Chapter 9 Ideal and Real Solutions

Ideal solution

Interaction between like and unlike molecules are the same.

A-A = A-B = B-B

Relation between partial pressure (gas phase) and solution concentration is described by Raoult's law for each component.

Real solution:

Activity (a) explains the deviation from ideal dilute solution.

9.1 Defining the Ideal Solution

Ideal gas = No interaction between the molecules

Liquid does have attractive interactions which are greatly varied.

Normal bp: Helium = 4.2K (Poor attraction)
Hafnium = 5400K (Great attraction)

Rault's law (Definition of ideal solution)

$$P_i = x_i P_i^* \qquad i=1,2 \qquad (9.1)$$

P_i = Partial pressure
P_i^* = Vapor pressure (A function of only T!!!)
x_i = Mole fraction of component i in liquid phase.

▶Partial pressure is proportional to the vapor pressure with the proportionality constant, mole fraction in the liquid.

▶Raoult's law holds for $0 \le x_i \le 1$ each substance.
In binary solution larger x_i is called solvent, smaller x_i solute.

▶Few solutions satisfy the Rault's law where A-A, A-B, and B-B have the same interactions. Benzene-toluene solution satisfies this since they have similar size, shape, and property. In real solution, solvent obeys Raoult's law since the solute is highly dilute.

Derivation of Raoult's law (Example 9.1)

Gas phase in equilibrium with solution, and its composition is determined by the dynamic balance between the gas and solution. (Figure 9.1)

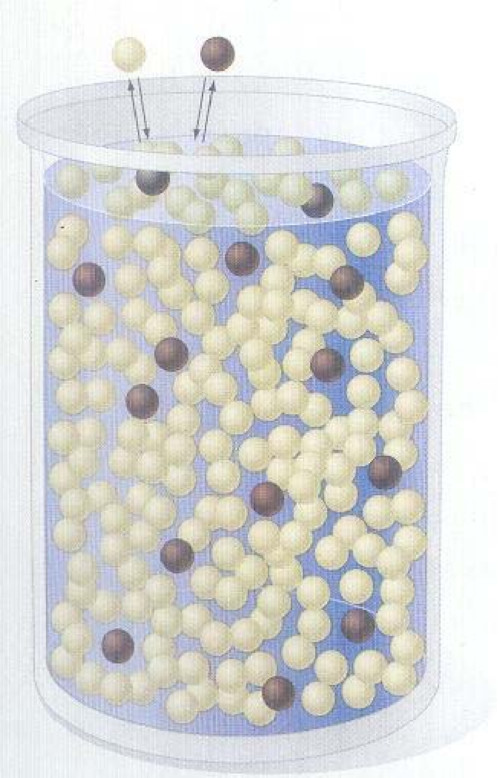


FIGURE 9.1

Schematic model of a solution. The white and black spheres represent solvent and solute molecules, respectively.

Figure 9.1 here

Example 9.1 here

EXAMPLE PROBLEM 9.1

Assume that the rates of evaporation, R_{evap}, and condensation, R_{cond}, of the solvent from the surface of pure liquid solvent are given by the expressions

$$R_{evap} = Ak_{evap}$$

$$R_{cond} = Ak_{cond}P^{*}_{solvent}$$

where A is the surface area of the liquid and k_{evap} and k_{cond} are the rate constants for evaporation and condensation, respectively. Derive a relationship between the vapor pressure of the solvent above a solution and above the pure solvent.

Solution

For the pure solvent, the equilibrium vapor pressure is found by setting the rates of evaporation and condensation equal:

$$R_{evap} = R_{cond}$$

$$Ak_{evap} = Ak_{cond}P^{*}_{solvent}$$

$$P^{*}_{solvent} = \frac{k_{evap}}{k_{cond}}$$

Next, consider the ideal solution. In this case, the rate of evaporation is reduced by the factor $x_{solvent}$.

$$R_{evap} = Ak_{evap}x_{solvent}$$

$$R_{cond} = Ak_{cond}P_{solvent}$$

and at equilibrium

$$R_{evap} = R_{cond}$$

$$Ak_{evap}x_{solvent} = Ak_{cond}P_{solvent}$$

$$P_{solvent} = \frac{k_{evap}}{k_{cond}}x_{solvent} = P^{*}_{solvent}x_{solvent}$$

The derived relationship is Raoult's law.

9.2 The Chemical Potential of a Component in the Gas and Solution Phases

At equilibrium, the chemical potential of component, i in the two phase is the same.

$$\mu_i^{solution} = \mu_i^{vapor} \qquad (9.2)$$

Chemical potential of component i in gas phase depends on its partial pressure, P_i, by (Section 6.3)

$$\mu_i^{vapor} = \mu_i^o + RT\ln\frac{P_i}{P^o} \qquad (9.3)$$

μ_i^o = pure i in the gas phase at the standard state pressure $P^o = 1$ bar (See eq 3).

@ equilibrium $\mu_i^{solution} = \mu_i^{vapor}$, then Eq (9.3) becomes:

$$\mu_i^{solution} = \mu_i^o + RT\ln\frac{P_i}{P^o} \qquad (9.4)$$

For pure liquid i in equilibrium with its vapor, $\mu_i^*(\text{liquid})=\mu_i^*(\text{vapor})=\mu_i^*$. Therefore, the chemical potential of the pure liquid is given by

$$\mu_i^* = \mu_i^o + RT\ln\frac{P_i^*}{P^o} \qquad (9.5)$$

If vapor pressure is measured, chemical potential is calculated.

(9.4) – (9.5) gives

$$\mu_i^{solution} = \mu_i^* + RT\ln\frac{P_i}{P_i^*} \qquad (9.6)$$

For an ideal solution, $P_i = x_i P_i^*$ (9.1)

(9.1)→(9.6)

$$\mu_i^{solution} = \mu_i^* + RT\ln x_i \qquad (9.7)$$

→Central equation for ideal solutions.

(See this is the same with Eq 6.44)

Chemical potential of component i in ideal solution – chemical potential of the pure i in vapor-liquid equil – mole fraction in the solution. This equation is most useful in describing the thermodynamics of solutions in which all components are volatile and miscible in all proportions. Recall the following equations.

$$\triangle G_{mixing} = nRT\sum_i x_i \ln x_i$$

$$\triangle S_{mixing} = -\left(\frac{\partial \triangle G_{mixing}}{\partial T}\right)_{P,n_1,n_2} = -nR\sum_i x_i \ln x_i$$

$$\triangle V_{mixing} = \left(\frac{\partial \triangle G_{mixing}}{\partial P}\right)_{T,n_1,n_2} = 0 \qquad \text{and}$$

$$\triangle H_{mixing} = \triangle G_{mixing} + T\triangle S_{mixing} = nRT\sum_i x_i \ln x_i - T\left(nR\sum_i x_i \ln x_i\right) = 0$$

9.3 Applying the Ideal Solution Model to Binary Solution

Recall the following equations.

For binary solution;

$$P_1 = x_1 P_1^*$$

$$P_2 = x_2 P_2^*$$

P_1, P_2 = Partial pressures of 1 and 2

P_1^*, P_2^* = Vapor pressures of 1 and 2

x_1, x_2 = Mole fractions of 1 and 2 in liquid

Dalton's law:

$$P_{total} = P_1 + P_2 = x_1P_1^* + (1-x_1)P_2^* = P_2^* + (P_1^*-P_2^*)x_1 \qquad (9.9)$$

Figure 9.2 Pressure vs liquid composition for benzene-dichloroethane binary solution (Note the vapor pressure at x_i=1).

→ Small deviation from Raoult's law is seen.

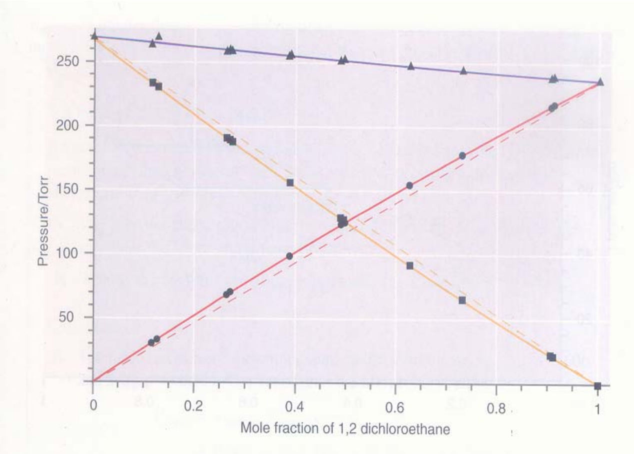


FIGURE 9.2

The vapor pressure of benzene (yellow), 1,2 dichloroethane (red), and the total vapor pressure (blue) above the solution is shown as a function of *x* 1,2 *dichloroethane*. The symbols are data points [J. v. Zawidski, *Zeitschrift für Physikalische Chemie*, 35 (1900) 129]. The solid curves are polynomial fits to the data. The dashed lines are calculated using Raoult's law.

Note: How are the lines drawn?

The mole fraction of each component in the gas phase (y_i) can also be calculated.

$$y_1 = \frac{P_1}{P_{total}} = \frac{x_1P_1^*}{P_2^* + (P_1^* - P_2^*)x_1} \qquad (9.10)$$

(P_{total}=P1+P2=$P_1^*x_1$ +$P_2^*x_2$ is being used.)

Rearrangement gives for x_1:

$$x_1 = \frac{y_1P_2^*}{P_1^* + (P_2^* - P_1^*)y_1} \qquad (9.11)$$

(9.11) → $P_{total} = P_2^* + (P_1^* - P_2^*)\,x_1$

$$P_{total} = \frac{P_1^* P_2^*}{P_1^* + (P_2^* - P_1^*)y_1} \qquad (9.12)$$

Rearrangement of (9.12) gives y_1 in terms of vapor pressures and the total pressure:

$$y_1 = \frac{P_1^* P_{total} - P_1^* P_2^*}{P_{total}(P_1^* - P_2^*)} \qquad (9.13)$$

The variation of total pressure (P_{total}) with x_1 is not the same with y_1 (See Figure 9.3). Q: How are the two equilibrium lines drawn?

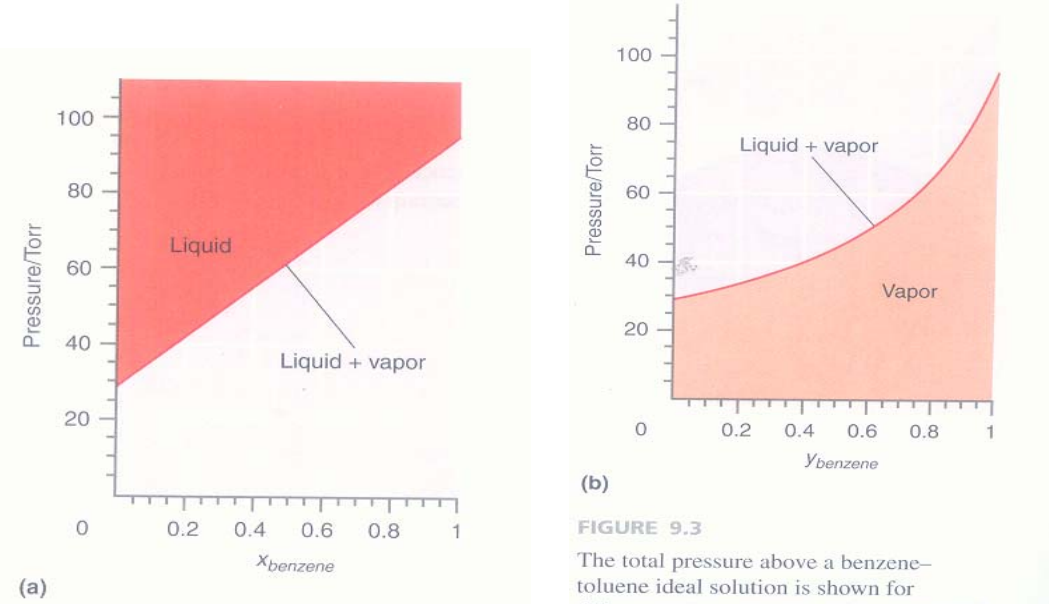


FIGURE 9.3

The total pressure above a benzene–toluene ideal solution is shown for different values of **(a)** the mole fraction of benzene in the solution and **(b)** the mole fraction of benzene in the vapor. Points on the curves correspond to vapor–liquid coexistence. Only the curves and the shaded areas are of physical significance as explained in text.

Determination of x_i-y_i (n_{liquid}-n_{vapor})@ given total pressure

Define an average composition (Z) in the whole system as:

$$Z_{benzene} = \frac{n^{liquid}_{benzene} + n^{vapor}_{benzene}}{\qquad} = \frac{n_{benzene}}{\qquad}$$

$$\overline{n_{toluene}^{liquid} + n_{toluene}^{vapor} + n_{benzene}^{liquid} + n_{benzene}^{vapor}} \qquad \overline{n_{total}}$$

Note that in liquid $Z_{benzene} = x_{benzene}$, in gas $Z_{benzene} = y_{benzene}$

Usefuness of P-Z diagram:

Consider a constant temperature process in which the pressure decreases along a → d (Figure 9.4: P-Z phase diagram for benzene-toluene solution)

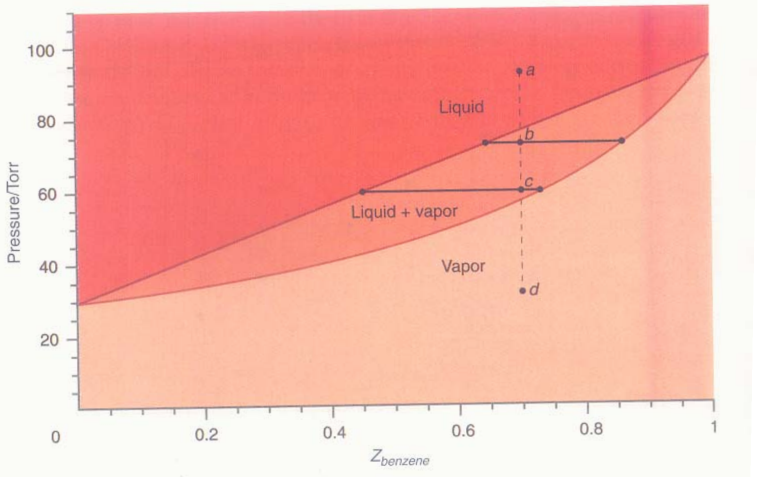


FIGURE 9.4

A P–Z phase diagram is shown for a benzene–toluene ideal solution. The upper curve shows the vapor pressure as a function of $x_{benzene}$. The lower curve shows the vapor pressure as a function of $y_{benzene}$. Above the two curves, the system is totally in the liquid phase, and below the two curves, the system is totally in the vapor phase. The area intermediate between the two curves shows the liquid–vapor coexistence region. The horizontal lines connecting the curves are called tie lines.

Q: How are the two equilibrium lines drawn?

In the Figure,

Composition of a = $x_{benzene}$

Composition of d = $y_{benzene}$

Upper curve: Vapor pressure vs $x_{benzene}$,

Lower curve: Vapor pressure vs $y_{benzene}$

Note for all pressures $y_{benzene} > x_{benzene}$

→ Benzene (more volatile) is enriched in vapor phase.

See two tie lines connecting $x_{benzene}$ and $y_{benzene}$ at constant P.

The relative amount of moles in two phases (See Figure 9.5):

$lb = Z_B - x_B = n_B^{tot}/n^{tot} - n_B^{liq}/n_{liq}^{tot}$ (15)

$bv = y_B - z_B = n_B^{vapor}/n_{vapor}^{tot} - n_B^{tot}/n^{tot}$ (16)

Multiply (15) by n_{liq}^{tot}, (16) by n_{vapor}^{tot} to obtain

$$lb\, n_{liq}^{tot} - bv\, n_{vapor}^{tot} = \frac{n_B^{tot}}{n^{tot}}(n_{liq}^{tot} + n_{vapor}^{tot}) - (n_B^{liq} + n_B^{vapor}) = n_B^{tot} - n_B^{tot} = 0$$

We conclude that

$$\frac{n_{liq}^{tot}}{n_{vap}^{tot}} = \frac{bv}{lb} \qquad (9.17)$$

(Lever rule) or

$$n_{liq}^{tot}(Z_B - x_B) = n_{vapor}^{tot}(y_B - Z_B) \qquad (9.18)$$

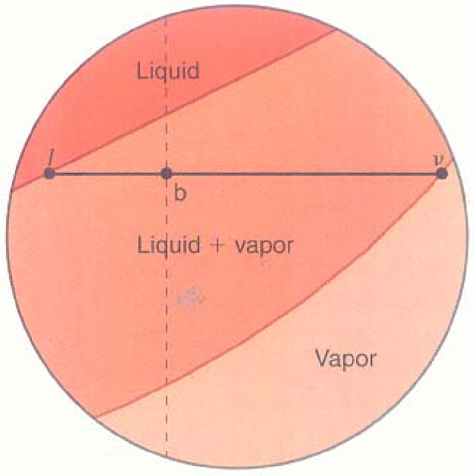


FIGURE 9.5

An enlarged region of the two-phase coexistence region of Figure 9.4 is shown. The vertical line through point *b* indicates a transition at constant system composition. The lever rule (see text) is used to determine what fraction of the system is in the liquid and vapor phases.

Figure 9.5

9.4 The T-Composition Diagram and Fractional Distillation

Figure 9.6: The boiling T vs Composition for benzene-toluene binary solution

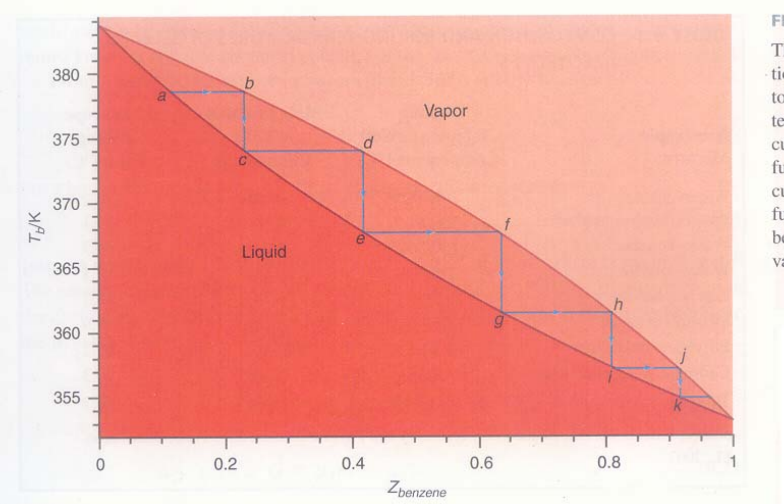


FIGURE 9.6

The boiling temperature of an ideal solution of the components benzene and toluene is plotted versus the average system composition, $Z_{benzene}$. The upper red curve shows the boiling temperature as a function of $y_{benzene}$, and the lower red curve shows the boiling temperature as a function of $x_{benzene}$. The area intermediate between the two curves shows the vapor–liquid coexistence region.

Figure 9.7: Fractional distillation column

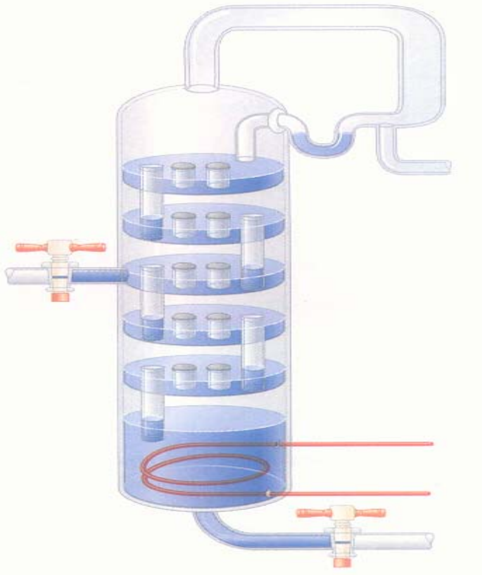


FIGURE 9.7

Schematic of a fractional distillation column. The solution to be separated into its components is introduced at the bottom of the column. The resistive heater provides the energy needed to vaporize the liquid. It can be assumed that the liquid and vapor are at equilibrium at each level of the column. The equilibrium temperature decreases from the bottom to the top of the column.

Note 1: Reboiler, condenser, and downcomers in Fig 9.7.
Note 2: Both Figures show 5.5 states where x_{BZ} changes from ca 0.1 to 0.9 with the given theoretical plate number. See many more plates are necessary to purify further since the two lines are close at the far right concentration.

Distillation is a major separation process of crude oil into gasoline, kerosene, diesel fuel...... naphtha. Naphtha is catalytically cracked under high pressure and high temperature into small molecules such as ethylene, propylene, BTX....→ Various monomers.

Fractional distillation is also used for real solution unless non-ideality is strong enough. If interaction between A-B > A-A and B-B, boiling point goes through a maximum at a specific concentration (maximum bp azeotrope). (See the strong intermolecular H bond of acetone-chloroform in Figure 9.8).

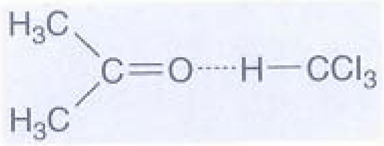


FIGURE 9.8

Hydrogen bond formation between acetone and chloroform leads to the formation of a maximum boiling azeotrope.

For this system, at maximum bp liquid and vapor composition lines are tangent to each other. → No separation by distillation is possible. (See Figure 9.9a)

On the other hand when interaction between A-B < A-A and B-B, boiling point goes through a minimum at a specific concentration (minimum bp azeotrope). (See Figure 9.9b)

See composition and bp of various azeotropes in Table 9.1.

Note the azeotropic composition is a function of total pressure (See Figure 9.10) → The mixture is first distilled at atmosphere, and the distillates are distilled under reduced pressure to avoid the azeotrope.

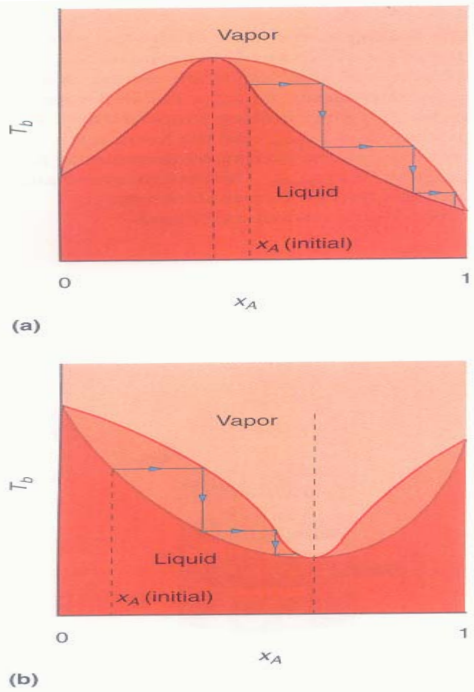


FIGURE 9.9

A boiling point diagram is shown for **(a)** maximum and **(b)** minimum boiling point azeotropes. The dashed lines indicate the initial composition of the solution and the composition of the azeotrope. The sequence of horizontal segments with arrows corresponds to successively higher (cooler) portions of the column.

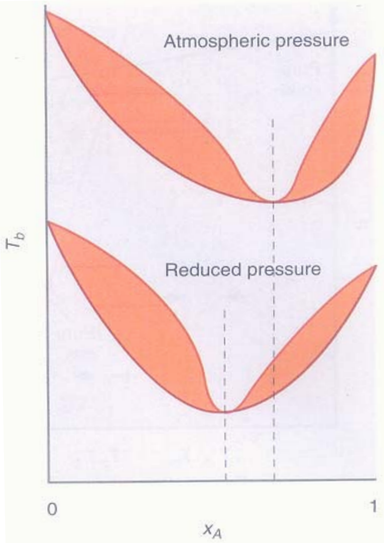


FIGURE 9.10

Because the azeotropic composition depends on the total pressure, pure B can be recovered from the A–B mixture by first distilling the mixture under atmospheric pressure and, subsequently, under a reduced pressure. Note that the boiling temperature is lowered as the pressure is reduced.

9.5 Gibbs-Duhem Equation

(Important in Polymer Physics)

From Eq 6.38

$$dG = -SdT + VdP + \sum_i \mu_i dn_i \qquad (9.19)$$

For binary solution at constant T and P,

$$dG = \mu_1 dn_1 + \mu_2 dn_2 \qquad (9.20)$$

Starting with infinitesimally small amount of a solution at constant T, P and composition, the amount of solution is gradually increased.
→ No change in chemical potential [$\mu_i = \partial G/\partial n_i)_{T,P,nj}$].

So, μ_i can be taken out of the integral:

$$\int_0^G dG' = \mu_1 \int_0^{n_1} dn'_1 + \mu_2 \int_0^{n_2} dn'_2 \qquad \text{or}$$

$$G = \mu_1 n_1 + \mu_2 n_2 \qquad (9.21)$$

Total differentiation of 9.21 gives:

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + n_1 d\mu_1 + n_2 d\mu_2 \qquad (9.22)$$

Letting 9.20 = 9.22 gives the Gibbs-Duhem Eq for binary solution as:

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad \text{or} \quad x_1 d\mu_1 + x_2 d\mu_2 = 0 \qquad (9.23)$$

→The chemical potentials of the components in a binary solution are not independent.

The change in chemical potential of the second component is determined by

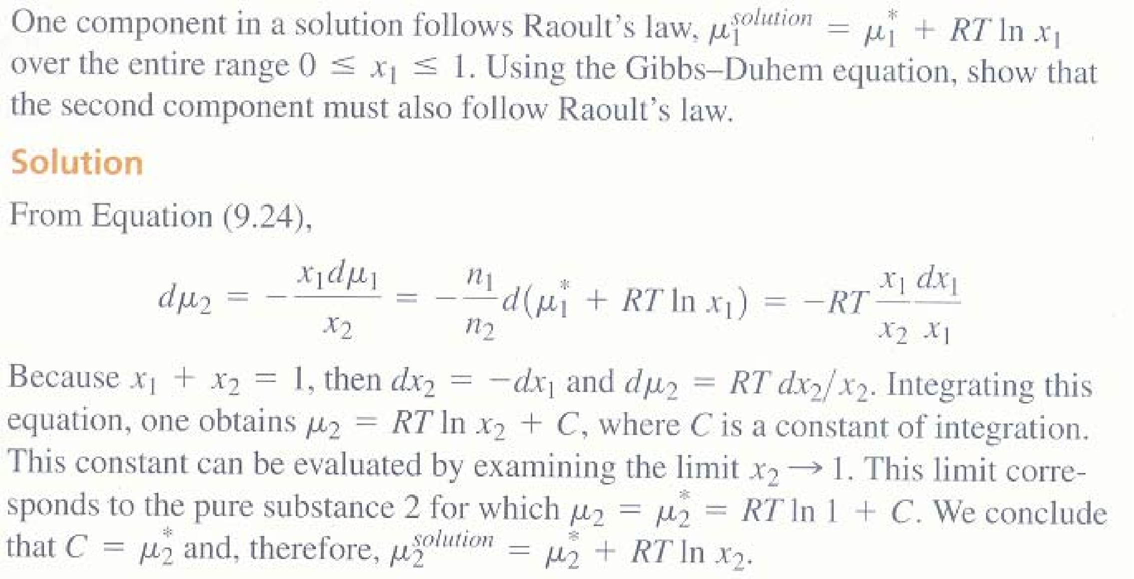
$$d\mu_2 = -\frac{n_1 d\mu_1}{n_2} \qquad (9.24)$$

Recall

$$\mu_i^* = \mu_i^o + RT\ln\frac{P_i^*}{P^o} \quad (9.5) \qquad \mu_i^{solution} = \mu_i^* + RT\ln\frac{P_i}{P_i^*} \quad (9.6)$$

Only with measurable vapor pressure, chemical potential is directly measured (9.5). Chemical potential of nonvolaile solute in volatile solvent (ex. sucrose or NaCl in water) can be calculate by Gibbs-Duhem eq (24).

EXAMPLE PROBLEM 9.5



One component in a solution follows Raoult's law, $\mu_1^{solution} = \mu_1^* + RT\ln x_1$ over the entire range $0 \le x_1 \le 1$. Using the Gibbs–Duhem equation, show that the second component must also follow Raoult's law.

Solution

From Equation (9.24),

$$d\mu_2 = -\frac{x_1 d\mu_1}{x_2} = -\frac{n_1}{n_2}d(\mu_1^* + RT\ln x_1) = -RT\frac{x_1}{x_2}\frac{dx_1}{x_1}$$

Because $x_1 + x_2 = 1$, then $dx_2 = -dx_1$ and $d\mu_2 = RT\,dx_2/x_2$. Integrating this equation, one obtains $\mu_2 = RT\ln x_2 + C$, where C is a constant of integration. This constant can be evaluated by examining the limit $x_2 \rightarrow 1$. This limit corresponds to the pure substance 2 for which $\mu_2 = \mu_2^* = RT\ln 1 + C$. We conclude that $C = \mu_2^*$ and, therefore, $\mu_2^{solution} = \mu_2^* + RT\ln x_2$.

Partial molar property of mixture ($\overline{M}_i$)

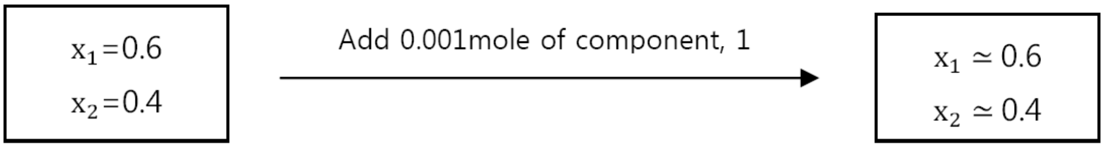
Partial molar volume of binary mixture for example.

Molar volume of the mixture, $V = x_1\overline{V}_1 + x_2\overline{V}_2$:

$\overline{V}_i$ = Partial molar volume of component i = f(x_i) defined by

$$\overline{V}_1 = \left.\frac{\partial V}{\partial n_1}\right)_{T_1,P_1,n_2}$$

Significance of partial molar volume

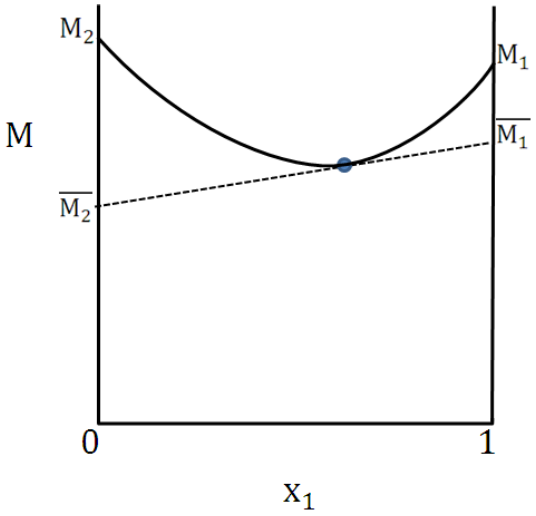


Volume= 1 L (Liquid) Volume = 1.0015 L

$$\overline{V}_1 = \left.\frac{\partial V}{\partial n_1}\right)_{T_1 P_1 n_2} \simeq \frac{(1.0015-1.0000)\text{L}}{0.001\ \text{mole}} = 1.5\ \frac{\text{L}}{\text{mole}}$$

Same is applied for other extensive properties as $\overline{U}$, $\overline{H}$, $\overline{S}$, $\overline{G}$.

Graphical representation of partial molar properties



$M = x_1\overline{M}_1 + x_2\overline{M}_2$ (1) (State function)

$\rightarrow dM = x_1 d\overline{M}_1 + \overline{M}_1 dx_1 + x_2 d\overline{M}_2 + \overline{M}_2 dx_2$

But,

$x_1 d\overline{M}_1 + x_2 d\overline{M}_2 = 0$ @const T & P (Gibbs-Duhem eq)

Then,

$dM = \overline{M}_1 dx_1 + \overline{M}_2 dx_2$ (2)

But,

$x_1 + x_2 = 1 \rightarrow dx_2 = -dx_1 \rightarrow (2)$

Then,

$\frac{dM}{dx_1} = \overline{M}_1 - \overline{M}_2$ (3)

From (1),

$\overline{M}_2 = \frac{M - x_1\overline{M}_1}{x_2} \rightarrow (3)$

$$\frac{dM}{dx_1} = \overline{M_1} - \frac{M - x_1\overline{M_1}}{x_2}$$

Multiply by x_2

$$x_2\frac{dM}{dx_1} = x_2\overline{M_1} - M + x_1\overline{M_1}$$

$$M + x_2\frac{dM}{dx_1} = (x_1 + x_2)\,\overline{M_1} = \overline{M_1}$$

i.e.

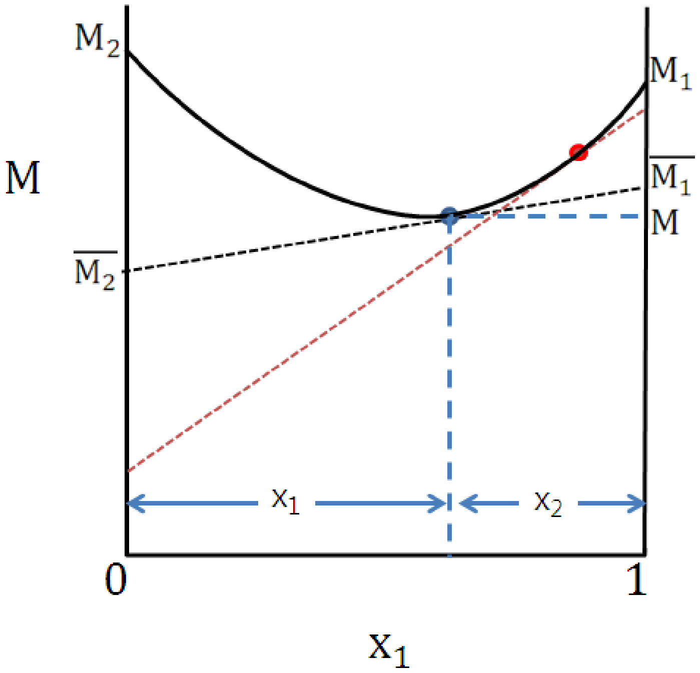
$$\overline{M_1} = M + x_2\frac{dM}{dx_1} \qquad (4)$$

Likewise,

$$\overline{M_2} = M - x_1\frac{dM}{dx_1}$$

Rearranging (4)

$$\frac{dM}{dx_1} = \frac{\overline{M_1} - M}{x_2}$$ (Extrapolation to x_1=1 should correspond to the $\overline{M_1}$)



$$\text{Slope} = \frac{\overline{M_1} - M}{x_2}$$

M=Molar property of mixture (mol/L),

$\overline{M_1}$ =Partial molar property of component 1.

Note: 1) $\overline{M_1}$ is the partial molar property of component 1. ($\overline{M_2}$ for 2)

2) Partial molar properties are tangents to the M curve at a specific composition.

3) At higher x_1, higher $\overline{M_1}$ and much lower $\overline{M_2}$ are obtained (Red line)

→ Partial molar property generally depends on the composition.

9.6 Colligative Properties

Properties depending only on the solute concentration, not on the nature (type, molecular weight of polymer homologue) of solute are called colligative property.
Examples: bp elevation, fp depression, osmotic pressure

We have seen that the vapor pressure of pure solvent decreases with the addition of solute (Raoult's law: Figure 9.1).

▶Chemical potential of solid does not change with the addition of solute since they are crystallized separately.
▶Chemical potential of gas (solvent) does not change with the addition of solute in solvent.
▶Only the liquid (solvent) chemical potential is affected by the formation of solution (by adding solute) following Figure 9.11a (See Eq 9.7, also given in Ex 9.5).

$$\rightarrow \mu_i^{solution} = \mu_i^* + RT\ln x_i \qquad (9.7)$$

See the same information in P-T diagram in Figure 9.11b.
Because the vapor pressure is lowered with the addition of solute (though nonvolatile) (EX 9.1, or Raoult law), liquid-gas coexistence curve intersects solid-gas coexistence curve at lower temperature than the pure solvent defining the triple point which is the origin of solid-liquid coexistence. That is, the solid-liquid coexistence (melting transition) shifts to lower temperature through the dissolution of nonvolatile solute. See the decrease of normal Tm from the Figure.

The bp elevation and fp depression effects depend only on the solute concentration, and not on the identity of the solute.

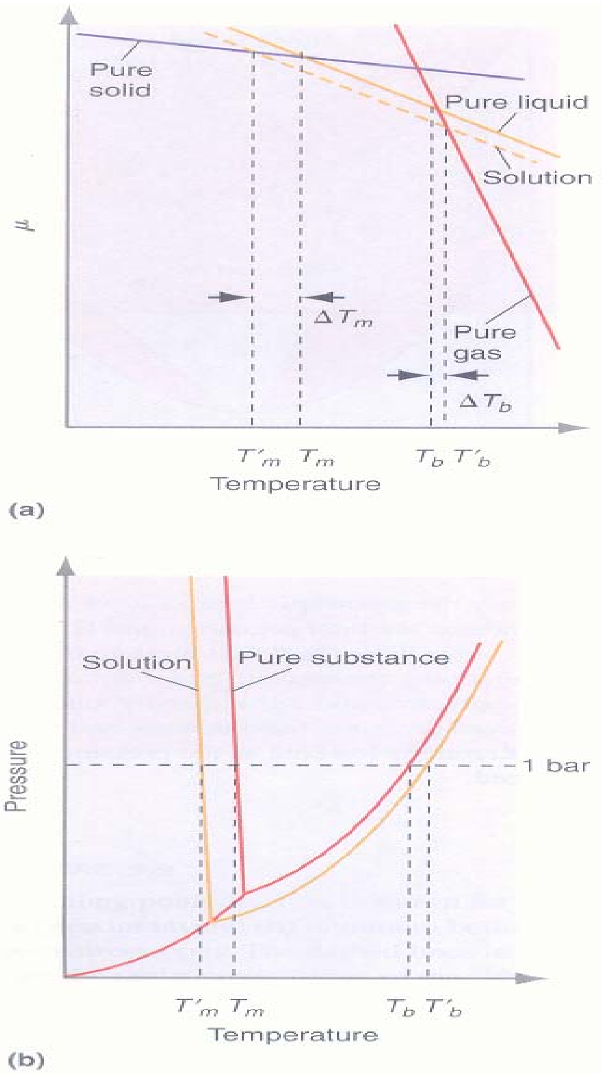


FIGURE 9.11

Illustration of the boiling point elevation and freezing point depression in two different ways: **(a)** These effects arise because the chemical potential of the solution is lowered through addition of the nonvolatile solute, while the chemical potential of the vapor and liquid is unaffected at constant pressure. **(b)** The same information from part (a) is shown using a P–T phase diagram.

Correct error in caption.