,P) - RT\ln x_i = RT\ln\gamma_i$$

$$\Rightarrow \bar{G}_i = G_i(T,P) + RT\ln(\gamma_i x_i)$$

$$\boxed{\mu_i = G_i(T,P) + RT\ln(\gamma_i x_i)} \longrightarrow (48)$$

From Eq^n. (45) using eq^n. (47), we get-

$$d\left(\frac{nG^E}{RT}\right) = \frac{nV^E}{RT}dP - \frac{nH^E}{RT^2}dT + \sum_i \ln\gamma_i \, dn_i \longrightarrow (49)$$

and,

$$\boxed{\ln\gamma_i = \left[\frac{\partial(nG^E/RT)}{\partial n_i}\right]_{T,P,n_j}} \longrightarrow (50)$$

Eq^n. (50) demonstrates that $\ln\gamma_i$ is a partial property with respect to G^E/RT.

The following forms of the summability and Gibbs/Duhem equations result from the fact that $\ln\gamma_i$ is a partial property with respect to G^E/RT.

(Lecture-44)

$$\boxed{\frac{G^E}{RT} = \sum_i x_i \ln \gamma_i} \longrightarrow (51)$$

$$\boxed{\sum_i x_i \, d \ln \gamma_i = 0} \longrightarrow (52)$$

↳ (cons T, P)

Problems: 1. A binary liquid mixture is in equilibrium with its vapor at a temperature T = 300 K. The liquid mole fraction x_1 of species 1 is 0.4 and the molar Excess Gibbs free energy is 200 J/mol. R = 8.314 J/mol-K, and γ_i denotes the liquid-phase activity coefficient of species i.

If $\ln \gamma_1 = 0.09$, find $\ln \gamma_2$.

Solution: We have,

$$\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \quad [\text{eq}^n\ 51]$$

$$\Rightarrow \frac{200 \text{ J/mol}}{(8.314 \text{ J/mol k})(300 \text{ K})} = 0.4 \times 0.09 + 0.6 \ln \gamma_2$$

$$0.0802 = 0.036 + 0.6 \ln \gamma_2$$

$$\Rightarrow 0.6 \ln \gamma_2 = 0.0442$$

$$\Rightarrow \underline{\underline{\ln \gamma_2 = 0.074}}$$

2. Minimum work (W) required to separate a binary mixture at a temp. T_0 and pressure P_0 is-

$$W = -RT_0\left[y_1 \ln\left(\frac{\hat{f}_1}{f_{pure,1}}\right) + y_2 \ln\left(\frac{\hat{f}_2}{f_{pure,2}}\right)\right]$$

where y_1 and y_2 are mole fractions, $f_{pure,1}$ and $f_{pure,2}$ are fugacities of pure species at T_0 and P_0 and $\hat{f}_1$ and $\hat{f}_2$ are fugacities of species in the mixture at T_0, P_0.

If the mixture is ideal then 'W' is ?

Soln. In case of ideal gas mixture,

$$\hat{f}_1 = y_1 P \quad \text{and} \quad \hat{f}_2 = y_2 P$$

$$\text{and} \quad f_{pure,1} = f_{pure,2} = P$$

Thus,
$$W = -RT_0\left[y_1 \ln\left(\frac{y_1 P}{P}\right) + y_2 \ln\left(\frac{y_2 P}{P}\right)\right]$$

$$W = -RT_0\left[y_1 \ln y_1 + y_2 \ln y_2\right]$$

Problem. The excess Gibbs energy of a binary liquid mixture at T and P is given by-

$$\frac{G^E}{RT} = (-2.6x_1 - 1.8x_2)x_1x_2$$

(a) Find expressions for $\ln\gamma_1$ and $\ln\gamma_2$ at T and P.

(b) Show that these expressions satisfy Gibbs/Duhem equation.

(c) Find $\ln\gamma_1^\infty$ and $\ln\gamma_2^\infty$.

Soln. : Since $\ln\gamma_i$ is a partial property w.r.t. G^E/RT, we can write,

$$\ln\gamma_1 = \frac{G^E}{RT} + x_2\frac{d(G^E/RT)}{dx_1}$$

and, $$\ln\gamma_2 = \frac{G^E}{RT} - x_1\frac{d(G^E/RT)}{dx_1}$$

Now, $$\frac{d}{dx_1}\left(\frac{G^E}{RT}\right) = \frac{d}{dx_1}\left[\underbrace{(-2.6x_1 - 1.8x_2)(x_1x_2)}_{\{-2.6x_1 - 1.8(1-x_1)\}x_1(1-x_1)}\right]$$

$$= (-2.6x_1 - 1.8 + 1.8x_1)(x_1 - x_1^2)$$

$$= -2.6x_1^2 + 2.6x_1^3 - 1.8x_1 + 1.8x_1^2 + 1.8x_1^2 - 1.8x_1^3$$

$$= (0.8x_1^3 + x_1^2 - 1.8x_1)$$

Thus,

$$\frac{d}{dx_1}\left(\frac{G^E}{RT}\right) = \frac{d}{dx_1}\left\{0.8x_1^3 + x_1^2 - 1.8x_1\right\}$$

$$= 0.8(3x_1^2) + 2x_1 - 1.8$$

$$= 2.4x_1^2 + 2x_1 - 1.8$$

Thus,

$$\ln\gamma_1 = (0.8x_1^3 + x_1^2 - 1.8x_1) + (1-x_1)(2.4x_1^2 + 2x_1 - 1.8)$$

$$= (0.8x_1^3 + x_1^2 - 1.8x_1) + 2.4x_1^2 + 2x_1 - 1.8 - 2.4x_1^3 - 2x_1^2 + 1.8x_1$$

$$\boxed{\ln\gamma_1 = -1.6x_1^3 + 1.4x_1^2 + 2x_1 - 1.8}$$

$$\ln\gamma_2 = (0.8x_1^3 + x_1^2 - 1.8x_1) - x_1(2.4x_1^2 + 2x_1 - 1.8)$$

$$= 0.8x_1^3 + x_1^2 - 1.8x_1 - 2.4x_1^3 - 2x_1^2 + 1.8x_1$$

$$\boxed{\ln\gamma_2 = -1.6x_1^3 - x_1^2}$$

For binary mixture, Gibbs/Duhem relation is-

$$x_1 d\ln\gamma_1 + x_2 d\ln\gamma_2 = 0$$

$$\Rightarrow x_1\frac{d\ln\gamma_1}{dx_1} + x_2\frac{d\ln\gamma_2}{dx_1} = 0$$

Thus, $\frac{d\ln\gamma_1}{dx_1} = -1.6(3x_1^2) + 1.4(2x_1) + 2 = -4.8x_1^2 + 2.8x_1 + 2$

$$\frac{d\ln\gamma_2}{dx_1} = \cancel{d} -1.6(3x_1^2) - 2x_1$$

$$= -4.8x_1^2 - 2x_1$$

Now,

$$x_1\left[-4.8x_1^2 + 2.8x_1 + 2\right] + x_2\left[-4.8x_1^2 - 2x_1\right]$$

$$= -4.8x_1^3 + 2.8x_1^2 + 2x_1 + \cancel{4.8x}\,(1-x_1)(-4.8x_1^2 - 2x_1)$$

$$= \cancel{-4.8x_1^3} + \cancel{2.8x_1^2} + \cancel{2x_1} \cancel{-4.8x_1^2} + \cancel{4.8x_1^3} - \cancel{2x_1} + \cancel{2x_1^2}$$

$= 0.$ Thus, satisfied.

$$\ln\gamma_1 = -1.6x_1^3 + 1.4x_1^2 + 2x_1 - 1.8$$

At $x_1 \to 0$

$$\boxed{\ln\gamma_1^\infty = -1.8}$$

$$\ln\gamma_2 = -1.6x_1^3 - x_1^2$$

At $x_2 \to 0$; $x_1 \to 1$

$$\ln\gamma_2^\infty = -1.6 - 1 = -2.6$$

$$\boxed{\ln\gamma_2^\infty = -2.6}$$

(Lecture-25)

Models for γ_i using Excess Gibbs energy

In general G^E/RT is a function of T, P, and composition, but for liquids at low to moderate pressures it is a very weak function of P. Therefore the pressure dependence of activity coefficients is usually neglected. Thus, for data at constant T:

$$\frac{G^E}{RT} = g(x_1, x_2, \ldots, x_N) \qquad (\text{cons}T)$$

For binary systems (species 1 and 2) the function most often represented by an equation is G^E/x_1x_2RT, which may be expressed as a power series in x_1:

$$\frac{G^E}{x_1x_2RT} = a + bx_1 + cx_1^2 + \ldots\ldots \qquad (\text{cons}T)$$

Because $x_2 = 1 - x_1$, mole fraction x_1 serves as the single independent variable.

An equivalent power series with certain advantages is known as the "Redlich/Kister expansion"

$$\frac{G^E}{x_1x_2RT} = A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \ldots\ldots \xrightarrow{} (1)$$

* In application, different truncations of this series are appropriate and in each case specific expressions for $\ln\gamma_1$ and $\ln\gamma_2$ are generated.

Case-I:

When $A = B = C \dots = 0$,

$$\frac{G^E}{RT} = 0 \; ; \; \ln\gamma_1 = 0 \; ; \; \ln\gamma_2 = 0$$

$$\gamma_1 = 1 \quad \& \quad \gamma_2 = 1$$

and the solution is ideal.

Case-II:

If $B = C = \dots = 0$, then

$$\boxed{\frac{G^E}{x_1 x_2 RT} = A} \longrightarrow (2)$$

A → Dimensionless

→ constant for a given temp.

↓

Two-suffix Margules equation

Now, $$\ln\gamma_1 = \frac{\partial}{\partial n_1}\left(\frac{n G^E}{RT}\right)$$

$$= \frac{\partial}{\partial n_1}\left[(n_1+n_2) A x_1 x_2\right]$$

$$= \frac{\partial}{\partial n_1}\left[A(n_1+n_2)\frac{n_1}{(n_1+n_2)} \cdot \frac{n_2}{(n_1+n_2)}\right]$$

$$= A \frac{\partial}{\partial n_1}\left[\frac{n_1 n_2}{n_1+n_2}\right] = A\left[\frac{(n_1+n_2)n_2 - n_1 n_2(1)}{(n_1+n_2)^2}\right]$$

$$= A\left[\frac{n_1 n_2 + n_2^2 - n_1 n_2}{(n_1+n_2)^2}\right] = \frac{A\, n_2^2}{(n_1+n_2)^2}$$

$$\boxed{\ln\gamma_1 = A x_2^2} \longrightarrow (3)$$

Similarly, $$\boxed{\ln\gamma_2 = A x_1^2} \longrightarrow (4)$$

Infinite-dilution values of the activity coefficients:

$$\ln\gamma_1^{\infty} = \lim_{x_1\to 0} \ln\gamma_1 = \lim_{x_2\to 1} A x_2^2 = A$$

$$\ln\gamma_2^{\infty} = \lim_{x_2\to 0} \ln\gamma_2 = \lim_{x_1\to 1} A x_1^2 = A$$

i.e. $\boxed{\ln\gamma_1^{\infty} = \ln\gamma_2^{\infty} = A} \longrightarrow (5)$

~~Problems~~:

If $G^E = A x_1 x_2$
$\hookrightarrow$ (unit of energy)

Then, $\ln\gamma_1 = \frac{\partial}{\partial n_1}\left[\frac{nG^E}{RT}\right] = \frac{\partial}{\partial n_1}\left[\frac{nAx_1x_2}{RT}\right]$

$$= \frac{A}{RT}\frac{\partial}{\partial n_1}\left[n x_1 x_2\right]$$

$$\boxed{\ln\gamma_1 = \frac{A}{RT} x_2^2} \longrightarrow (6)$$

and, $\boxed{\ln\gamma_2 = \frac{A}{RT} x_1^2} \longrightarrow (7)$

problems: consider a binary mixture of cyclohexane (a) and dodecane (b) at 39.33°c. Activity coefficients at infinite dilution have been reported to be:

$$\gamma_a^\infty = 0.88 \; ; \quad \gamma_b^\infty = 0.86$$

Use these data to estimate the value of the two-suffix Margules parameter A in terms of J/mol.

solution: we have,

$$\ln \gamma_a = \frac{A}{RT} x_b^2$$

At infinite dilution of 'a', the mole fraction of 'b' goes to 1: thus,

$$\ln \gamma_a^\infty = \frac{A}{RT}$$

$$\Rightarrow \frac{A}{RT} = \ln(0.88) = -0.13$$

$$\Rightarrow A = (-0.13)(8.314 \tfrac{J}{mol.k})(273.15 + 39.33)k$$

$$\therefore \underline{A = -338 \text{ J/mol}}$$

Again,

$$\ln \gamma_b = \frac{A}{RT} x_a^2$$

$$\Rightarrow \ln \gamma_b^\infty = \frac{A}{RT}$$

$$\Rightarrow \frac{A}{RT} = \ln(0.86) = -0.15$$

$$\therefore \underline{A = -390 \text{ J/mol}}$$

Thus, $A_{average} = \frac{-338 - 390}{2} = \underline{\underline{-364 \text{ J/mol}}}$

Case-III: If $C = \cdots = 0$, then (Lecture-46)

$$\frac{G^E}{x_1 x_2 RT} = A + B(x_1 - x_2) = A + B(2x_1 - 1) \longrightarrow (8)$$

If we define $A + B = A_{21}$ and $A - B = A_{12}$,

then, $$\frac{G^E}{x_1 x_2 RT} = A_{21} x_1 + A_{12} x_2 \longrightarrow (9)$$

Eqn. (8) & Eqn. (9) are three-suffix Margules equation.

$$\ln \gamma_1 = \left[\frac{\partial (nG^E/RT)}{\partial n_1}\right]_{T,P,n_2}$$

$$= \frac{\partial}{\partial n_1}\left[(n_1+n_2)\, x_1 x_2 (A_{21}x_1 + A_{12}x_2)\right]$$

$$= \frac{\partial}{\partial n_1}\left[\cancel{(n_1+n_2)}\frac{n_1}{\cancel{(n_1+n_2)}} \cdot \frac{n_2}{(n_1+n_2)}\left\{A_{21}\frac{n_1}{n_1+n_2} + A_{12}\frac{n_2}{n_1+n_2}\right\}\right]$$

$$= \frac{\partial}{\partial n_1}\left[\frac{n_1 n_2}{(n_1+n_2)}\left\{\frac{A_{21}n_1}{n_1+n_2} + \frac{A_{12}n_2}{n_1+n_2}\right\}\right]$$

$$= \frac{\partial}{\partial n_1}\left[(A_{21}n_1 + A_{12}n_2)\frac{n_1 n_2}{(n_1+n_2)^2}\right]$$

$$= (A_{21}n_1 + A_{12}n_2)\frac{\partial}{\partial n_1}\left[\frac{n_1 n_2}{(n_1+n_2)^2}\right] + \frac{n_1 n_2}{(n_1+n_2)^2}\frac{\partial}{\partial n_1}\left[A_{21}n_1 + A_{12}n_2\right]$$

$$= (A_{21}n_1 + A_{12}n_2)\left\{\frac{(n_1+n_2)^2 n_2 - n_1 n_2 (2(n_1+n_2))}{(n_1+n_2)^4}\right\} + \frac{n_1 n_2}{(n_1+n_2)^2} A_{21}$$

$$= (A_{21}n_1 + A_{12}n_2)\left\{\frac{(n_1+n_2)^2 n_2}{(n_1+n_2)^4} - \frac{2n_1n_2(n_1+n_2)}{(n_1+n_2)^4}\right\} + \frac{n_1n_2A_{21}}{(n_1+n_2)^2}$$

$$= (A_{21}n_1 + A_{12}n_2)\left[\frac{n_2}{(n_1+n_2)^2} - \frac{2n_1n_2}{(n_1+n_2)^3}\right] + \frac{n_1n_2}{(n_1+n_2)^2}A_{21}$$

$$= (A_{21}\cancel{n}x_1 + A_{12}\cancel{n}x_2)\left[\frac{x_2}{\cancel{n}} - \frac{2x_1x_2}{\cancel{n}}\right] + x_1x_2A_{21}$$

$$= (A_{21}x_1 + A_{12}x_2)(x_2 - 2x_1x_2) + x_1x_2A_{21}$$

$$= A_{21}x_1x_2 - 2A_{21}x_1^2x_2 + A_{12}x_2^2 - 2A_{12}x_1x_2^2 + x_1x_2A_{21}$$

$$= 2A_{21}x_1x_2 + A_{12}x_2^2 - 2A_{12}x_1x_2^2 - 2A_{21}x_1^2x_2$$

$$= x_2\left[2A_{21}x_1 + A_{12}x_2 - 2A_{12}x_1x_2 - 2A_{21}x_1^2\right]$$

= ~~$x_2\left[2A_{21}x_1(1-x_1) + A_{12}x_2(1-2A_{12}x_1)\right]$~~

= ~~$x_2\left[A_{21}x_1 + A_{21}x_1 + A_{12}x_2 - 2A_{12}x_1x_2 - 2A_{21}x_1^2\right]$~~

= ~~$x_2\left[A_{21}x_1(1-2x_1) + A_{12}x_2(1-2x_1) + A_{21}x_1\right]$~~

= ~~$x_2\left[(A_{21}x_1 + A_{12}x_2)(1-2x_1) + A_{21}x_1\right]$~~

~~Replacing x_2 by $1-x_1$,~~

= ~~$(1-x_1)\left[\{A_{21}x_1 + A_{12}(1-x_1)\}(1-2x_1) + A_{21}x_1\right]$~~

$$= x_2\left[2A_{21}x_1(1-x_1) + A_{12}x_2 - 2A_{12}x_1x_2\right]$$

$$= x_2\left[2A_{21}x_1x_2 + A_{12}x_2 - 2A_{12}x_1x_2\right]$$

$$= x_2^2\left[A_{12} + 2A_{21}x_1 - 2A_{12}x_1\right]$$

$$= x_2^2\left[A_{12} + 2(A_{21} - A_{12})x_1\right]$$

Thus, $\boxed{\ln\gamma_1 = x_2^2\left[A_{12} + 2(A_{21}-A_{12})x_1\right]} \rightarrow (10)$

Similarly, $\boxed{\ln\gamma_2 = x_1^2\left[A_{21} + 2(A_{12}-A_{21})x_2\right]} \rightarrow (11)$

For the limiting conditions of infinite dilution,

$\boxed{\ln\gamma_1^\infty = A_{12}}$ and $\boxed{\ln\gamma_2^\infty = A_{21}}$

Another well-known equation results when the reciprocal expression x_1x_2RT/G^E is expressed as a linear function of x_1:

$$\frac{x_1x_2}{G^E/RT} = \cancel{A'(x} \; A' + B'(x_1 - x_2) = A' + B'(2x_1 - 1)$$

$$= A'(x_1 + x_2) + B'(x_1 - x_2)$$

$$= (A' + B')x_1 + (A' - B')x_2$$

when new parameters are defined by the equation,

$$A' + B' = \frac{1}{A'_{21}} \quad \text{and} \quad A' - B' = \frac{1}{A'_{12}}$$

then,

$$\frac{x_1 x_2}{G^E/RT} = \frac{x_1}{A'_{21}} + \frac{x_2}{A'_{12}} = \frac{A'_{12} x_1 + A'_{21} x_2}{A'_{12} A'_{21}}$$

$$\boxed{\frac{G^E}{x_1 x_2 RT} = \frac{A'_{12} A'_{21}}{A'_{12} x_1 + A'_{21} x_2}} \longrightarrow (12)$$

The activity coefficients implied by this equation are:

$$\boxed{\ln \gamma_1 = \frac{A'_{12}}{\left(1 + \frac{A'_{12} x_1}{A'_{21} x_2}\right)^2}} \longrightarrow (13)$$

$$\boxed{\ln \gamma_2 = \frac{A'_{21}}{\left(1 + \frac{A'_{21} x_2}{A'_{12} x_1}\right)^2}} \longrightarrow (14)$$

These are known as <u>Van Laar equations</u>.

when $x_1 = 0$; $\ln \gamma_1^{\infty} = A'_{12}$

& $x_2 = 0$; $\ln \gamma_2^{\infty} = A'_{21}$

* Wilson equation (two parameters for a binary system)

* NRTL equation (three parameters for a binary system)
  ↳ (Non-random two-Liquid model)

* UNIQUAC ~~equation~~ Model
  ↳ Universal quasichemical

* UNIFAC Model
  ↳ Uniquac Functional-group activity coefficients.

The molecular basis for ideality is that the forces between the molecules of both components of the mixture should be identical. i.e. all interactions between like and unlike molecules, should be same.

Consider two components A and B. In pure components, the intermolecular attractive interactions will be of types A-A and B-B, whereas in the binary solutions in addition to these two interactions, A-B type of interactions will also be present. If the intermolecular attractive forces between the A-A and B-B are nearly equal to those between A-B, this leads to the formation of ideal solution. A perfectly ideal solution is rare but some solutions are nearly ideal in behaviour.

Ideal-solution behaviour is often approximated by liquid phase wherein the molecular species are not too different in size and are of the same chemical nature.

Thus, a mixture of isomers, such as ortho-, meta-, and para-xylene, conforms very closely to ideal solution behaviour.

So do mixtures of adjacent members of a homologous series, for example -

n-hexane/n-heptane
ethanol/propanol
benzene/toluene.

other examples:

acetone/acetonitrile
acetonitrile/nitromethane.