Chapter 5. Simple Mixtures
(Binary Alloy Phase Diagram)

5A.1 Partial Molar Quantities

The partial molar volume of a substance in a mixture of some general composition **is defined** as the increase of volume that occurs when 1 mole of the substance is added to an infinitely large sample of the solution.

$$\Delta V(T, p, x_A) = V_{A,m}(T, p, x_A)\Delta n_A \qquad x_A + x_B = 1$$

where ΔV is the volume change, $V_{A,m}(x_A, x_B)$ is the underlined partial molar volume of A when the solution has a composition of the mole fraction x_A and x_B, and Δn_A is the amount of A added.

The partial molar volume is **dependent** on the composition.

The addition of A is limited to an infinitesimal amount.

$$dV(T, p, x_A) = V_{A,m}(T, p, x_A)dn_A \qquad \textbf{\textcolor{red}{at } T \textbf{ and } P}$$

When dn_B and dn_A are added to the solution (x_A, x_B),

$$dV = V_{A,m}(x_A, x_B)dn_A + V_{B,m}(x_A, x_B)dn_B \qquad (1)$$

Since dV is complete differential,

$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{n_A} dn_B \qquad (2)$$

Comparing eq (1) with eq (2),   ❋ ❋ ❋

$$V_{A,m} = \left(\frac{\partial V}{\partial n_A}\right)_{n_B}, \qquad V_{B,m} = \left(\frac{\partial V}{\partial n_B}\right)_{n_A} \qquad (3)$$

$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{n_A} dn_B \qquad (5) \qquad \text{at } \textbf{\textit{T}} \text{ and } \textbf{\textit{P}}$$

If the partial molar volumes **at a composition x_A, x_B** are $V_{A,m}$

and $V_{B,m}$, then the total volume of a sample containing an amount n_A of A

and n_B of B is $(x_A = \dfrac{n_A}{n}, x_B = \dfrac{n_B}{n}; n = n_A + n_B)$

$$V = n_A V_{A,m}(x_A, x_B) + n_B V_{B,m}(x_A, x_B)$$

(6)

Derivation Eq. (5A.3) p. 181

One A atom and two B atoms = nonsense

One mole of A atoms and two moles of B atoms = OK

Provided the relative composition is held constant as the amount of A and B are increased, the partial molar quantities are both constant.

$$\mu_A = G_{A,m} = \left(\frac{\partial G}{\partial n_A} \right)_{p,T,n_B}$$

Therefore, the Gibbs function for a sample containing an amount n_A of A, n_B of B, etc. is:

$$G = n_A \mu_A + n_B \mu_B + \cdots = \sum_i n_i \mu_i \qquad (7)$$

(5A.5)

It is known from eq (6) that the volume of the system would appear to change both because n changes and because V_m changes when the concentrations are varied by small amounts.

$$dV = n_A dV_{A,m} + n_B dV_{B,m} + V_{A,m} dn_A + V_{B,m} dn_B \qquad (8)$$

at T and P

From eq (1) and (8), we obtain $\quad dV = V_{A,m}(x_A, x_B) dn_A + V_{B,m}(x_A, x_B) dn_B$

$$n_A dV_{A,m} + n_B dV_{B,m} = 0 \Rightarrow n_A dV_{A,m} = -n_B dV_{B,m} \qquad (9)$$

(5A.12)

The Gibbs-Duhem equation

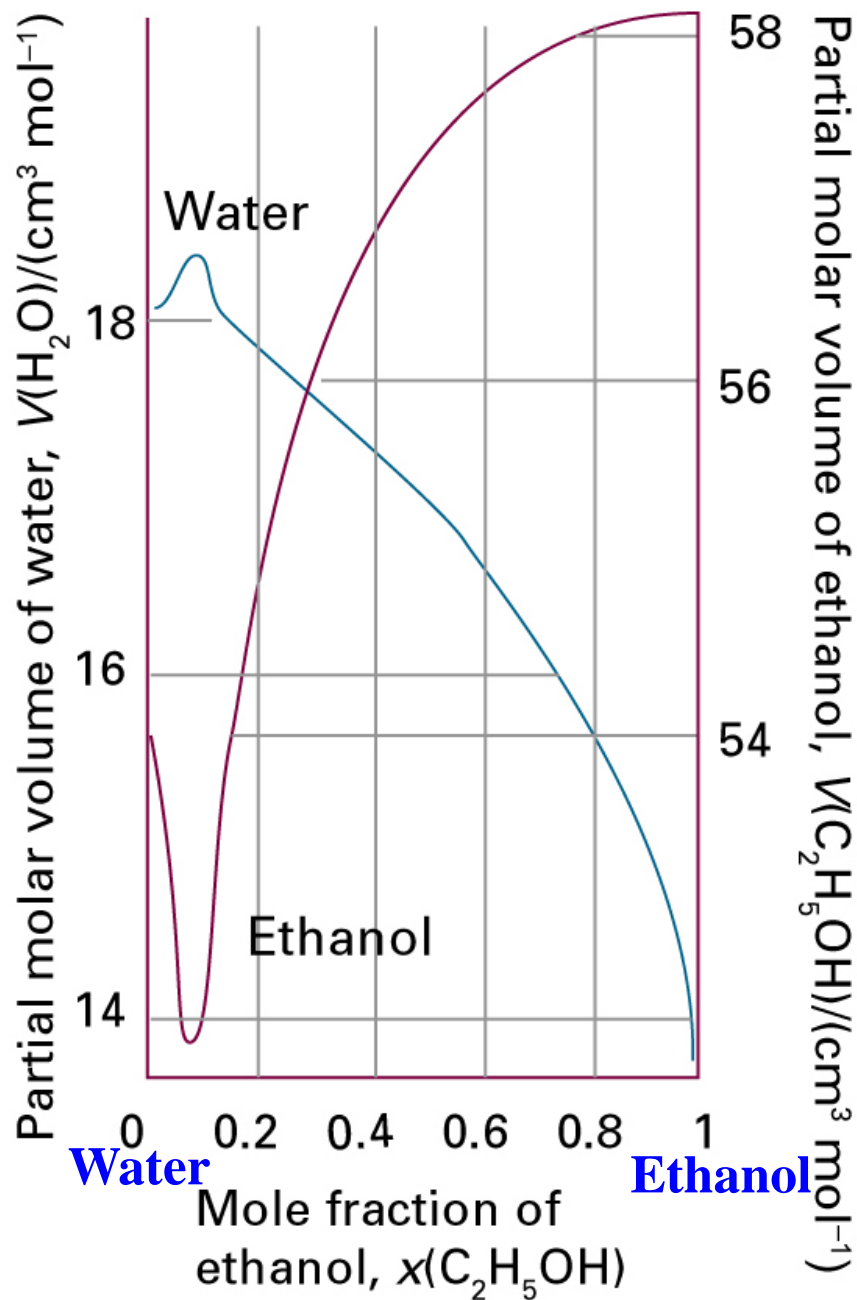This means that if $V_{A,m}$ increases, then $V_{B,m}$ must decrease.

Figure 5A.1

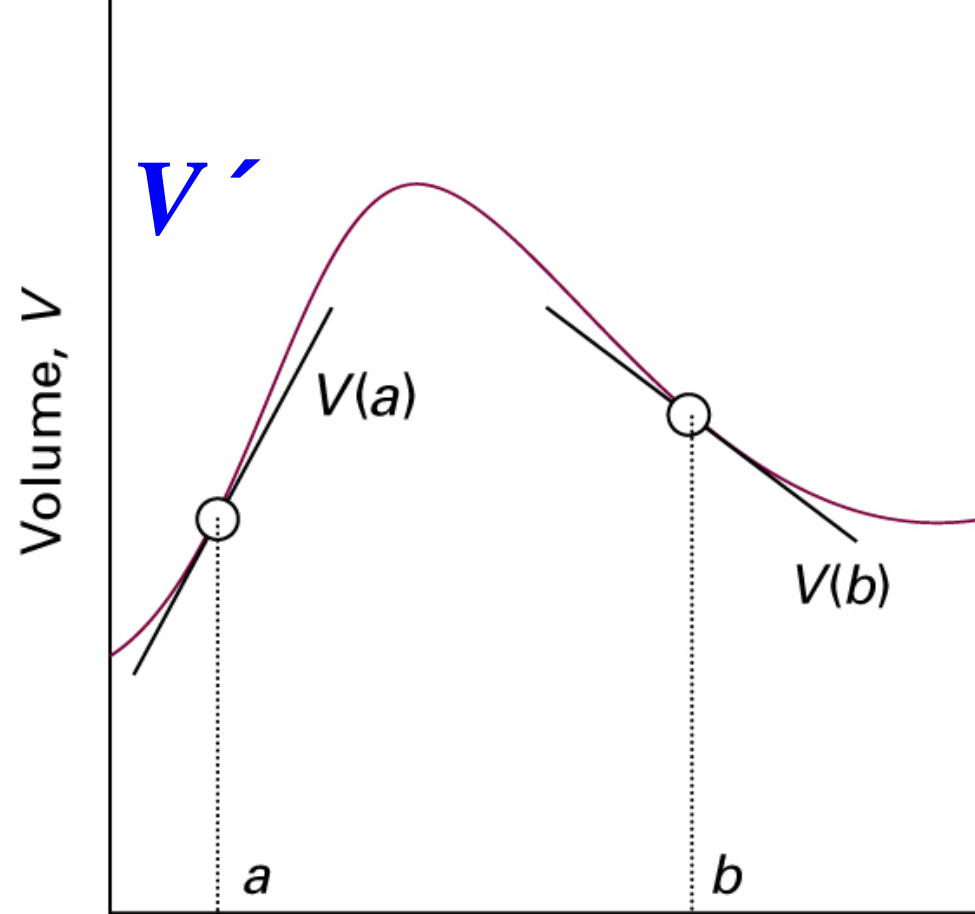The partial molar volumes of water and ethanol at 25˚C.

Note the different scales (water on the left, ethanol on the right).

V'

Volume, V

$V(a)$

$V(b)$

a b

Amount of A, n_A

n_A (not x_A)

Fix n_B n_C n_D n_E . . .

Figure 5A.2

The partial molar volume of a substance is the slope of the variation of the total volume of the sample plotted against the amount of each atom.

In general, partial molar quantities vary with the composition, as shown by the different slopes at the amounts a or b.

Note that the partial molar volume at b is negative: the overall volume of the sample decreases as A is added.
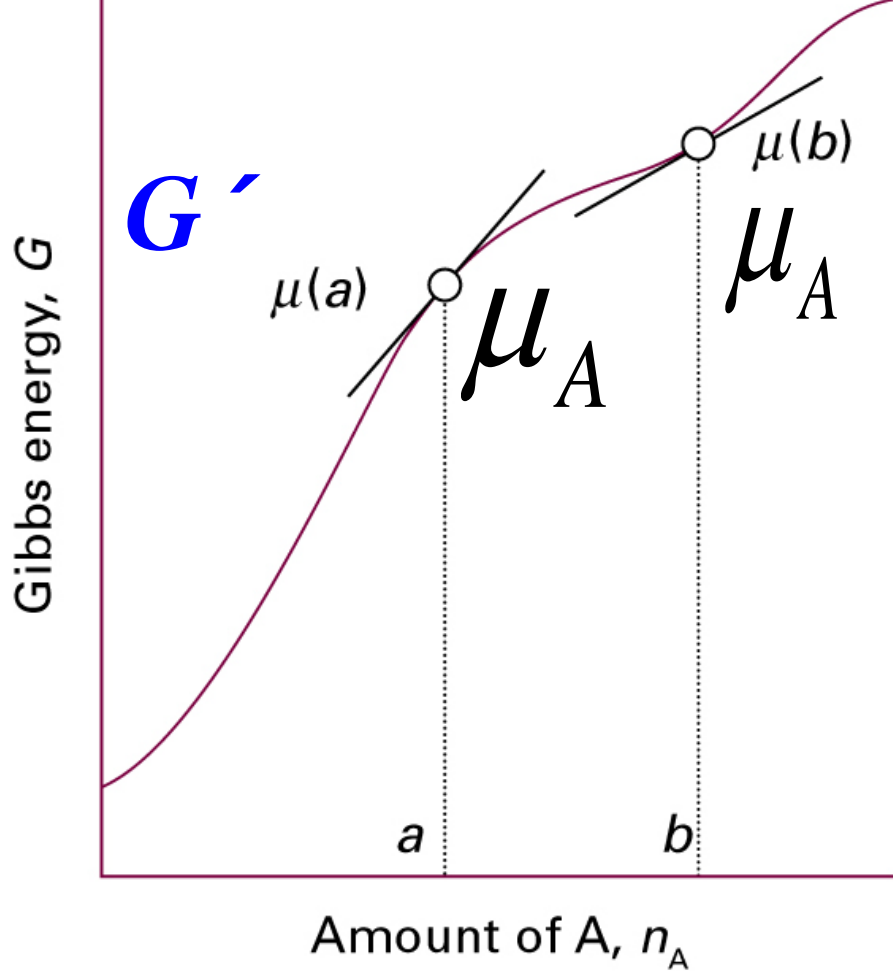
Figure 5A.4

The [chemical potential](#) of a substance is the slope of the total Gibbs energy of a mixture with respect to the amount of substance of interest.

In general, the chemical potential varies with composition, as shown for the two values at a and b.

Only in this case, the chemical potentials are positive. **<- wrong**

<- meaningless

절대 다 믿지 말 것

(Reference Point)

G'

μ_A μ_A

n_A (not x_A)

Fix n_B n_C n_D n_E . . .

For the partial molar Gibbs function,
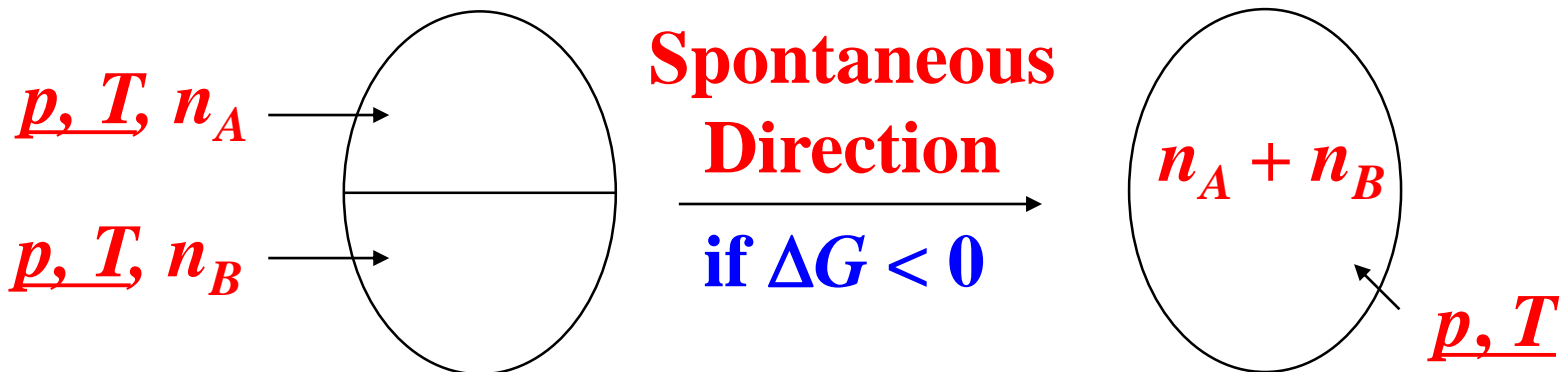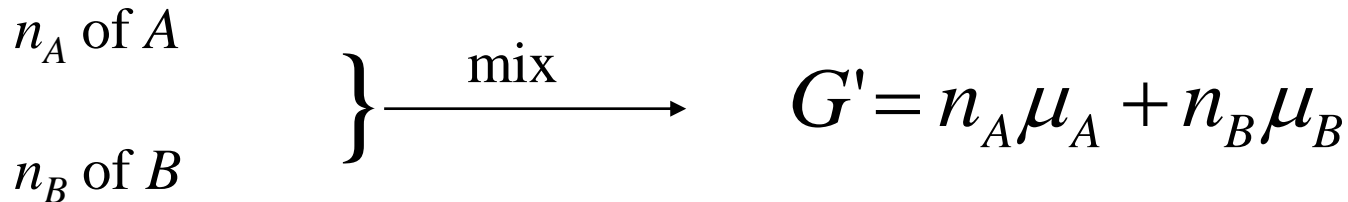
$$\sum_i n_i d\mu_i = 0 \qquad \underline{\text{at } T \text{ and } P} \qquad (10)$$

Gibbs-Duhem Equation

5A.2 Thermodynamics of Mixing

For a mixture:

$$
\left.
\begin{array}{l}
n_A \text{ of } A \\[2em]
n_B \text{ of } B
\end{array}
\right\}
\xrightarrow{\text{mix}}
\quad G' = n_A \mu_A + n_B \mu_B
$$

p, T, n_A

p, T, n_B

Spontaneous Direction

if $\Delta G < 0$

$n_A + n_B$

p, T

Ideal Gas $P + T$

$\mu(p,T) = \mu^0(T) + RT\ln p$

Initial state (before mixing)

$$G'_i = n_A\{\mu_A^0(T) + RT\ln p\} + n_B\{\mu_B^0(T) + RT\ln p\} \quad \textbf{\textit{before mixing}}$$

After mixing, each gas exerts a partial pressure whose sum $\boldsymbol{p_A + p_B = p}$,

$$G'_f = n_A\{\mu_A^0(T,p) + RT\ln p_A\} + n_B\{\mu_B^0(T,p) + RT\ln p_B\} \quad \textbf{\textit{after mixing}}$$

where $p_A + p_B = p.$ 　　　　　　　　　　　　　　[예: $p = 1$ atm]

For an ideal gas, Dalton's law is applicable.

$$x_A = \frac{p_A}{p}, \; x_B = \frac{p_B}{p} \quad \text{where } x_A \text{ and } x_B \text{ are mole fractions of gas A and B.}$$
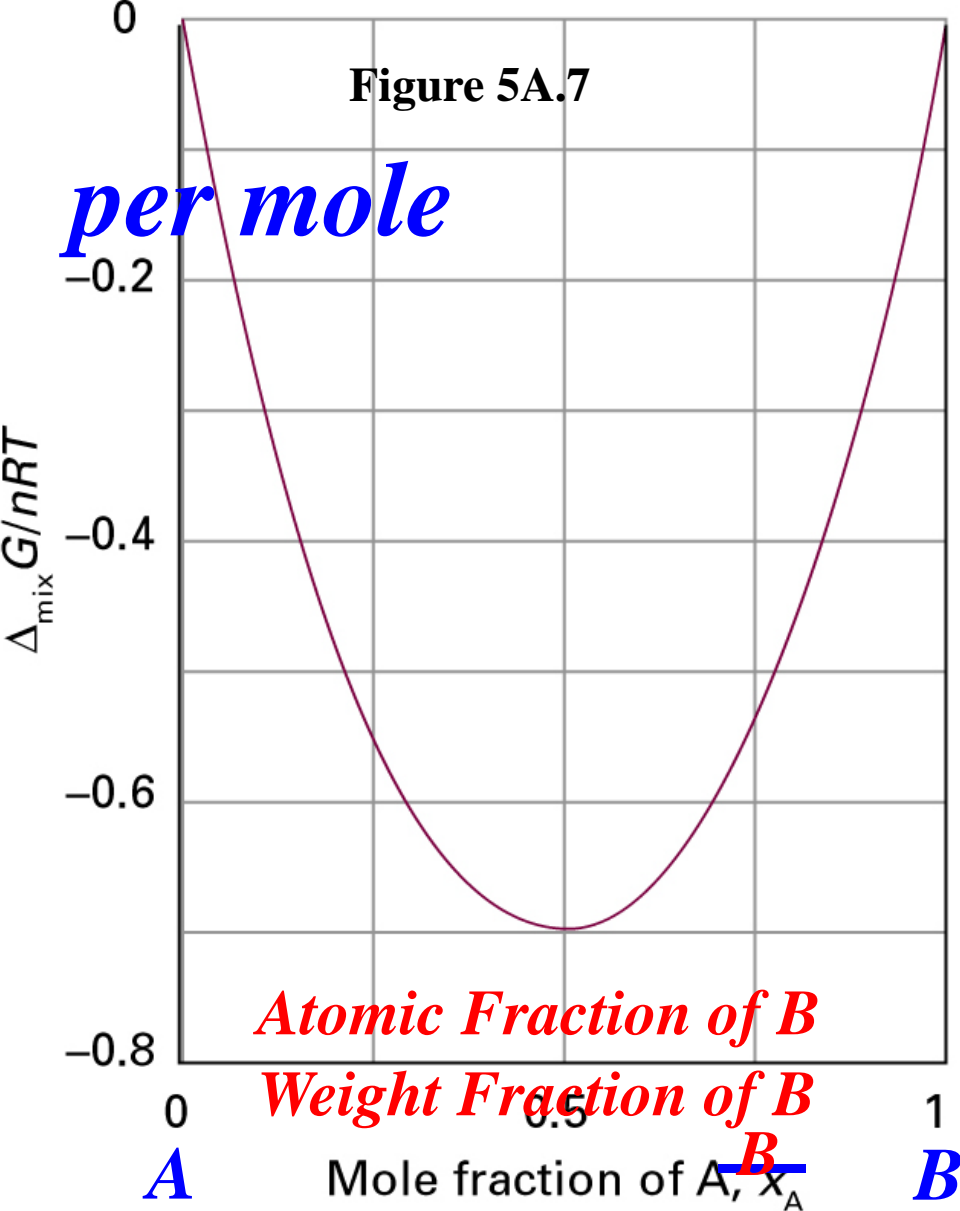
의미

$$\Delta G'_{mix} = G_f - G_i = n_A RT\ln\frac{p_A}{p} + n_B RT\ln\frac{p_B}{p} \qquad \textbf{(5A.16)}$$
$$\textbf{(5A.17)}$$

$$= nx_A RT\ln x_A + nx_B RT\ln x_B = nRT\{x_A\ln x_A + x_B\ln x_B\} \; ^{(11)}$$

where $x_A = \dfrac{n_A}{n}, \; x_B = \dfrac{n_B}{n}.$

Ideal Gas
Ideal Solution (later)

$$\Delta G'_{mix} = nRT\{x_A \ln x_A + x_B \ln x_B\}$$

(5A.16)

Figure 5A.7

per mole

$\Delta_{mix}G/nRT$

Atomic Fraction of B

Weight Fraction of B

B

Mole fraction of A, x_A

A   *B*

This expression confirms that the mixing of ideal gases is a <u>natural process</u>.

Both x_A and x_B are less than unity, and so their logarithms are negative.

The Gibbs energy of mixing of two perfect gases and (as discussed <u>later</u>) of two

<u>gases, liquids or solids of an ideal solution.</u>

The Gibbs energy of mixing is negative for all compositions and temperatures.

$$\mu_i(p,T,n_A,n_B,n_C,\ldots) = \mu_i^0(p,T) + RT \ln x_i$$

5A.2(b) Other Thermodynamic Mixing Functions

$$\left(\frac{\partial G}{\partial T}\right)_{p,n_j} = -S \qquad \Delta G'_{mix} = G_f - G_i = nRT\{x_A \ln x_A + x_B \ln x_B\}$$

$$\Delta S'_{mix} = -\left(\frac{\partial \Delta G'_{mix}}{\partial T}\right)_{p,n_A,n_B}$$

$$= -nR\{x_A \ln x_A + x_B \ln x_B\} \qquad (12) \qquad \textbf{(5A.17)}$$

constant P & T

(later) $$a_i(T, p, x_j) = x_i \qquad \textbf{for ideal solution}$$

$$\Delta G'_{mix} = nRT\{x_A \ln a_A + x_B \ln a_B\}$$

$$\Delta S'_{mix} = -nR\{x_A \ln x_A + x_B \ln x_B\} \quad \text{(5A.17)}$$
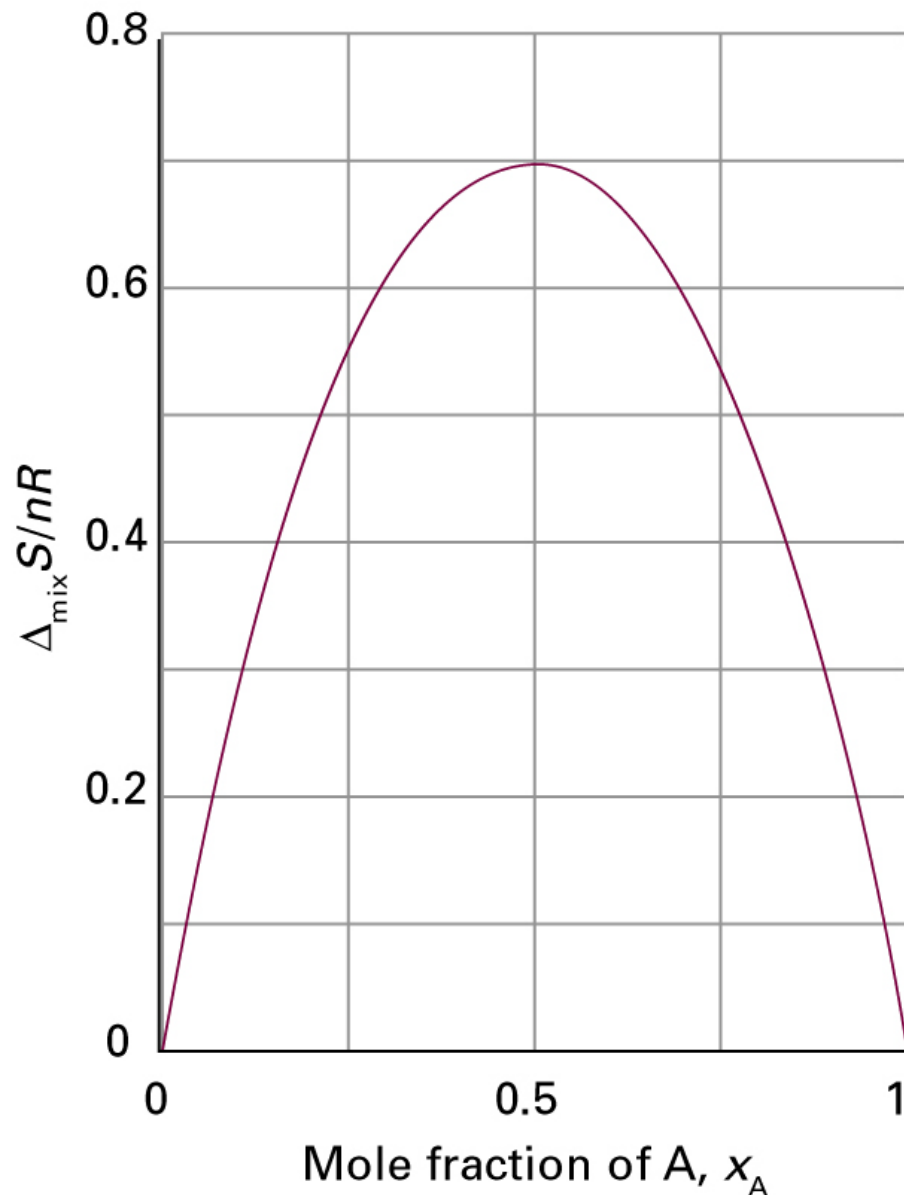
Figure 5A.9

The entropy of mixing of **an ideal solution**.

The entropy increases for all compositions and temperatures, so ideal solutions mix spontaneously in all proportions.

Because there is **no transfer of heat** to the surroundings for ideal solution, the entropy of the surroundings is unchanged.

Hence, the graph also shows the total entropy of the system plus the surroundings when perfect gases mix.

$$\Delta G'_{mix} = nRT\{x_A \ln x_A + x_B \ln x_B\}$$

Enthalpy of mixing of two ideal gases

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

$$\Delta H = \Delta G + T\Delta S = 0$$

$\because$ No interaction between molecules

Volume change of mixing

$$\left(\frac{\partial G'}{\partial p}\right)_{T,n} = V', \qquad \left(\frac{\partial \Delta G'_{mix}}{\partial p}\right)_{T,n} = \Delta V'_{mix}$$

$\Delta G'_{mix}$ is independent of pressure for a perfect gas.

$$\Delta V'_{mix} = 0$$

$\because$ No interaction

Internal energy change

$$\Delta E_{mix} = \Delta H_{mix} - p\Delta V_{mix} = 0$$

Ideal Gas
Ideal Solution

$$\Delta H_{mix} = 0$$

$$\Delta E_{mix} = 0$$

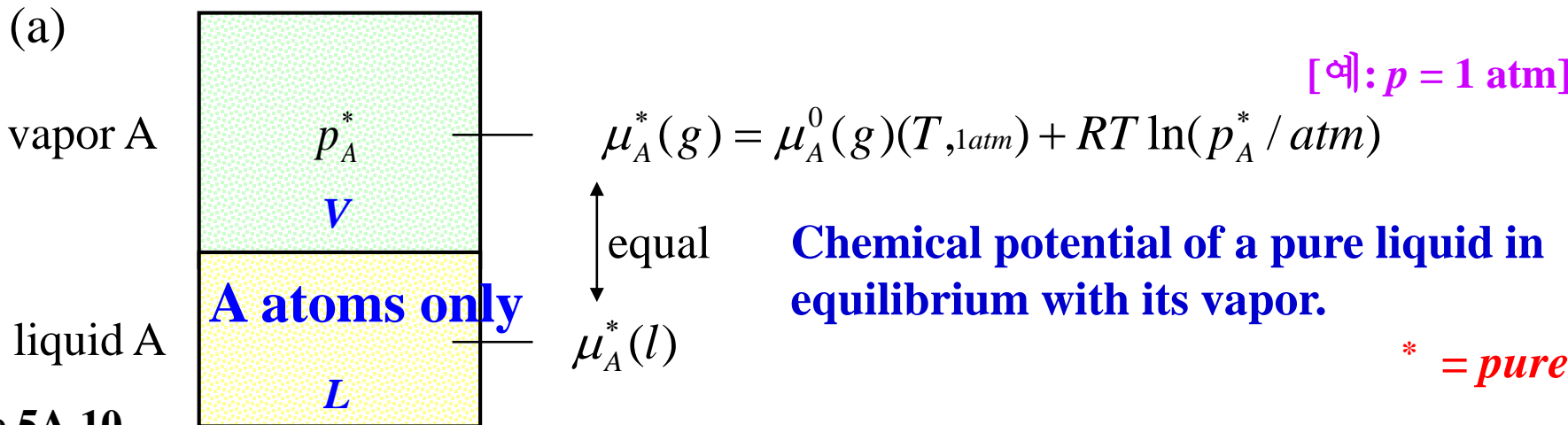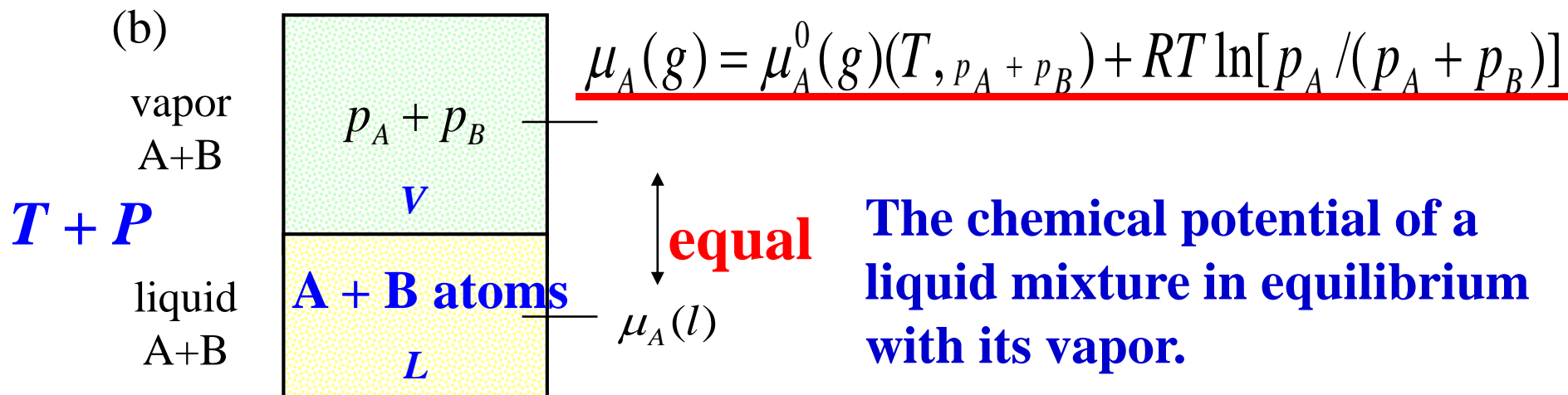$$\Delta V_{mix} = 0$$

5A.3 Chemical Potential of Liquids

(a)

[예 : $p = 1$ atm]

vapor A $\quad p_A^*$

$$\mu_A^*(g) = \mu_A^0(g)(T, 1atm) + RT\ln(p_A^*/atm)$$

V

equal $\quad$ **Chemical potential of a pure liquid in equilibrium with its vapor.**

liquid A $\quad \mu_A^*(l)$

L

$* = pure$

Figure 5A.10

(b)

vapor
A+B $\quad p_A + p_B$

$$\mu_A(g) = \mu_A^0(g)(T, p_A + p_B) + RT\ln[p_A/(p_A + p_B)]$$

V

$T + P$ $\quad$ **equal** $\quad$ **The chemical potential of a liquid mixture in equilibrium with its vapor.**

liquid
A+B $\quad$ **A + B atoms** $\quad \mu_A(l)$

L

System with only *A* and *B* atoms

At equilibrium, $\mu_A(l) = \mu_A(g)$.

$$\mu(p,T) = \mu^0(T) + RT \ln p$$

$$\mu(l) = \mu(g) = \mu^0(T, \text{1atm}) + RT \ln(p/atm)$$

Assume that the <u>vapor is ideal</u>.

(16)

One component system,

$$\mu_A^*(l)(T, p_A^*) = \mu_A^*(g)(T, p_A^*) = \mu_A^0(g)(T, \text{1atm}) + RT \ln(p_A^*/atm) \qquad \text{* = pure}$$

where p_A^* is the <u>vapor pressure of the pure liquid</u>. (17)

- -

<u>Two or more</u> component system, $\qquad p = p_A + p_B$

$$\mu_A(l)(T, p) = \mu_A(g)(T, p) = \mu_A^0(g)(T, p_A + p_B) + RT \ln[p_A/(p_A + p_B)]$$

$$= \mu_A^0(g)(T, p_A^*) + RT \ln[p_A/p_A^*] \qquad (18)$$

System with only
_A_ and _B_ atoms

$$= \mu_A^*(g)(T, p_A^*) + RT \ln[p_A/p_A^*] \qquad (19)$$

$$= \mu_A^*(l)(T, p_A^*) + RT \ln[p_A/p_A^*]$$

Equilibrium (Universe) with Only *A* and *B*

In Equilibrium

A(g) + B(g)

○ — $\mu_A(g, p)$

‖ **Equal**

○ — $\mu_A(l)$

A(l) + B(l)

L or *S*
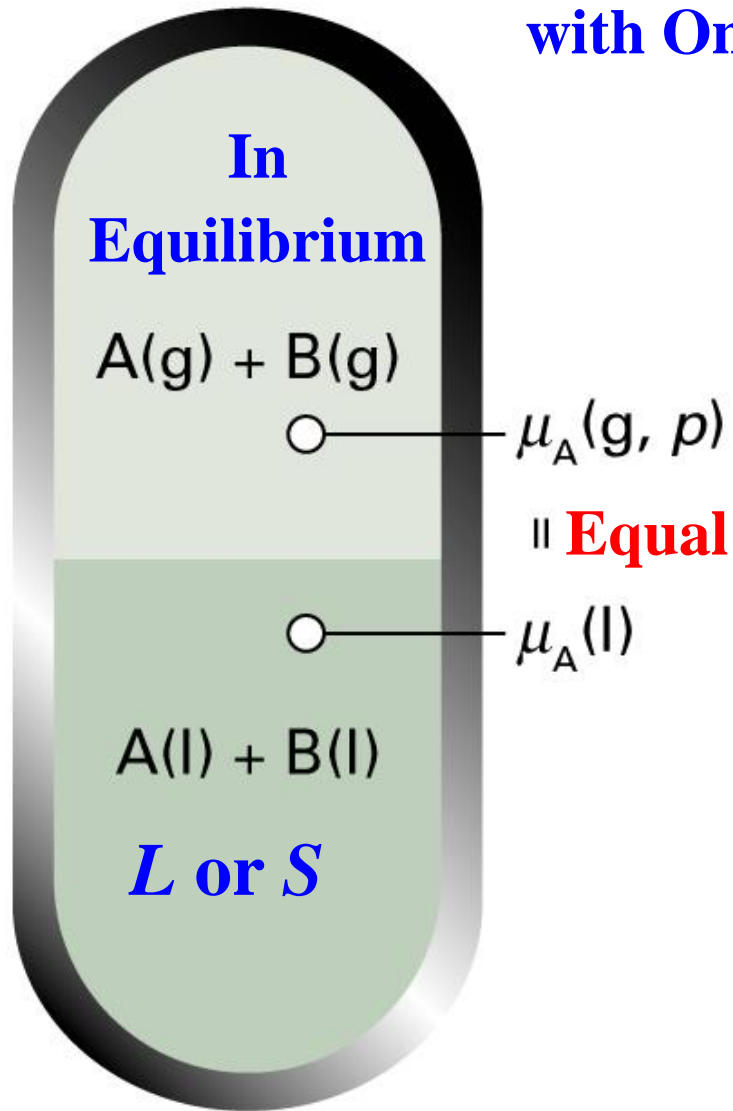
Figure 5A.10

The chemical potential of the gaseous form of a substance A is equal to the chemical potential of its condensed phase.

The equality is preserved if a solute is also present.

Because the chemical potential of A in the vapor depends on its partial vapor pressure, it follows that the chemical potential of liquid A can be related to its partial vapor pressure.

5A.3(a) Chemical Potential: Ideal Solution (Raoult's law)

$$p_B = x_B p_B^*$$

Vapor Pressure and Mole Fraction in Liquid (20)

where x_B is the mole fraction of B, and $0 < p_B < p_B^*$.   * = *pure***

System obeying the Raoult's law is the ideal solution: e.g., benzene and toluene, because **two components are chemically similar**. System deviated from the Raoult's law is non-ideal solution.

Inserting eq (20) into eq (19), one knows

$$\mu_A(l)(T, p) = \mu_A^*(l)(T, p_A^*) + RT \ln x_A \qquad (21)$$

"an alternative definition of an **Ideal Solution****"**

Gibbs function at **initial state (before mixing)**

$$G_i(l)(T, p) = n_A \mu_A^*(l)(T, p_A^*) + n_B \mu_B^*(l)(T, p_B^*)$$

$p_B^*(T)$ = **Equilibrium Vapor Pressure**

Gibbs function at **final state (after mixing)**

* = pure

$$G_f(T, p) = n_A \mu_A(l)(T, p) + n_B \mu_B(l)(T, p)$$

$$= n_A \left\{ \mu_A^*(l)(T, p_A^*) + RT \ln x_A \right\} + n_B \left\{ \mu_B^*(l)(T, p_B^*) + RT \ln x_B \right\}$$

The change of the Gibbs function on mixing

(from ppt 5-17)

$$\Delta G'_{mix}(p, T) = G_f - G_i = nRT \left(x_A \ln x_A + x_B \ln x_B \right) \quad \overset{\text{(Ideal)}}{(22)}$$

From eq (22) which describes an ideal solution, ΔG has a negative value since x_A and x_B are less than unity, indicating the mixing is a spontaneous process.

$$\underline{\mu_i(p, T, n_A, n_B, n_C, \ldots) = \mu_i^0(p, T) + RT \ln a_i} \text{ (later)}$$

$$a_i(T, p, x_j) = x_i \quad \textbf{Ideal Solution}$$

Ideal Solution

Figure 5A.11

The total vapor pressure and the two partial vapor pressures of an **ideal binary mixture** are proportional to the mole fractions of the components.

Equilibrium Vapor Pressure with Only *A* and *B*
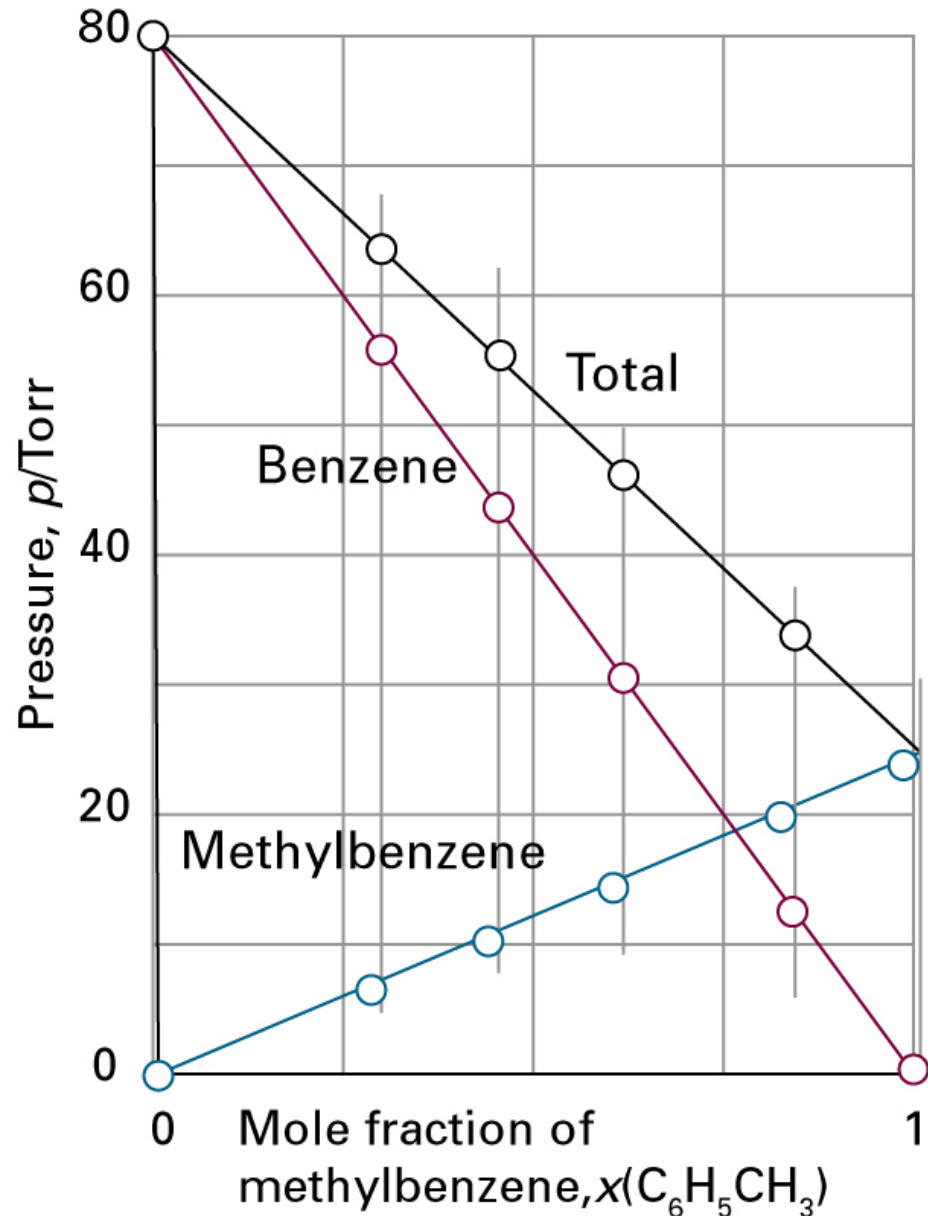
Figure 5A.12
Two similar liquids, in this case benzene and methylbenzene (toluene), behave almost ideally, and the variation of their vapor pressures with composition

resembles that for **an ideal solution**.

Equilibrium Vapor Pressure with Only *A* and *B*
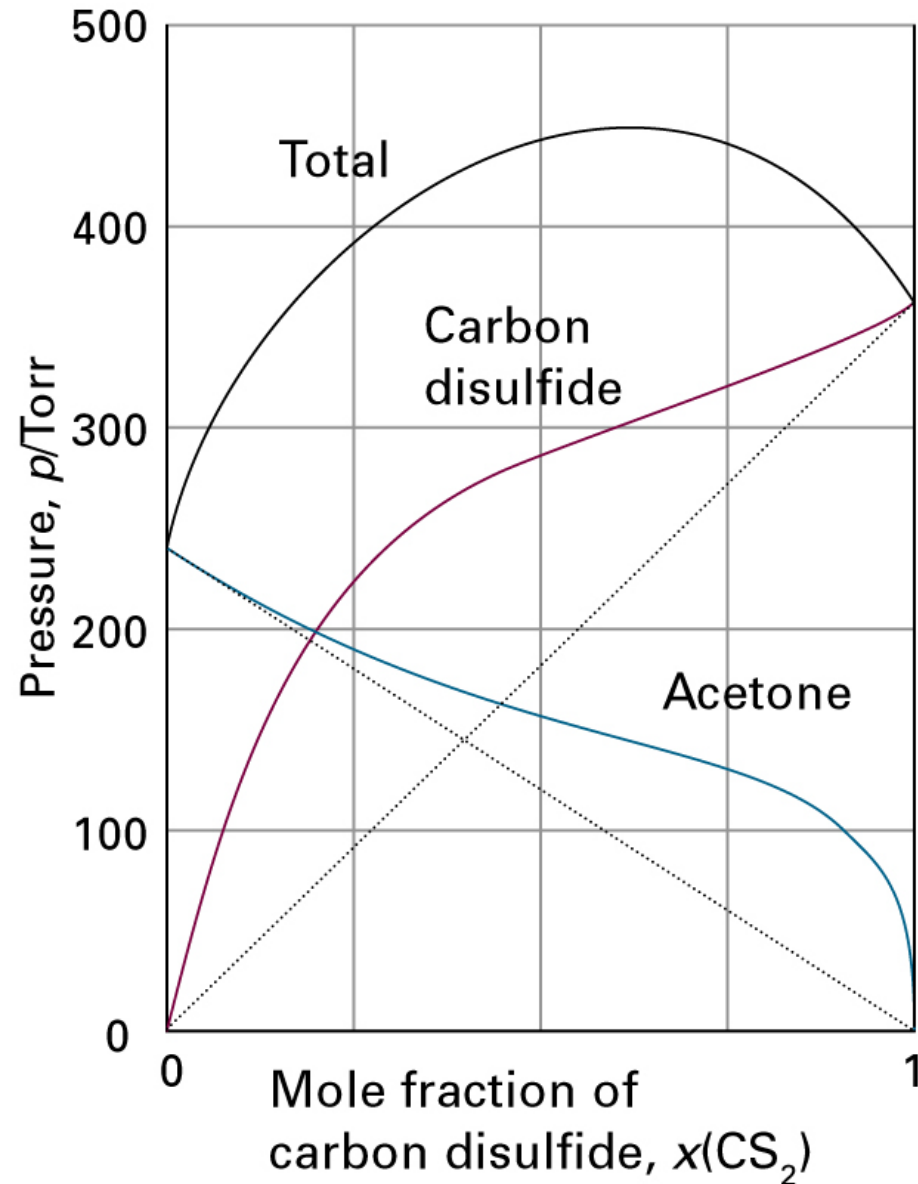
Figure 5A.13
Strong **deviations from ideality** are shown by dissimilar liquids (in this case carbon disulfide and acetone (propanone)).

5B.1(b) Excess Functions and Regular Solutions

Excess function: the difference between the observed thermodynamics function of mixing and function for an ideal solution

$$S^E = \Delta S_{mix} - \Delta S_{mix}^{ideal}$$

Regular-Solution Model: $\underline{H^E \neq 0, \ S^E = 0}$

Suppose the excess enthalpy **(per mole)** depends on the composition as

$$H^E = R\beta x_A x_B$$

~independent of temperature
(*derivation in the Thermodynamics class*)

where β is a dimensionless parameter that is a measure of the energy of **A-B interactions relative to that of the A-A and B-B interactions**.

$$\Delta G_{mix} = RT\{x_A \ln x_A + x_B \ln x_B\} + \{R\beta x_A x_B\}$$

entropy term   *enthalpy term*

[*different from Eqs. (5B.6) and (5B.7)*]

Hate Each Other

$$H^E = R\beta x_A x_B$$

> 0
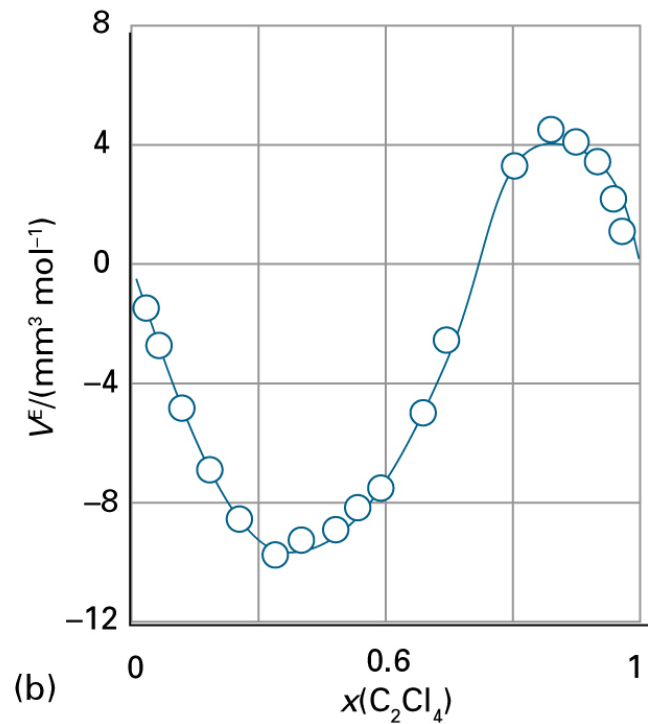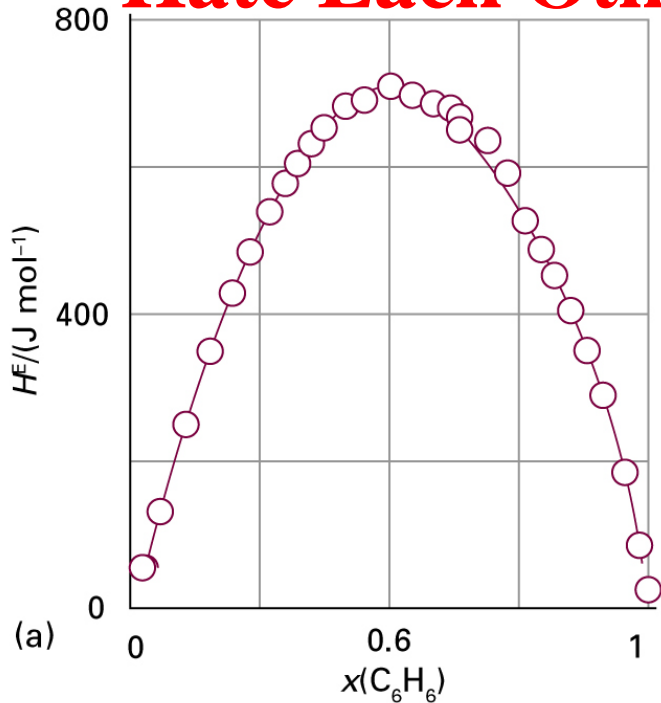
Figure 5B.3
Experimental excess function at 25°C.

$$H^E = \Delta H_{mix} - \Delta H_{mix}^{ideal}$$

(a) H^E for benzene/cyclohexane; this graph shows that the mixing is endothermic (because $\Delta H_{mix} = 0$ for an ideal solution).

(b) The excess volume, V^E, for tetrachloroethene/cyclopentane; this graph shows that there is a contraction at low tetrachloroethene mole fractions, but an expansion at high mole fractions (because $\Delta V_{mix} = 0$ for an ideal mixture).

$$H^E = nR\beta x_A x_B$$

$$H^E = \Delta H_{mix} - \Delta H_{mix}^{ideal}$$

✳ ✳ ✳

(a)

Hate each other

Like each other

(b)

Hatred

Dislike

At Finite Temperature
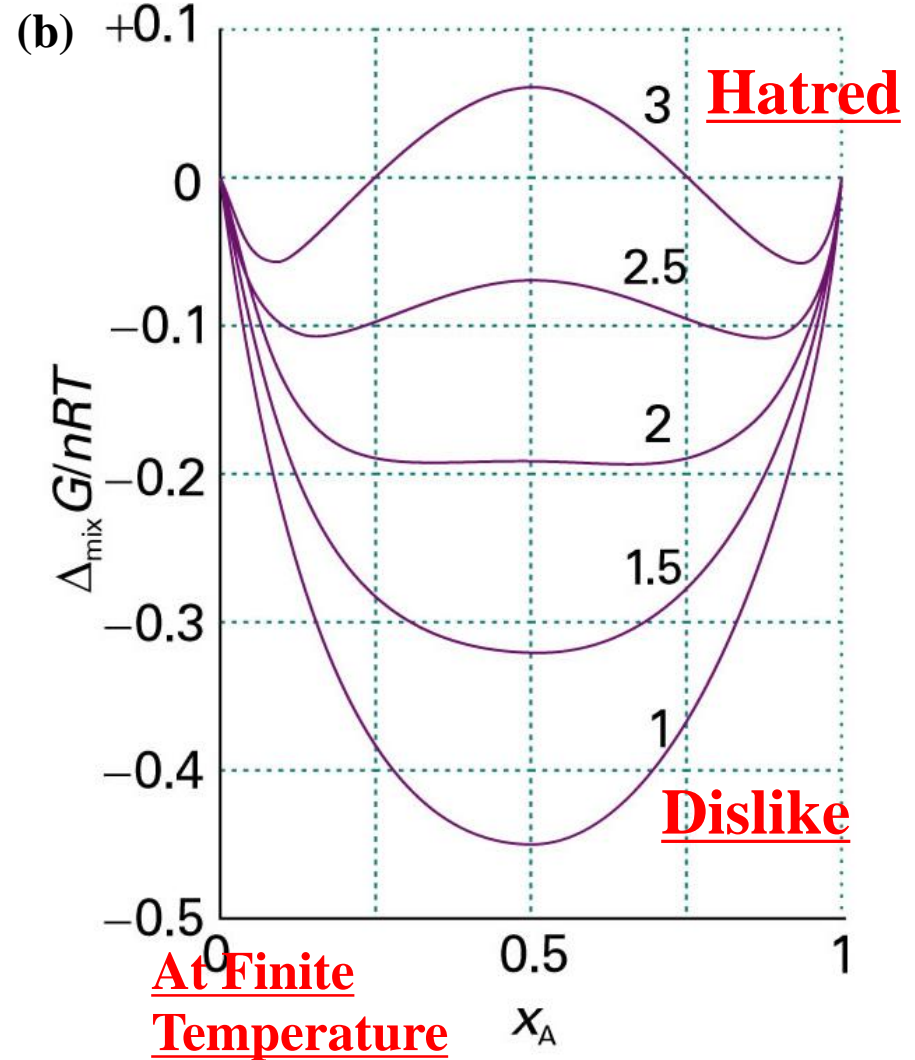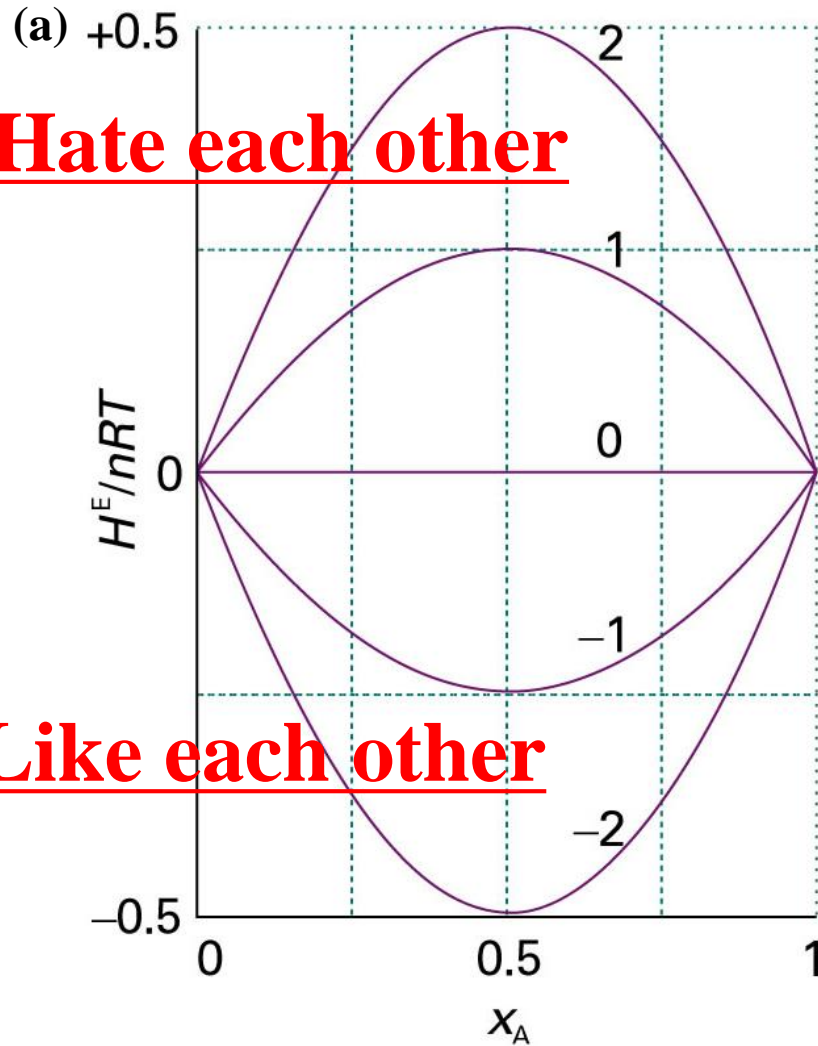
Figures 5B.4 & 5B.5 The excess enthalpy according to a model in which it is proportional to $\beta x_A x_B$ for different values of the parameter β. (b) The Gibbs free energy of mixing **for different values of the parameter β**.

[different from Eq. (5B.6)] 24

5B.2 Solutions of Nonvolatile Solutes: Colligative Properties (총괄성)

The elevation of boiling point

The depression of freezing point

Two assumptions:

1. The solute is involatile: the solvent vapor is only the gas present.

2. The involatile solute does not dissolve much in solid solvent.

Principle

The Gibbs free energy of the liquid solution is lowered by the presence of the solute, causing that the boiling point is raised and the freezing point lowered. (See Fig. 5.15)

G' or G
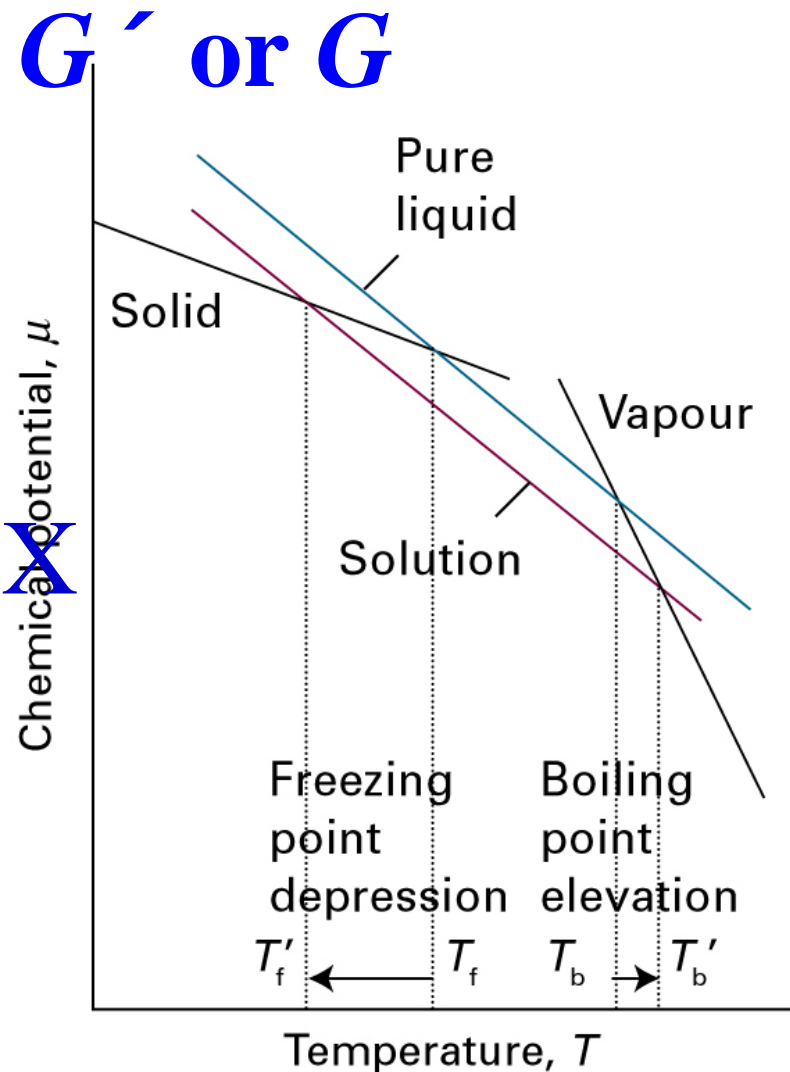
$$\mu_s(l) = \mu_s^*(l) + RT \ln x_s$$

Figure 5B.6
The **Gibbs free energy of S, L, & V** in the presence of a solute. The lowering of the liquid's G has a greater effect on the freezing point than on the boiling point because of the angles at which the lines intersect (which are determined by entropies). *[different from Fig. 5B.6]*

$*\ = pure$

V

p_A^*

p_A

involatile

L

(a)   (b)
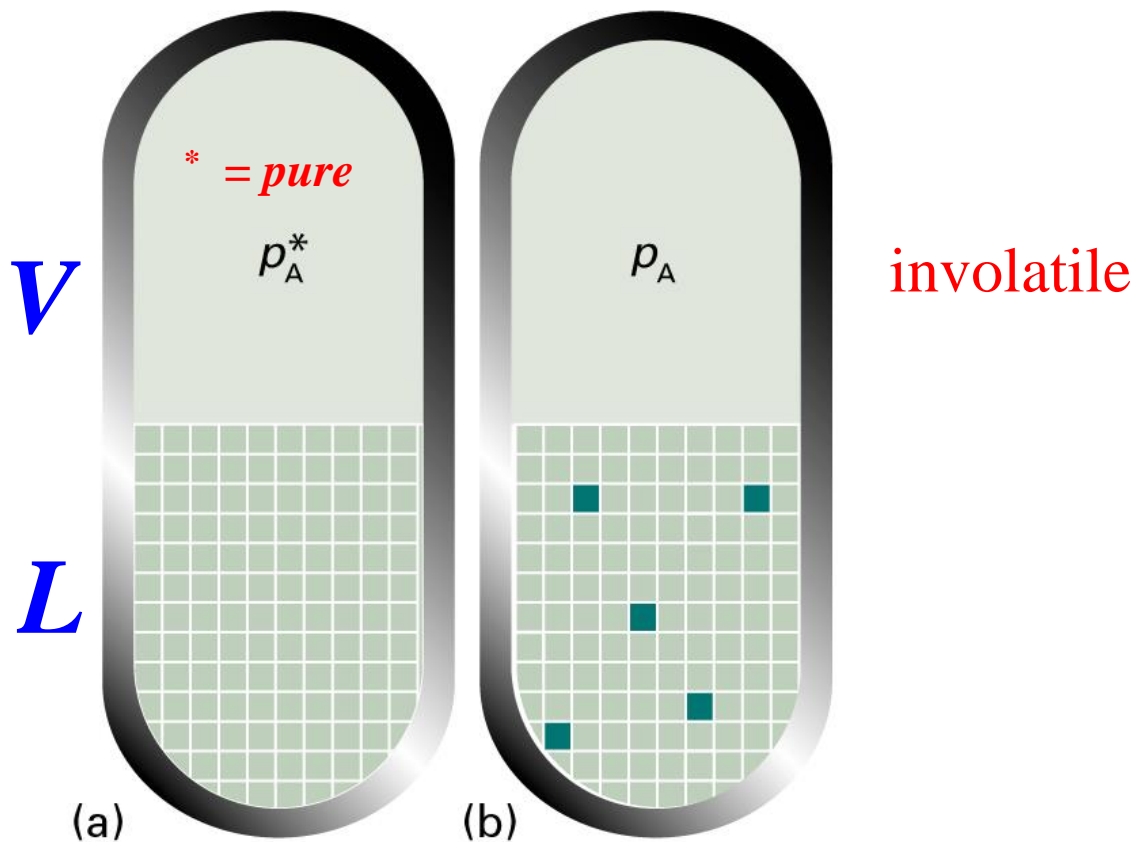
Figure 5B.7

The vapor pressure of a pure liquid represents a balance between the increased disorder arising from vaporization and the decreased disorder of the surroundings. (a) Here the structure of the liquid is represented highly schematically by the grid of squares. (b) When solute (the dark squares) is present, the disorder of the condensed phase is relatively higher than that of the pure liquid, and there is a decreased tendency to acquire the disorder characteristic of the vapor.

Elevation of boiling point

At equilibrium between the solvent vapor and the solvent in solution (See Figure 5.17)

$$\mu_s^*(g) = \mu_s(l) = \mu_s^*(l) + RT \ln x_s \qquad (A)$$

From eq (A)

$$\ln x_s = \ln(1 - x_s) = \frac{\mu_s^*(g) - \mu_s^*(l)}{RT} = \frac{\Delta G_{vap,m}(T)}{RT} \qquad (B)$$

where $\Delta G_{vap,m}$ is the molar Gibbs function for vaporization of the pure solvent and x_s is the mole fraction of the solute ($x_S + x_s = 1$).

$$x_s \sim 0 \to T \cong T^* \ (\text{boing point})$$

$$\ln 1 = \frac{\Delta G_{vap,m}(T^*)}{RT^*} \qquad (C)$$

A(g)

$\mu_A^*(g,p)$

$=$

$\mu_A(l)$

A(l) + B
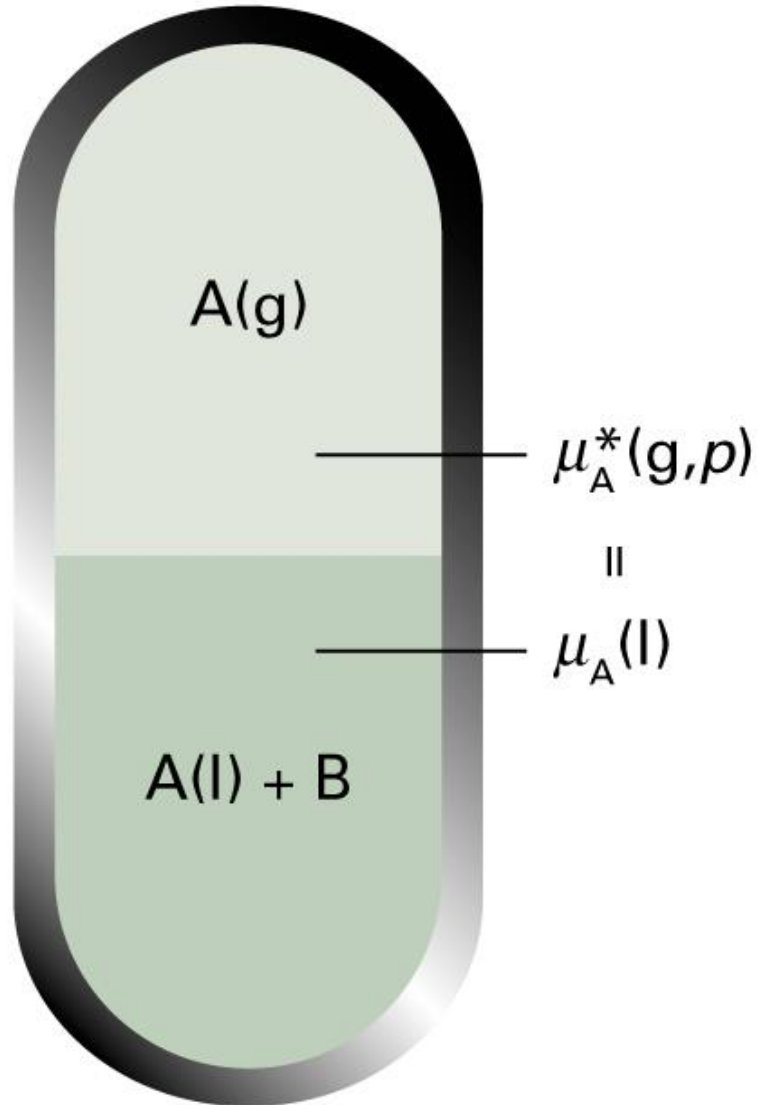
Figure 5.17
The heterogeneous equilibrium involved in the calculation of the elevation of boiling point is between A in the pure vapor and A in the mixture, A being the solvent and B an involatile solute.

Subtracting eq (C) from eq (B) and using $\Delta G = \Delta H - T\Delta S$ leads to

$$\ln(1-x_s) - \ln 1 = \left\{\frac{\Delta G_{vap,m}(T)}{RT}\right\} - \left\{\frac{\Delta G_{vap,m}(T^*)}{RT^*}\right\}$$

$$= \left\{\frac{\Delta H_{vap,m}(T)}{RT}\right\} - \left\{\frac{\Delta S_{vap,m}(T)}{R}\right\} - \left\{\frac{\Delta H_{vap,m}(T^*)}{RT^*}\right\} \quad (D)$$

$$+ \left\{\frac{\Delta S_{vap,m}(T^*)}{R}\right\}$$

$$If \ x < 1, \ \ln(1-x) = -x - \frac{x^2}{2} \cdots \approx -x$$

$$\Delta H(T) \cong \Delta H(T^*),$$
$$\Delta S(T) \cong \Delta S(T^*)$$

Since the boiling point elevation is small if $x_s \ll 1$,

thus eq (D) becomes

$$x_s = \left(\frac{\Delta H_{vap,m}}{R} \right) \left(\frac{1}{T} - \frac{1}{T^*} \right) \tag{E}$$

Approximation: $\dfrac{1}{T} - \dfrac{1}{T^*} = \dfrac{T^* - T}{TT^*} \cong -\dfrac{\Delta T}{T^{*2}}$, where $T - T^* = \Delta T$

$$\therefore \Delta T \cong \left(\frac{RT^{*2}}{\Delta H_{vap,m}} \right) x_s$$

Boiling point elevation can be used to determine the relative molecular mass of soluble, involatile materials.

Freezing point depression

At the freezing point the chemical potentials of the pure solid and thecontaminated solvent are equal: (See Figure 5.18)

$$\mu_S^* \left(s \right) = \mu_S \left(l \right) = \mu_S^* \left(l \right) + RT \ln x_S$$

Similarly to above,

$$\therefore \Delta T \cong \left(\frac{RT^{*2}}{\Delta H_{melt,m}} \right) x_s \qquad \text{(F)}$$

where $\Delta T = T^* - T$ is the freezing point depression, T^* is the freezing point of the pure solid, and $\Delta H_{melt,m}$ is the molar enthalpy of fusion (melting).

A(l) + B

$\mu_A(l)$

=

$\mu_A^*(s)$

A(s)
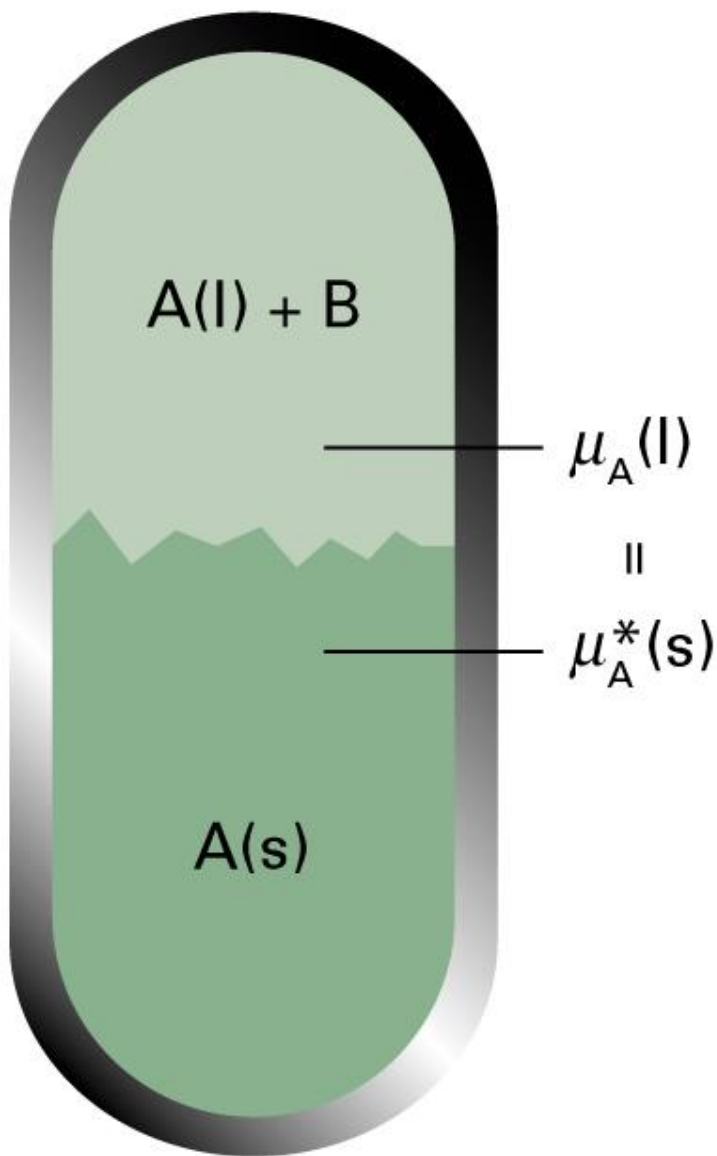
Figure 5.18
The heterogeneous equilibrium involved in the calculation of the lowering of freezing point is between A in the pure solid and A in the mixture, A being the solvent and B a solute that is insoluble in solid A.

5B.2(e) Osmosis   (삼투)

The chemical potential of the solvent on both sides of the semipermeable membrane must be equal. Because of the random distribution of solute, __the chemical potential of a solvent__ in a mixture is less than that of the pure solvent (an entropy effect), and so the pure solvent has a thermodynamic tendency to flow into the solution.
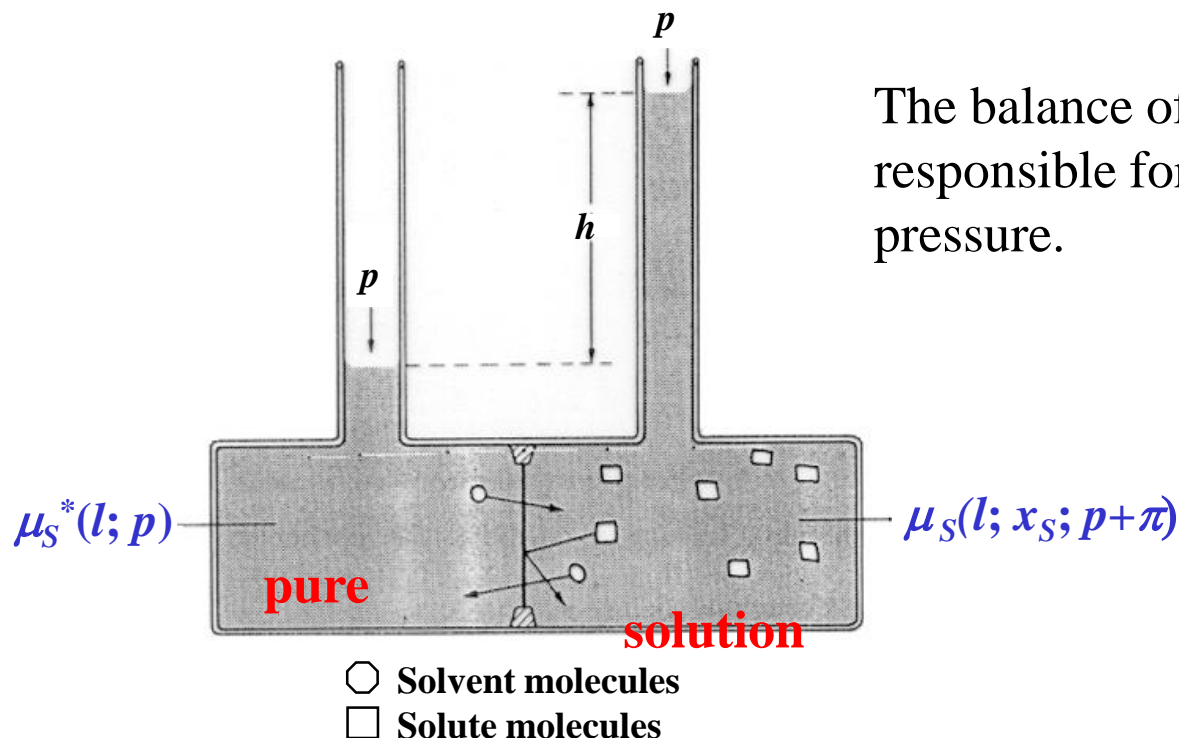
The balance of effects responsible for osmotic pressure.

p

h

p

$\mu_S^*(l; p)$

$\mu_S(l; x_S; p+\pi)$

pure

solution

○ **Solvent molecules**
□ **Solute molecules**

$$\mu_S^*(l;p) = \mu_S(l;x_S;p+\pi) \qquad (a)$$

$$\mu_S(l;x_S;p+\pi) = \mu_S^*(l;p+\pi) + RT \ln x_S \qquad (b)$$

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V(p)dp$$

$$\mu_S^*(l;p+\pi) = \mu_S^*(l;p) + \int_{p}^{p+\pi} V_m^* dp \qquad (c)$$

Inserting eq (c) into eq (b),

$$\mu_S(l;x_S;p+\pi) = \mu_S^*(l;p) + \int_{p}^{p+\pi} V_m^* dp + RT \ln x_S \qquad (d)$$

From eqs (a) and (d),

$$\mu_S^*(l; p) = \mu_S^*(l; p) + \int_p^{p+\pi} V_m^* dp + RT \ln x_S$$

$$\therefore -RT \ln x_S = \int_p^{p+\pi} V_m^* dp$$

$$x_S = 1 - x_s$$

$\ln(1 - x_s) \cong -x_s$ when $x_s \ll 1$. V_m^* is not a function of pressure.

$$RTx_s = \pi V_m^*$$

$$x_s = \frac{n_s}{n_S + n_s} \cong \frac{n_s}{n_S}$$

$$RTn_s = \pi V_m^* n_S = \pi V$$

where $V_m^* n_S$ is the actual volume of the solvent (V).

van't Hoff equation

$$\pi V = n_s RT$$
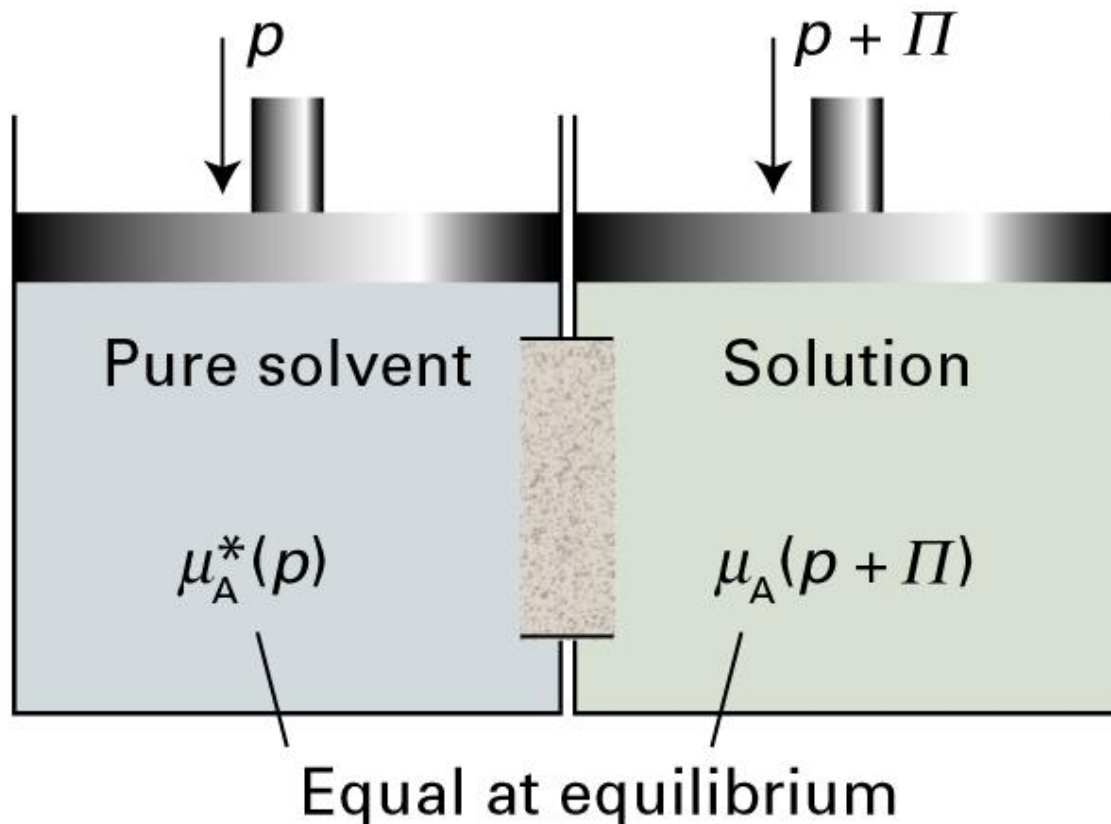
Figure 5.22
The equilibrium involved in the calculation of osmotic pressure, Π, is between pure solvent A at a pressure p on one side of the semipermeable membrane and A as a component of the mixture on the other side of the membrane, where the pressure is $p + \Pi$.

Solution

Height proportional to osmotic pressure

Solvent

Semipermeable membrance
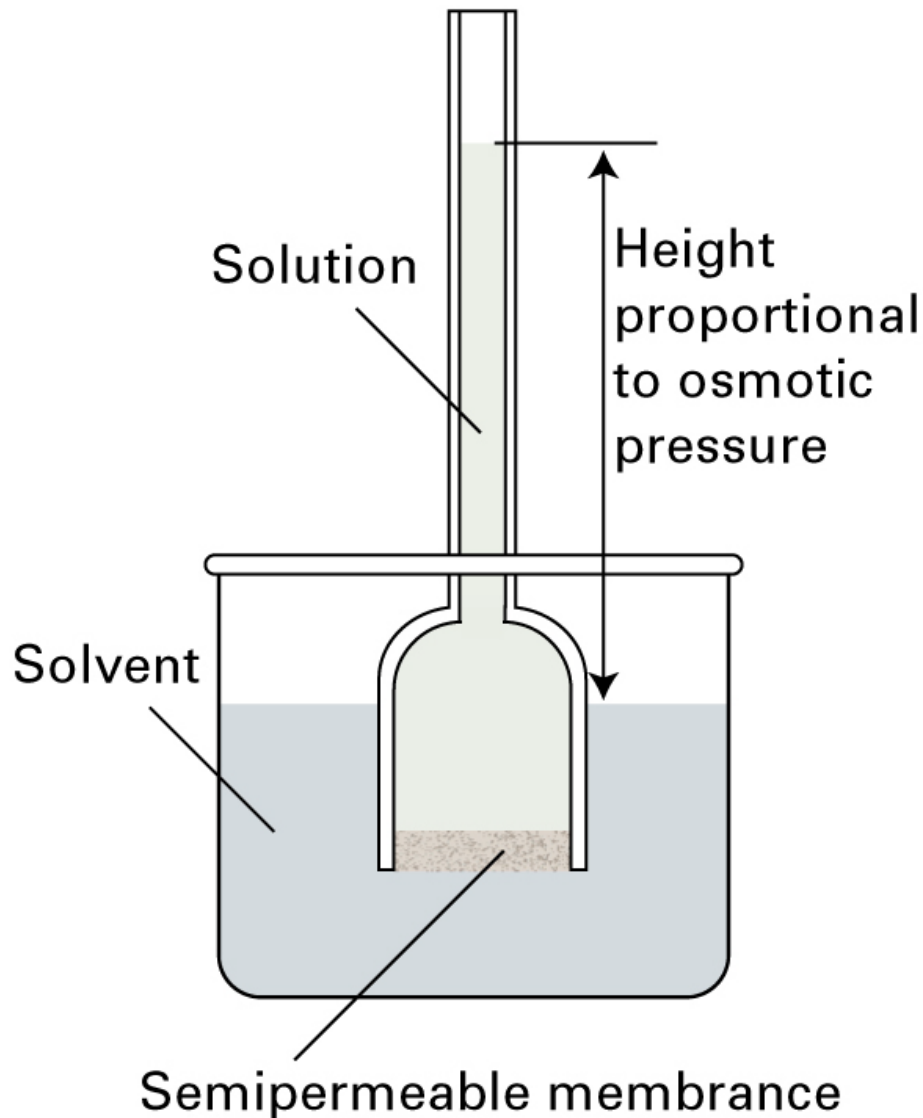
Figure 5.23
In a simple version of the osmotic pressure experiment, A is at equilibrium on each side of the membrane when enough has passed into the solution to cause a hydrostatic pressure difference.

Phase Rule   (*Lecture Note*)

F = number of degrees of freedom

$$\underline{F = C + 2 - P}$$

P = number of phases in equilibrium

C = number of components

(Derivation) For a system of *C* components and *P* phases

- The pressure and temperature: 2 variables

- Since $x_1 + x_2 + \cdots + x_c = 1$, one of the mole fractions is fixed if all the others have been specified. Specifying *C* – 1 mole fractions specifies the composition of a phase. There are *P* phases, and so the total number of composition variables is *P*(*C* – 1).

- The total number of variables = $P(C - 1) + 2$

-160509(월)
-160511(수) 휴강
-160516(월) Quiz 2

The presence of equilibria between phases reduces the freedom.

- Let the chemical potential of one of the components be μ_j.

- At equilibrium,

$$\underline{\mu_j(\text{phase}1) = \mu_j(\text{phase}2) = \cdots = \mu_j(\text{phase}P)}$$

- (P - 1) equations have to be specified by the components j. There are C components, and so the total number of equations that have to be satisfied is $C(P\text{-}1)$. Every equation reduces the freedom to vary one of the $P(C\text{-}1)+2$ variables.

$$\therefore \underline{F} = P(C-1) + 2 - C(P-1) = \underline{C + 2 - P}$$
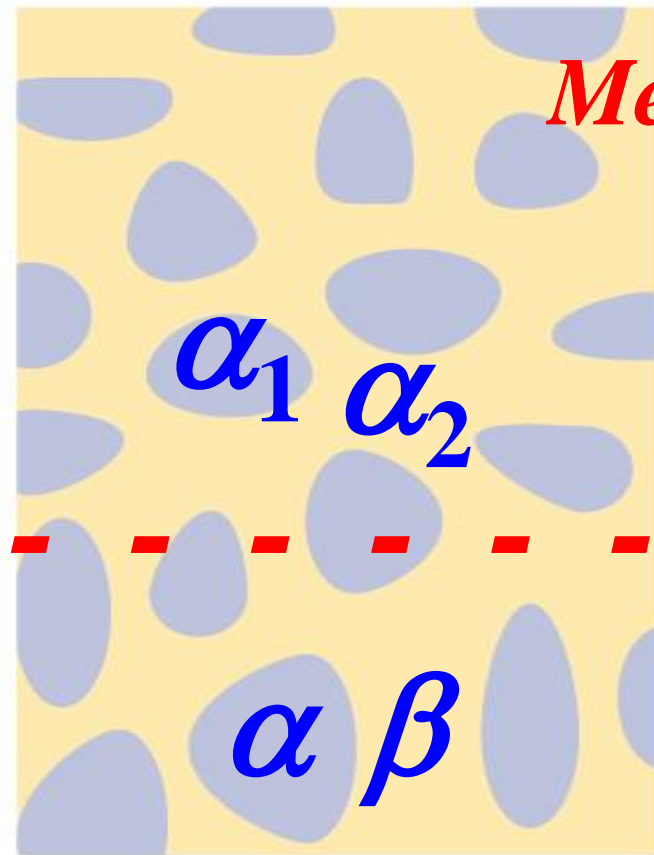
(a) A single-phase solution, in which the composition is uniform on a microscopic scale.
(b) Regions of one composition are embedded in a matrix of a second composition.

Solid Liquid Vapour phase diagram showing Pressure, p versus Temperature, T, with the Triple point at T_3 and the Critical point at T_c.
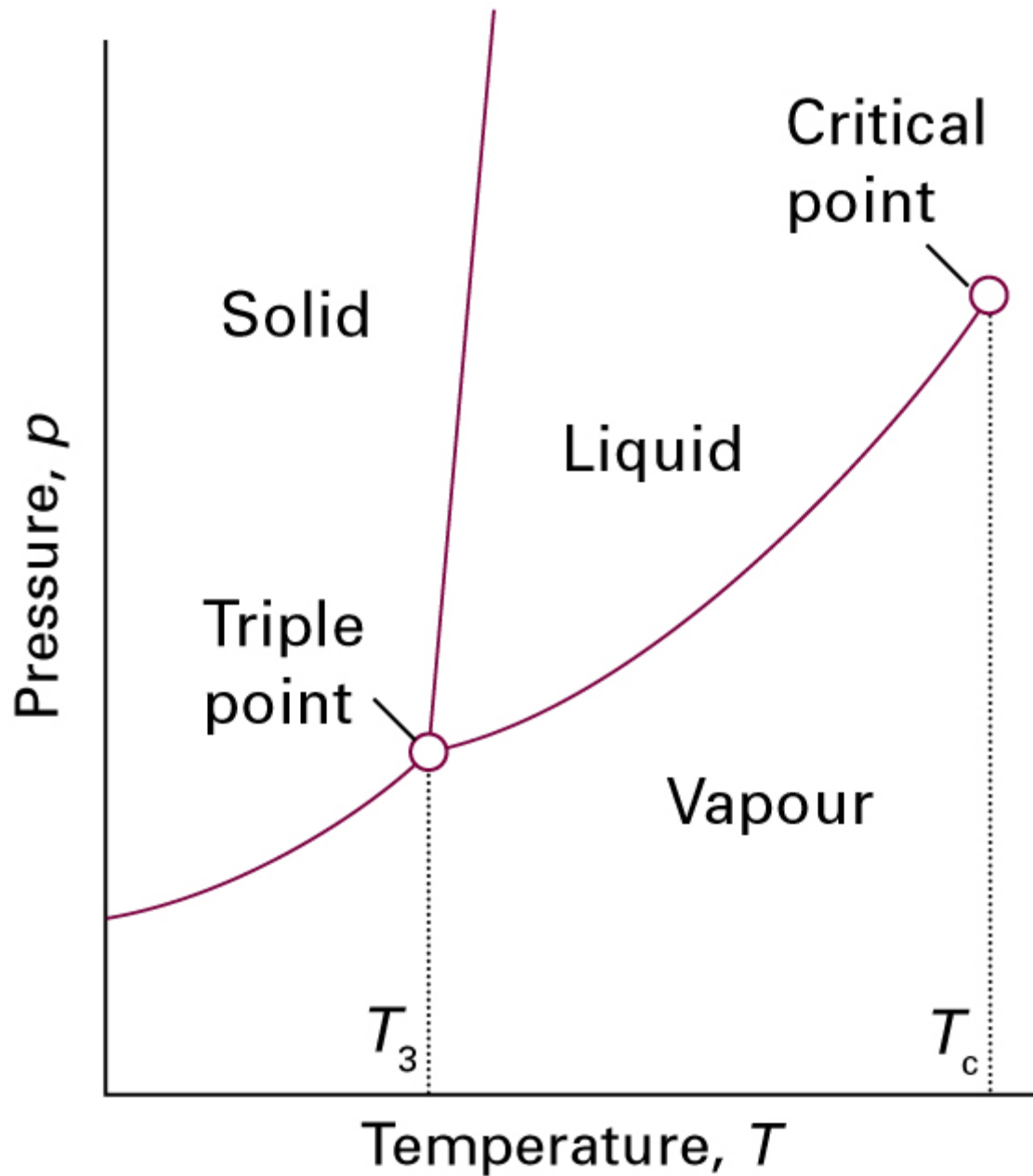
$$F = C + 2 - P = 3 - P$$
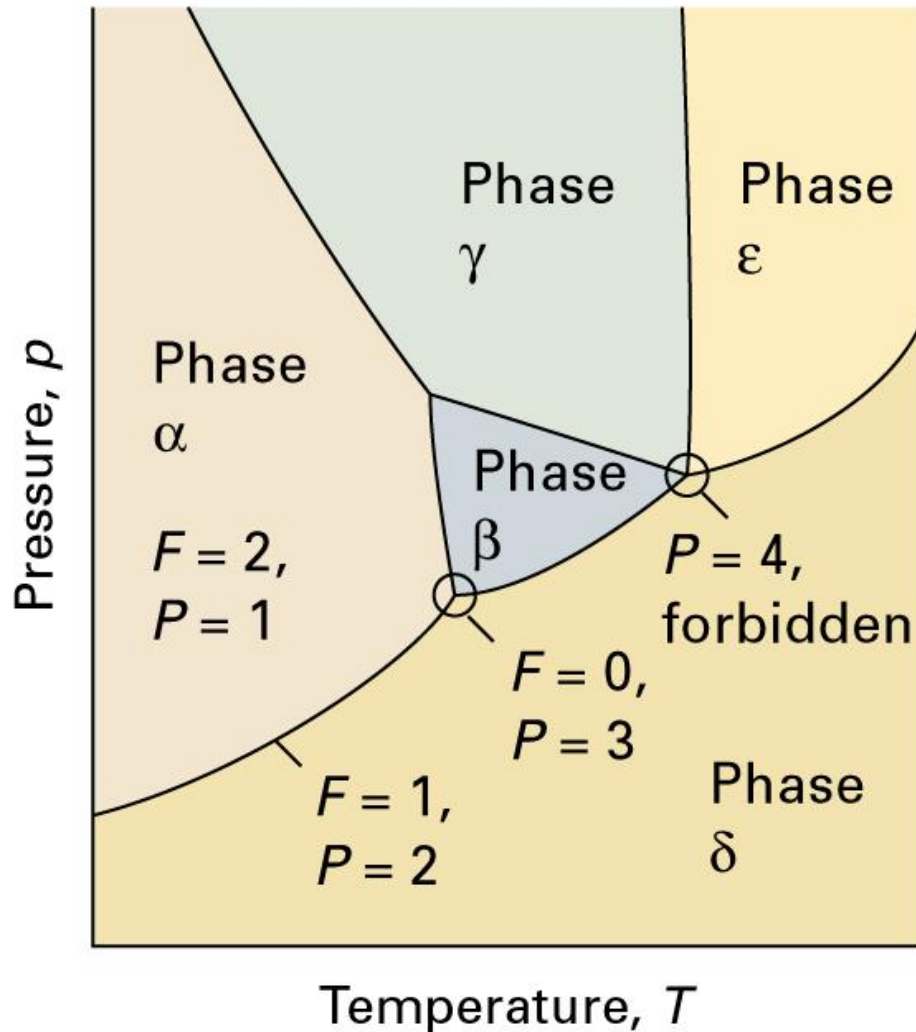
The typical regions of
<u>a one-component phase diagram</u>.
The lines represent conditions under
which the two adjoining phases are in
equilibrium. A point represents the
unique set of conditions under which
three phases coexist in equilibrium.

**<u>Four phases cannot mutually
coexist in equilibrium.</u>**

One component systems

$C = 1$

$\therefore F = 3 - P$

$$F = C + 2 - P$$

Two-component systems

$C = 2$

$\therefore F = 4 - P$

For simplicity we can agree to keep the pressure constant (at 1 *atm*) and so one of the degrees of freedom has been discarded. Now $F'=3-P$.

$F'=3-P$ $\rightarrow$ a maximum value of 2. One of these remaining degrees of freedom is the temperature and the other is the composition. Hence, one form of the phase diagram is <u>a map of temperature and composition</u> at which each phase is stable.

5C.1(a) Vapor-Pressure Diagrams

For an <u>ideal solution</u>,

$$p_A = x_A p_A^*$$

$$p_B = x_B p_B^*$$

where p_A^* and p_B^* are the vapour pressure of the pure liquids at that temperature.

$$
\begin{aligned}
p = p_A + p_B &= x_A p_A^* + x_B p_B^* \\
&= x_A p_A^* + (1 - x_A) p_B^* \\
&= p_B^* + (p_A^* - p_B^*) x_A
\end{aligned}
\qquad (1)
$$
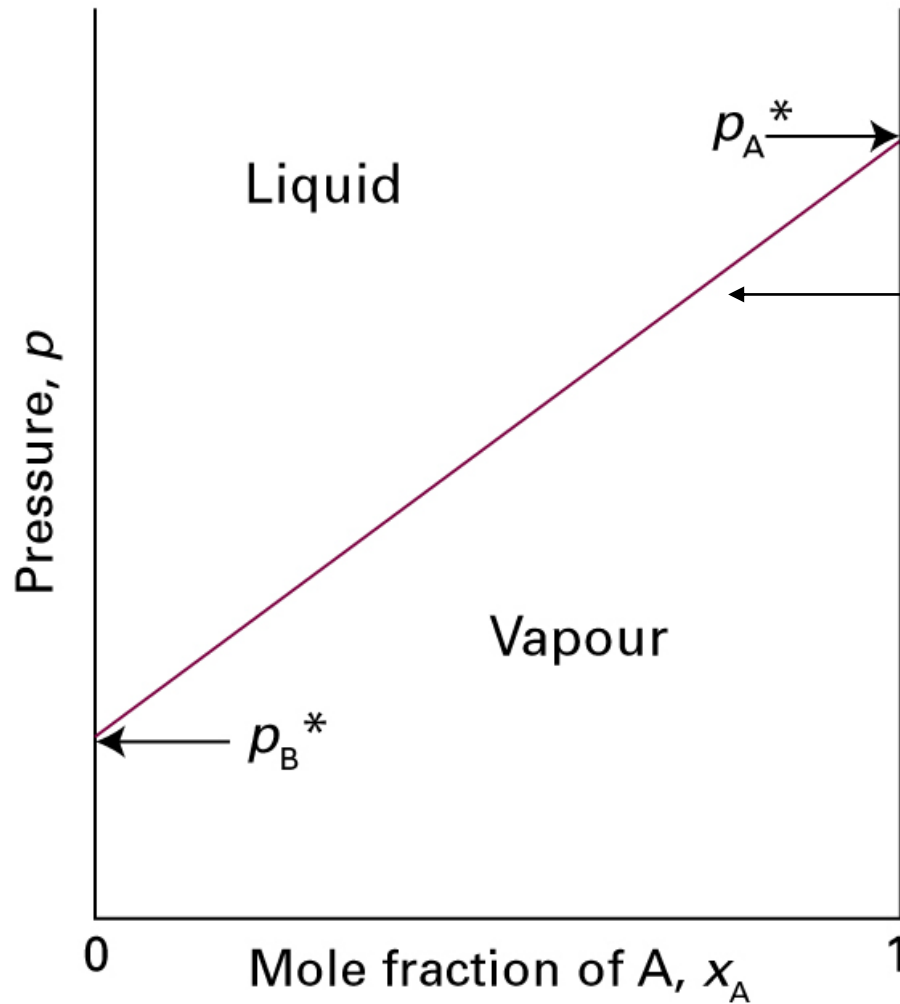
$$p = p_B^* + (p_A^* - p_B^*)x_A$$

Figure 5C.1
The variation of the total vapor pressure of a binary mixture with the mole fraction of A in the liquid when **<u>ideal solution</u>** (Raoult's law) is obeyed.

5C.1(c) Derivation of <u>Lever Rule</u>

(Lecture Note)

Let the overall composition be z_A, z_B, the amount of liquid $n(l)$, and of vapor $n(g)$. The total amount of material is n, and so

$$nz_A = n(l)x_A + n(g)y_A$$

and

$$nz_A = [n(l) + n(g)]z_A = n(l)z_A + n(g)z_A$$

therefore

$$n(l)(x_A - z_A) + n(g)(y_A - z_A) = 0$$

or

$$\frac{n(g)}{n(l)} = \frac{z_A - x_A}{y_A - z_A} = \frac{l}{l'}$$

Phase Diagram: **Weight %**, **Atomic %**, or **Mole %**

Equilibrium (Universe)
with Only *A* Atoms

(a)

(b)

(c)
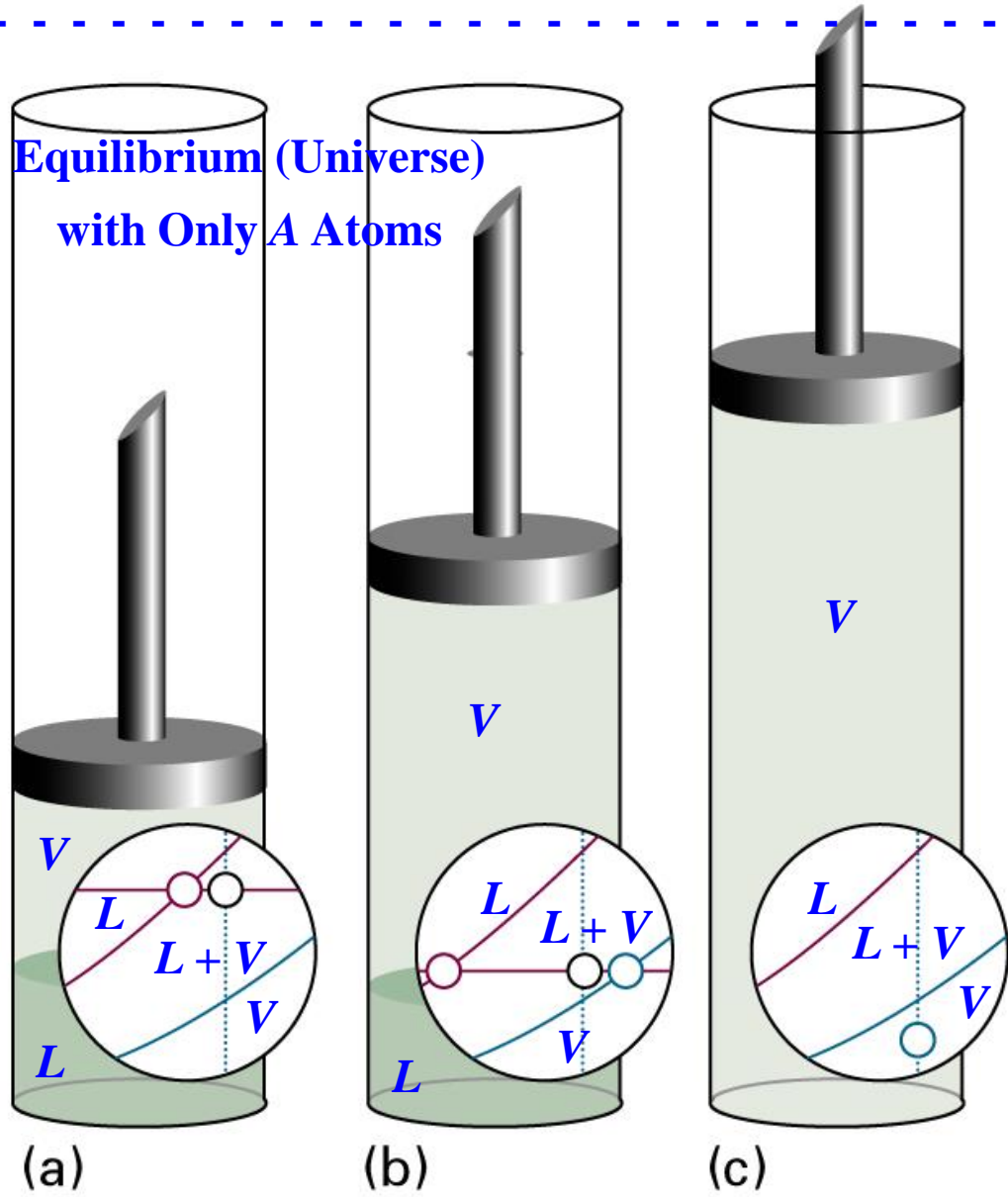
Figure 5C.6 *(skip)*

(a) A liquid in a container exists in equilibrium with its vapor. The superimposed fragment of the phase diagram shows the compositions of the two phases and their abundances (by the lever rule).

(b) When the pressure is changed by drawing out a piston, the compositions of the phases adjust as shown by the tie line in the phase diagram.

(c) When the piston is pulled so far out that all the liquid has vaporized and only the vapor is present, the pressure falls as the piston is withdrawn and the point on the phase diagram moves into the one-phase region.

It is more common **to distill** at constant pressure by raising the temperature.
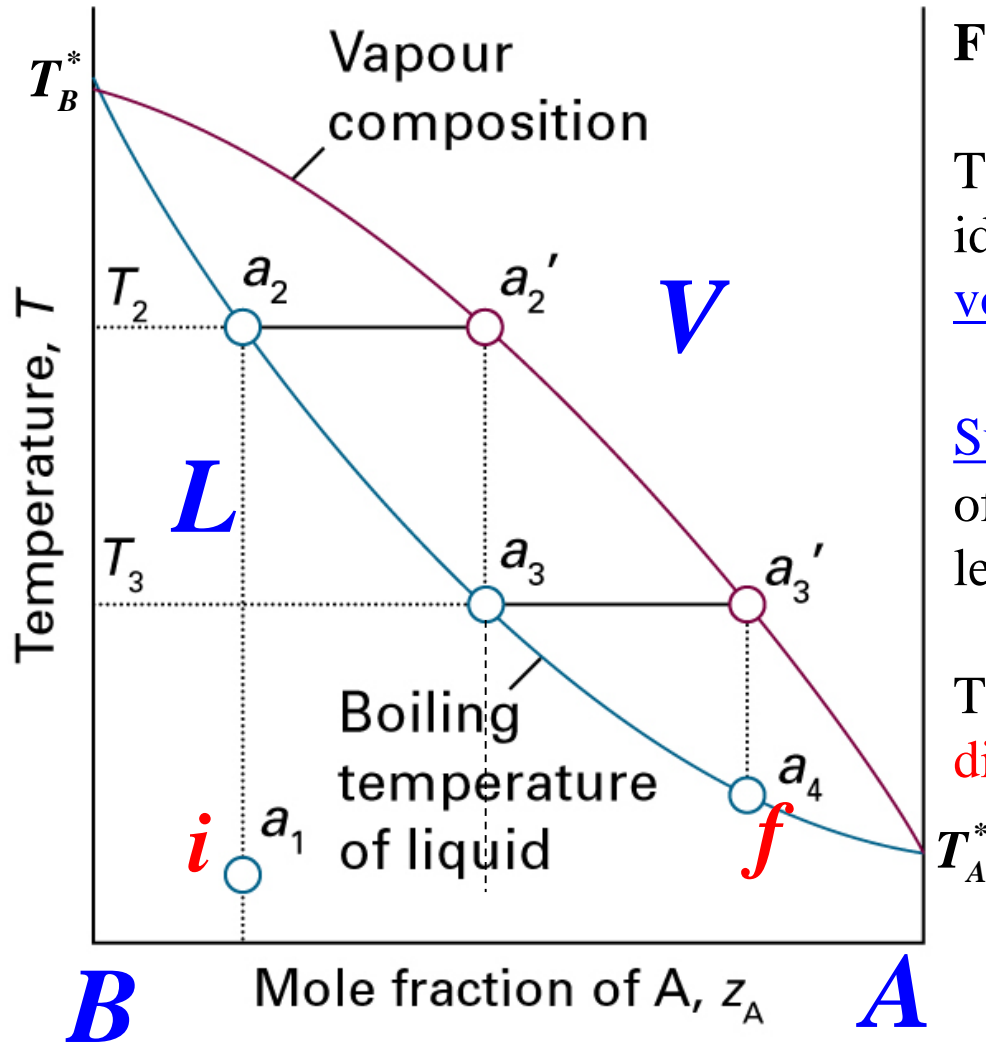
Figure 5C.10   증류

The phase diagram corresponding to an ideal mixture with the component <u>A more volatile</u> than component *B*.

<u>Successive</u> **boiling and condensation** of a liquid originally of composition a_1 leads to a condensate that is pure *A*.

The separation technique is called fractional distillation.

$G^S(x)$

$G^L(x)$

V (or L)

L (or S)

Vapour composition

Boiling temperature of liquid

Temperature, T

Mole fraction of A, z_A

a_4 a_4'

a_3 a_3'

a_2 a_2'

b a

0 1
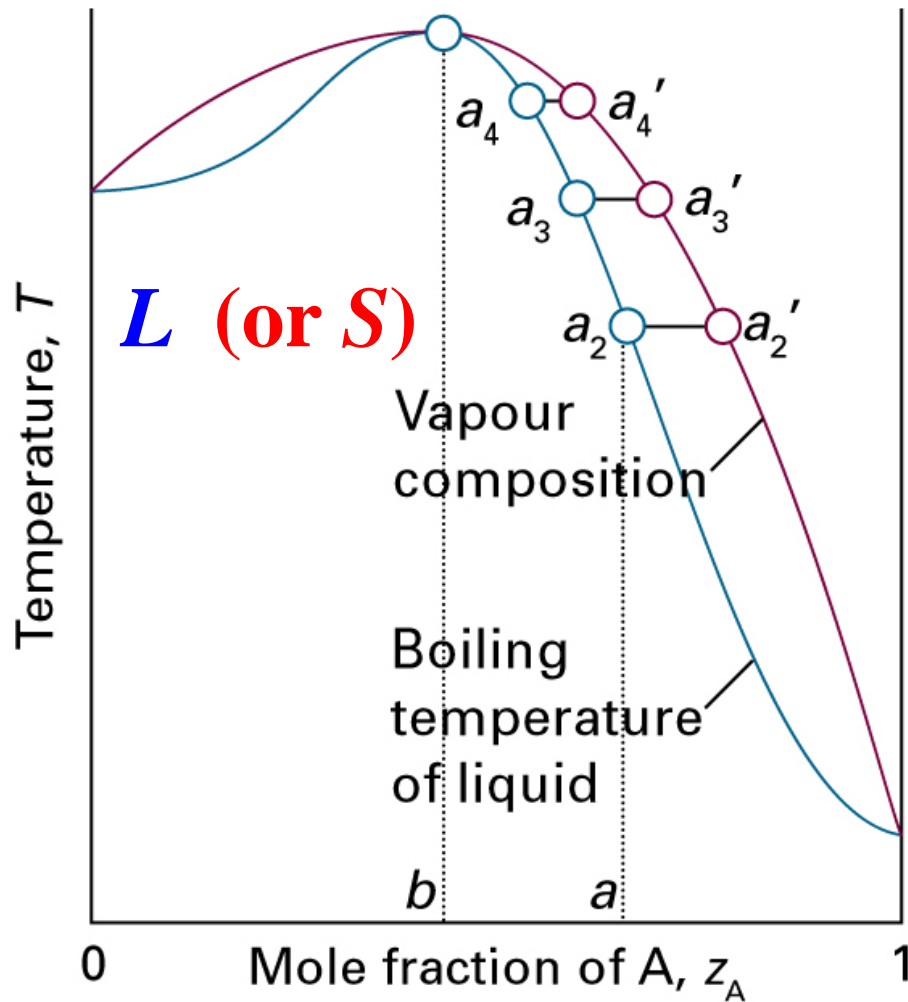
Figure 5C.12
When the liquid of composition a is distilled, the composition of the remaining liquid changes towards b but no further.

$G^S(x)$

$G^L(x)$
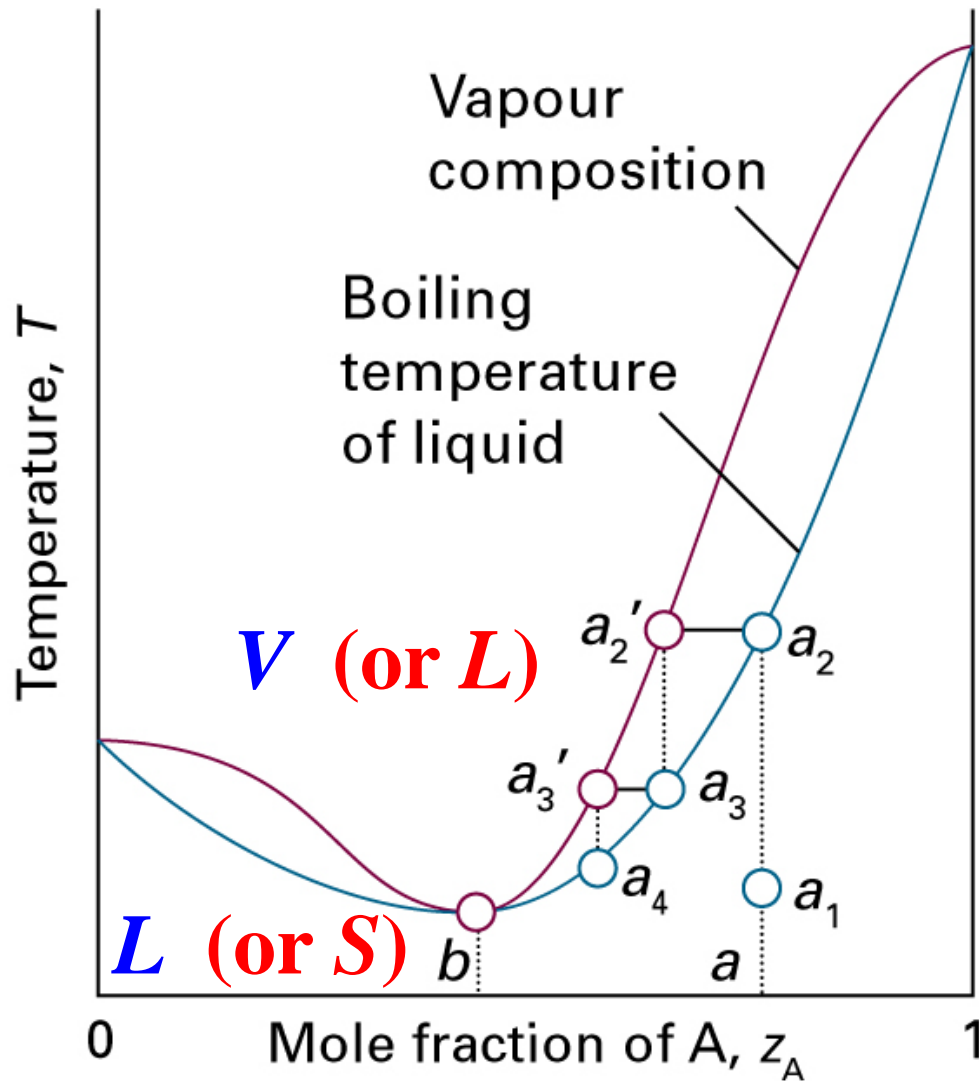
Figure 5C.13
When the mixture at *a* is fractionally <u>distilled</u>, the vapor in equilibrium in the fractionating column moves towards *b* and then remains unchanged.

5C.3 Liquid-Liquid (or Solid-Solid) Phase Diagrams

$$C=2, \quad \therefore F = 4 - P$$

Under conditions where the two liquids mix completely, only one phase is present and so *F'*=2, which indicates that both the temperature and composition may be varied independently. When <u>the two liquids do not mix</u>, like oil and water, *P*=2 and so *F*=2.

Consider two **partially miscible liquids** A and B.

The upper critical solution temperature is the temperature above which phase separation does not occur at any composition. It may seem quite natural that there should be upper critical solution temperatures, where the more violent molecular motion overcomes the tendency of molecules of the same species to stick together in swarms and therefore to form two phases.

However, some systems show a lower critical solution temperature beneath which they mix in all proportions and above which they form two layers: e.g. water/ triethylamine. Some systems show both UCST and LCST: e.g. water/nicotine (see Figure 5C.23).
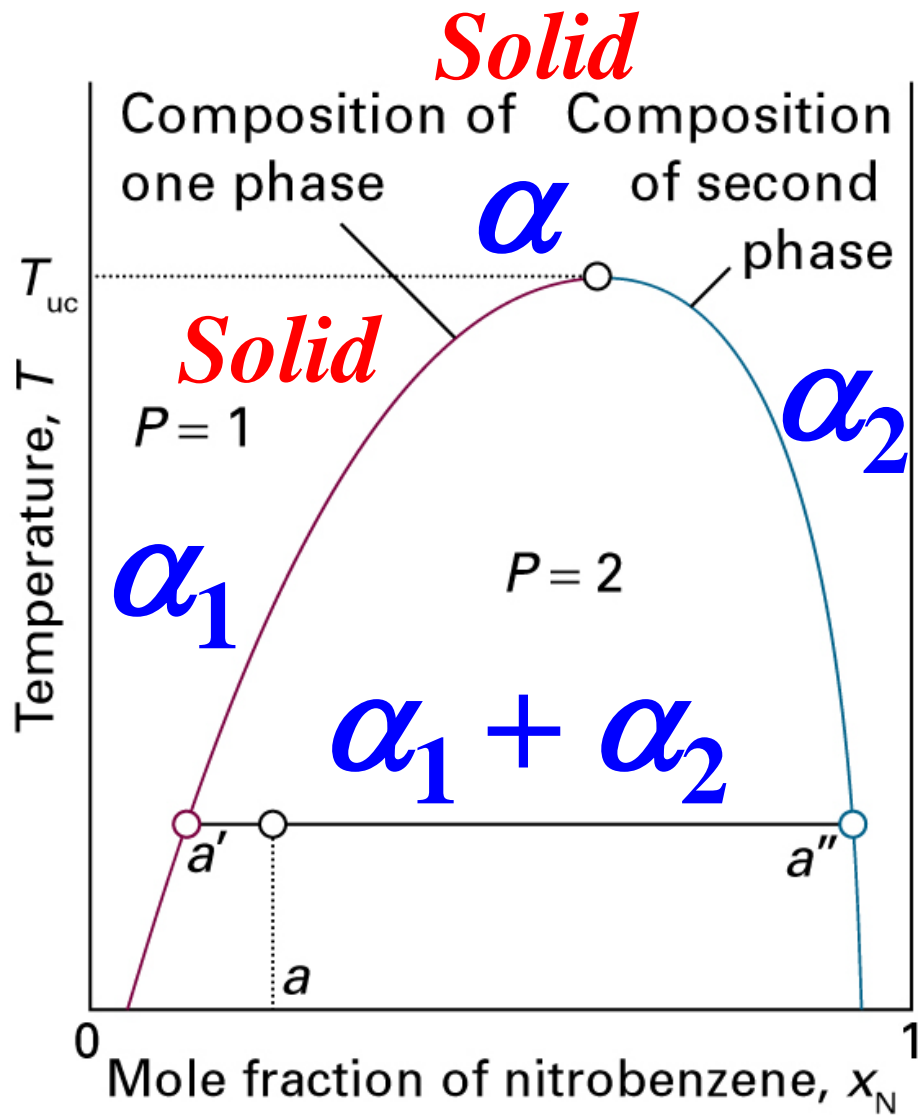
Figure 5C.15

The region below the curve corresponds to the compositions and temperatures at which the liquids form two phases.

The upper critical temperature is the temperature above which the two liquids are miscible in all proportions.
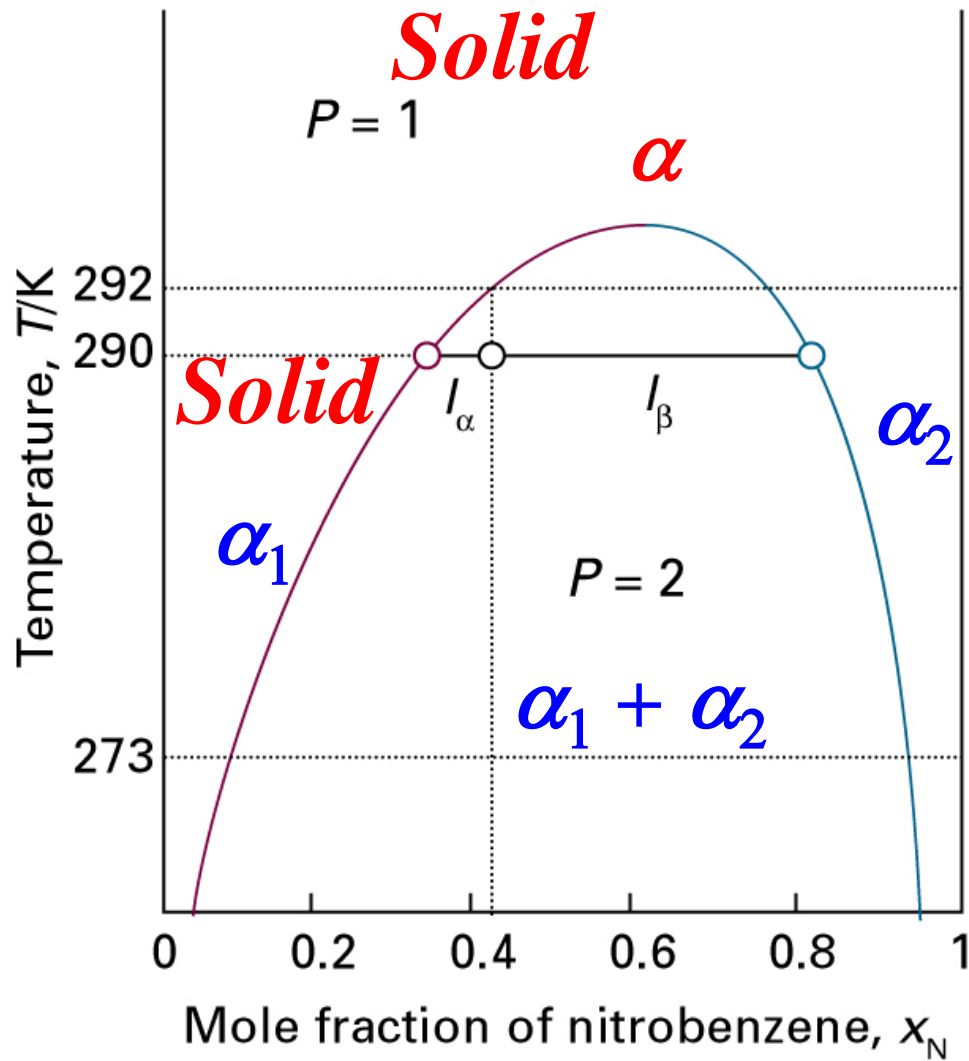
Figure 5C.16
The temperature-composition diagram for hexane and nitrobenzene at 1 *atm* again, with the points and lengths discussed in the text.
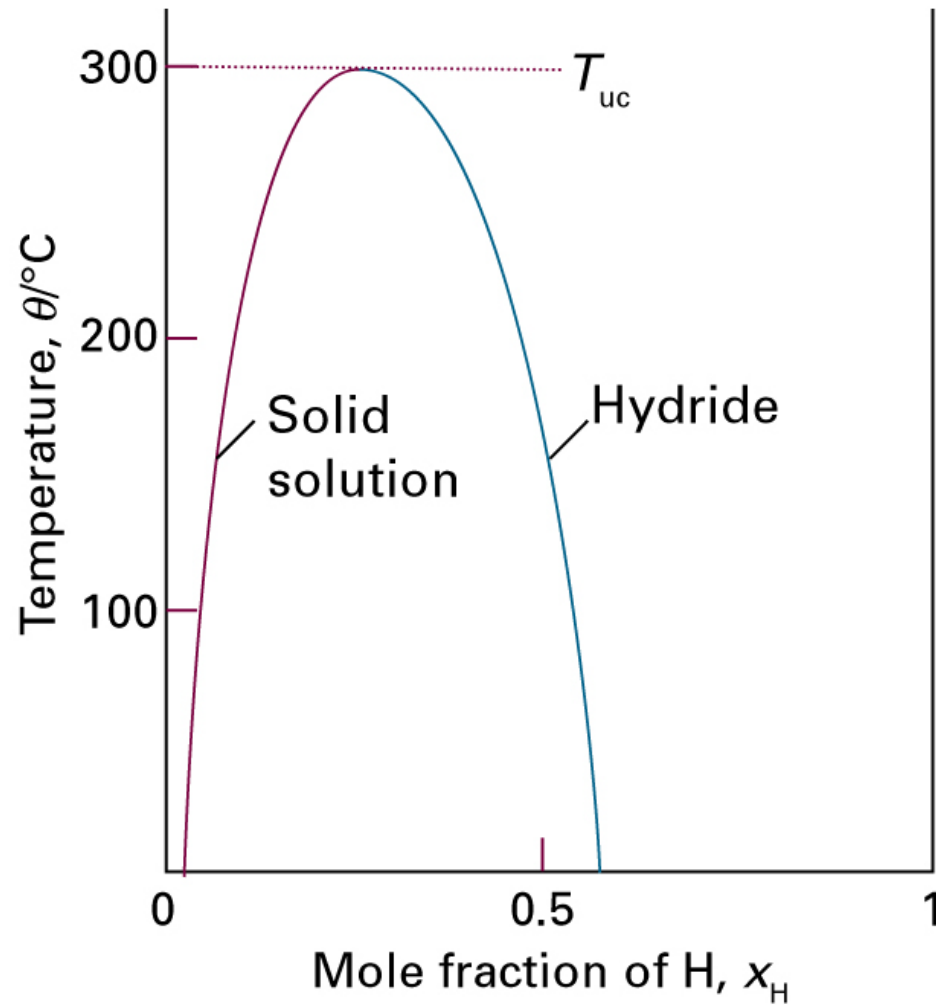
Figure 5C.17
The phase diagram for palladium and palladium hydride, which has an
upper critical temperature at 300˚C.
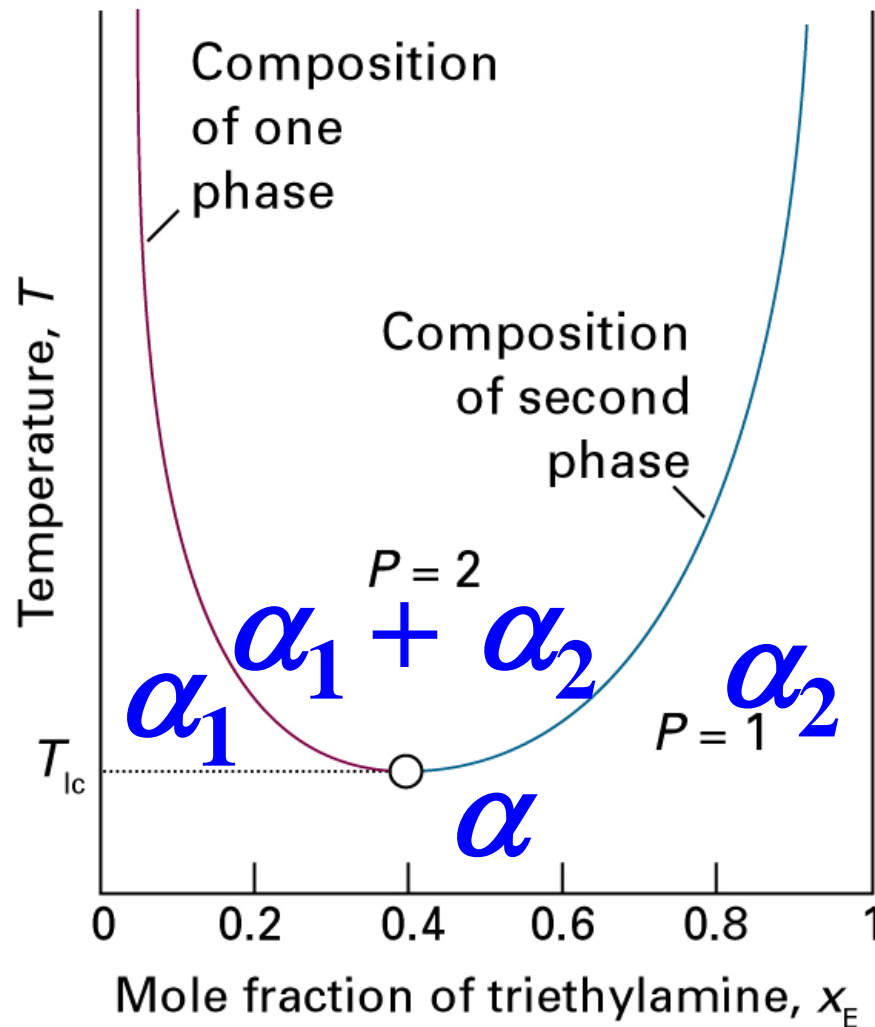
Figure 5C.22

The temperature-composition diagram for water and triethylamine. This system shows a lower critical temperature at 292 K. The labels indicate the interpretation of the boundaries.
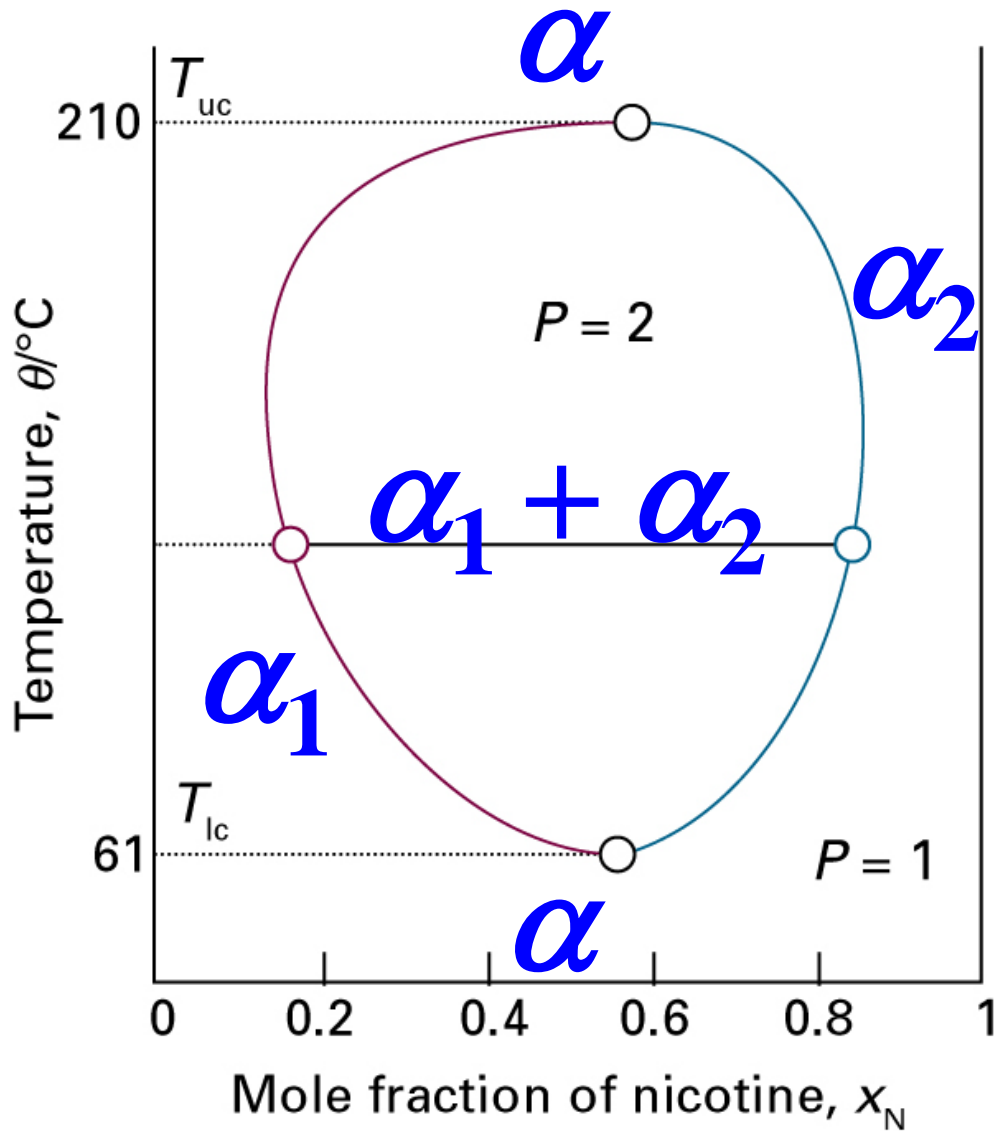
Figure 5C.23
The temperature-composition diagram for water and nicotine, which has both upper and lower critical temperatures.

Phase diagram for two components that become fully miscible before they boil.
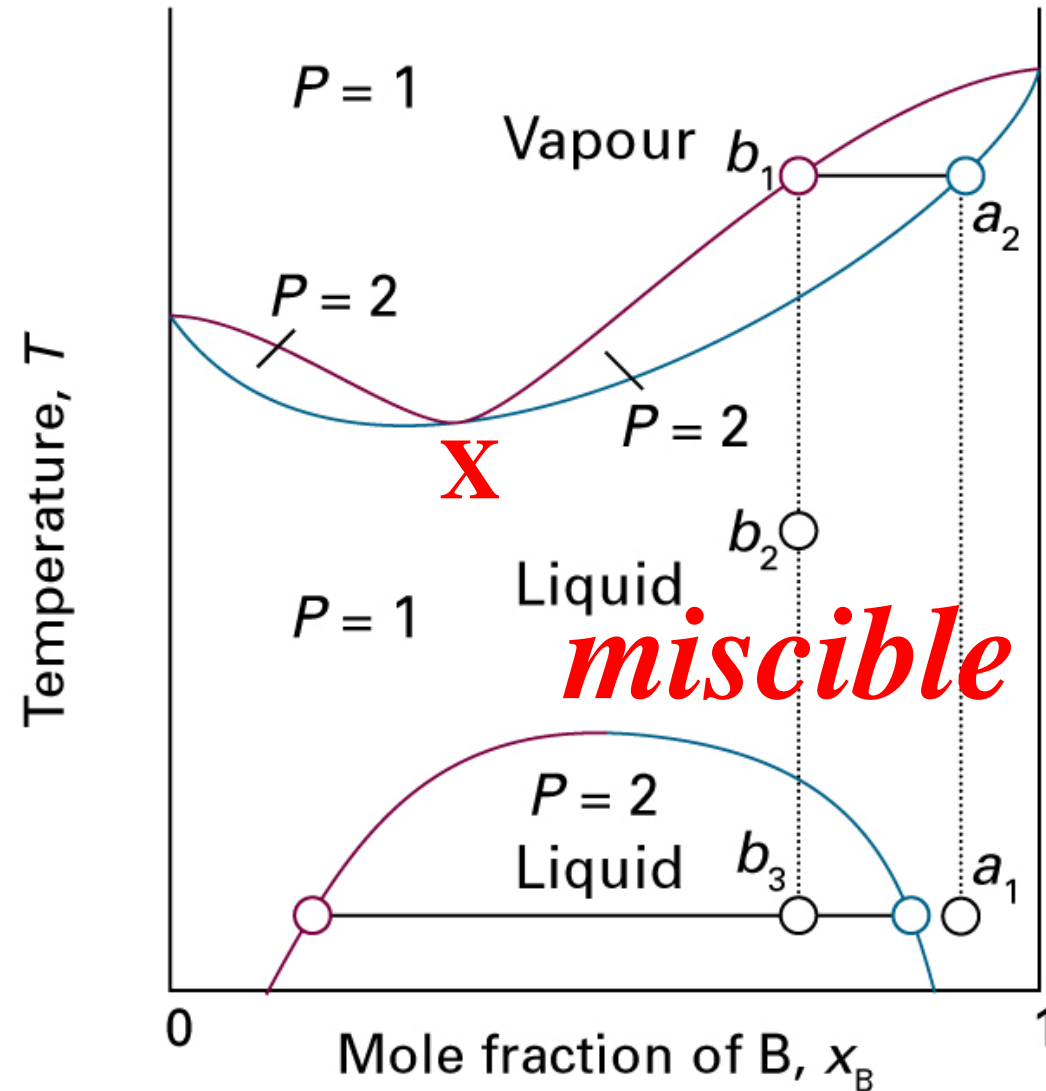
Figure 5C.24
The temperature-composition diagram for a binary system in which the upper critical temperature is less than the boiling point at all compositions.

Eutectic Phase Diagram (p. 212)

Binary system in which boiling occurs before the two liquids are fully miscible.
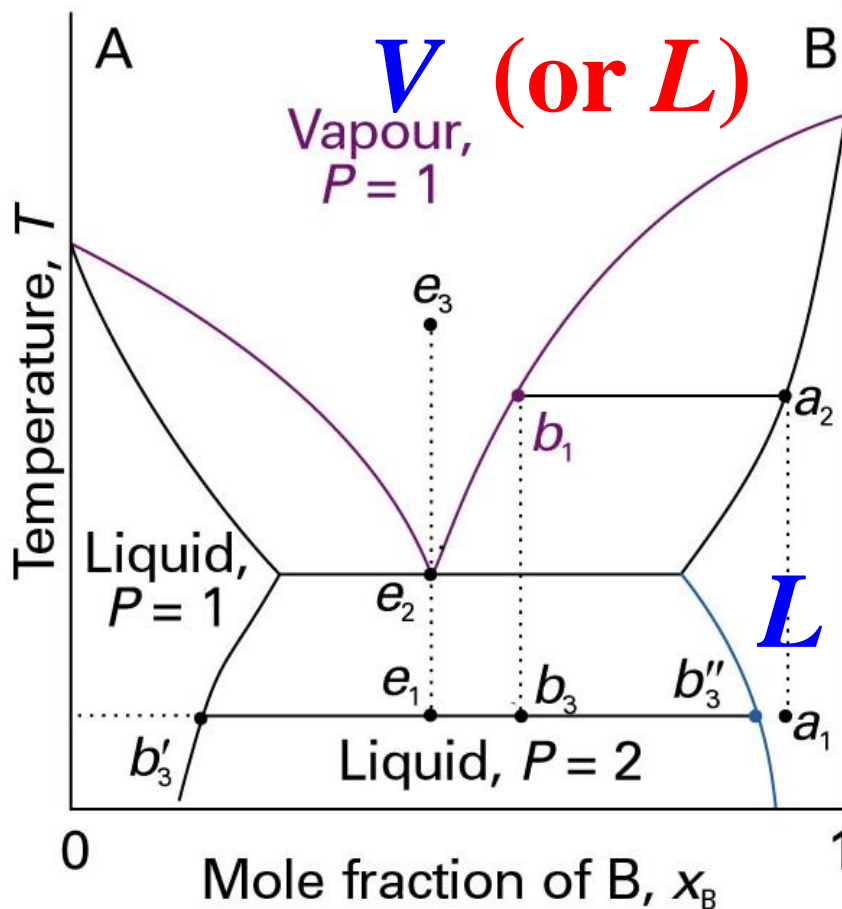
Figure 5C.25
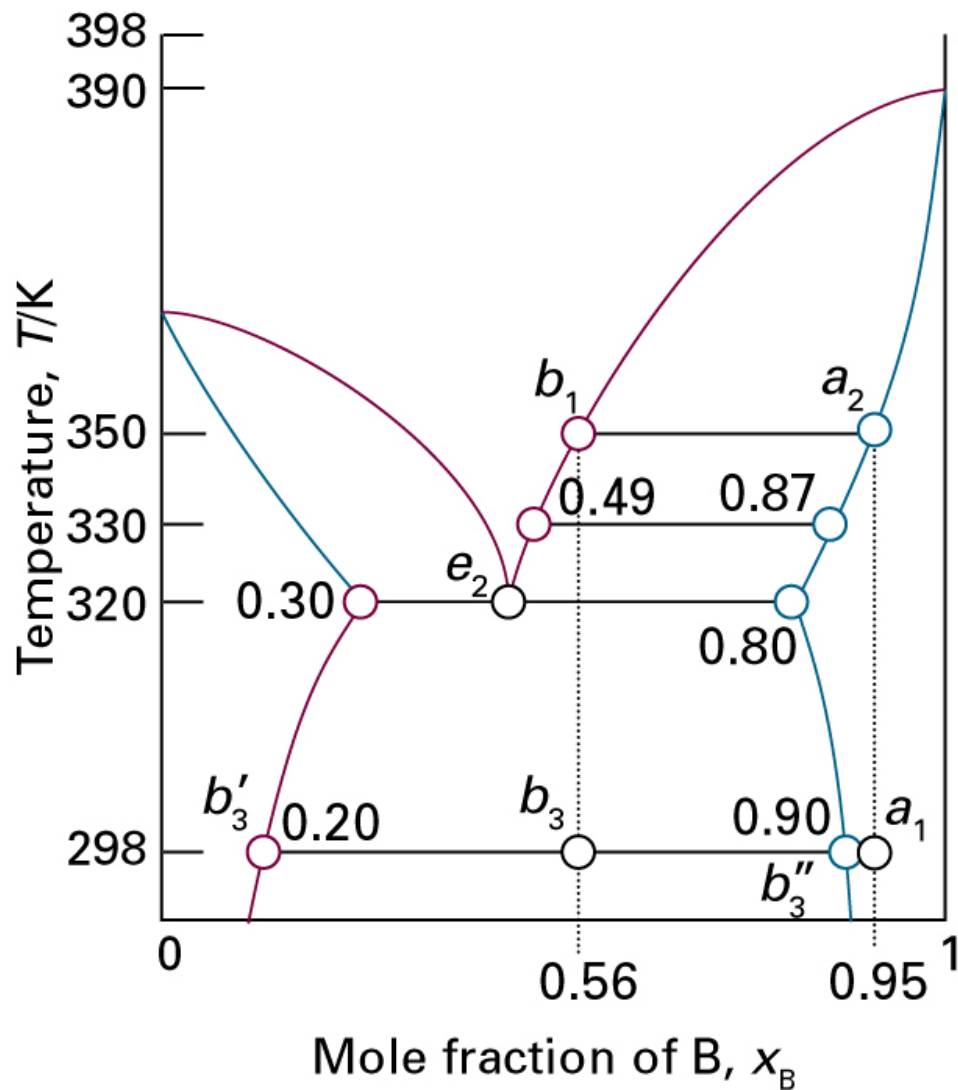The temperature-composition diagram for a binary system in which boiling occurs before the two liquids are fully miscible.

Figure 5C.26
The points of the phase diagram in Figure 5C.25 that are discussed in Example 5C.3.

5C.4 Liquid-Solid Phase Diagrams

Solid and liquid phases may both be present in a system at temperatures below the boiling point. An example is a pair of metals that are (almost) completely immiscible right up to their melting points (such as antimony and bismuth).

Consider the two-component liquid of composition a_1 in Figure 5.51. The change that occur may be expressed as follows.

(1) $a_1 \rightarrow a_2$. The system enters the two-phase region labeled "Liquid+B". Pure solid B begins to come out of solution and the remaining liquid becomes richer in A.

(2) $a_2 \rightarrow a_3$. More of the solid forms, and the relative amounts of the solid and liquid (which are in equilibrium) are given by the lever rule. At this stage there are roughly equal amounts of each. The liquid phase is richer in A than before (its composition is given by b_3) because some B has been deposited.

(3) $a_3 \rightarrow a_4$. At the end of this step, there is less liquid than a_3, and its composition is given by e. This liquid now freezes to give a two-phase system of pure B and pure A.
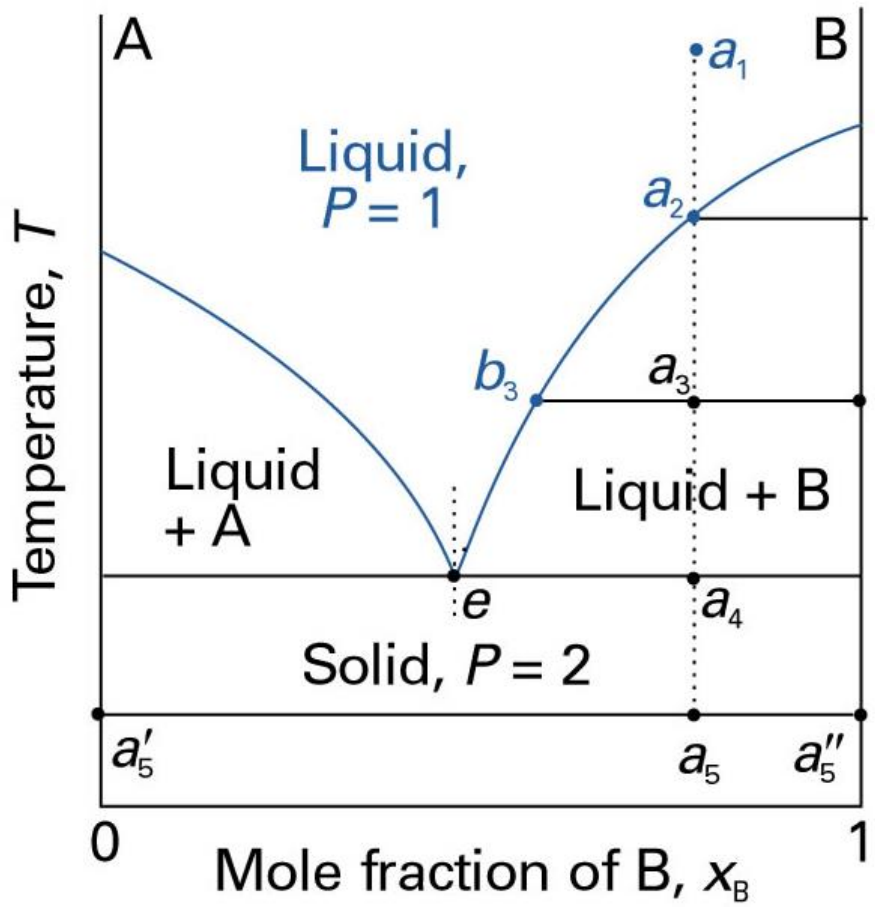
5C.4(a) Eutectics

Figure 5C.27

The temperature-composition phase diagram for two almost immiscible solids and their completely miscible liquids.

Note the similarity to Figure 5C.25.

The **eutectic point** e corresponds to the eutectic composition + temperature, having the lowest melting point.

Heat-capacity measurements (or heating/cooling curves) are used to construct the phase diagram.

Figure 5C.28

The cooling curves for the system shown in Figure 5C.25.

For a, the rate of cooling slows at a_2 because solid B deposits from liquid.

There is a complete halt at a_4 while the eutectic solidifies. This halt is longest for the eutectic e.
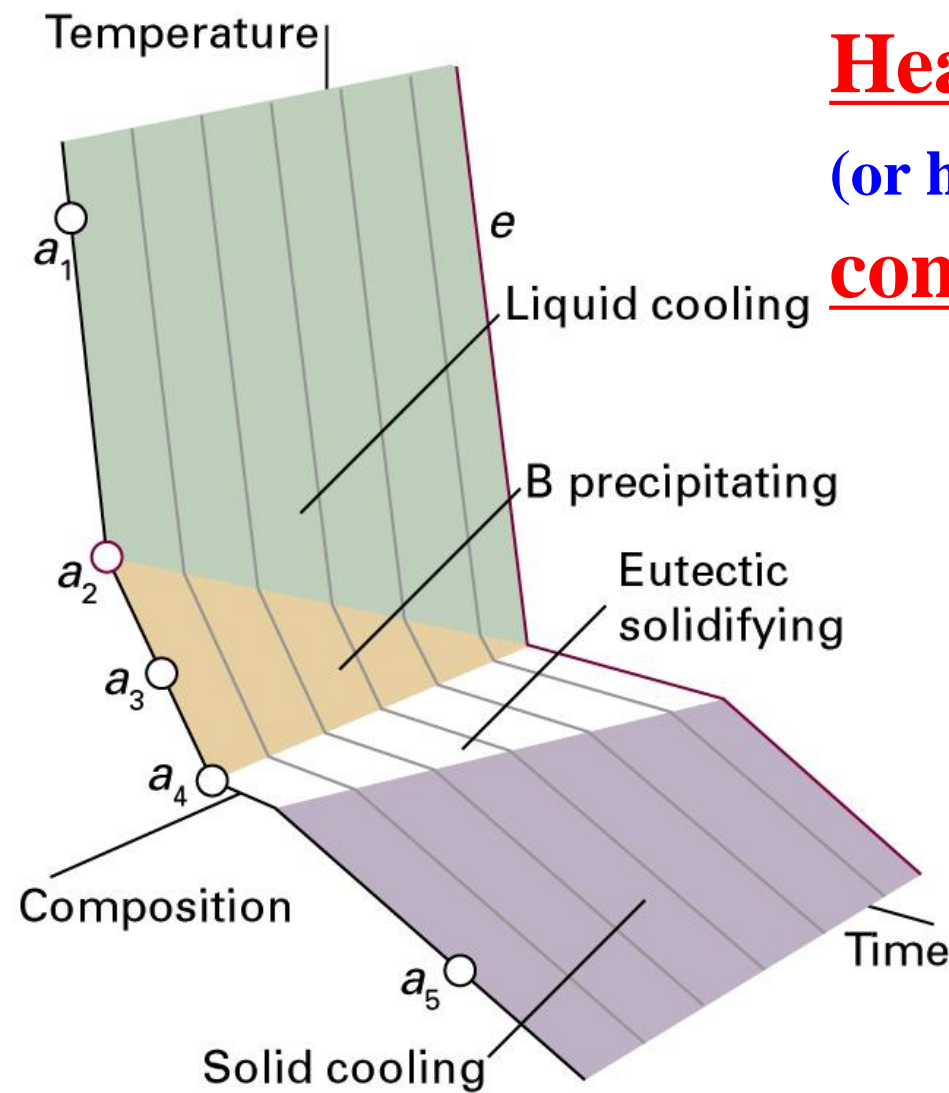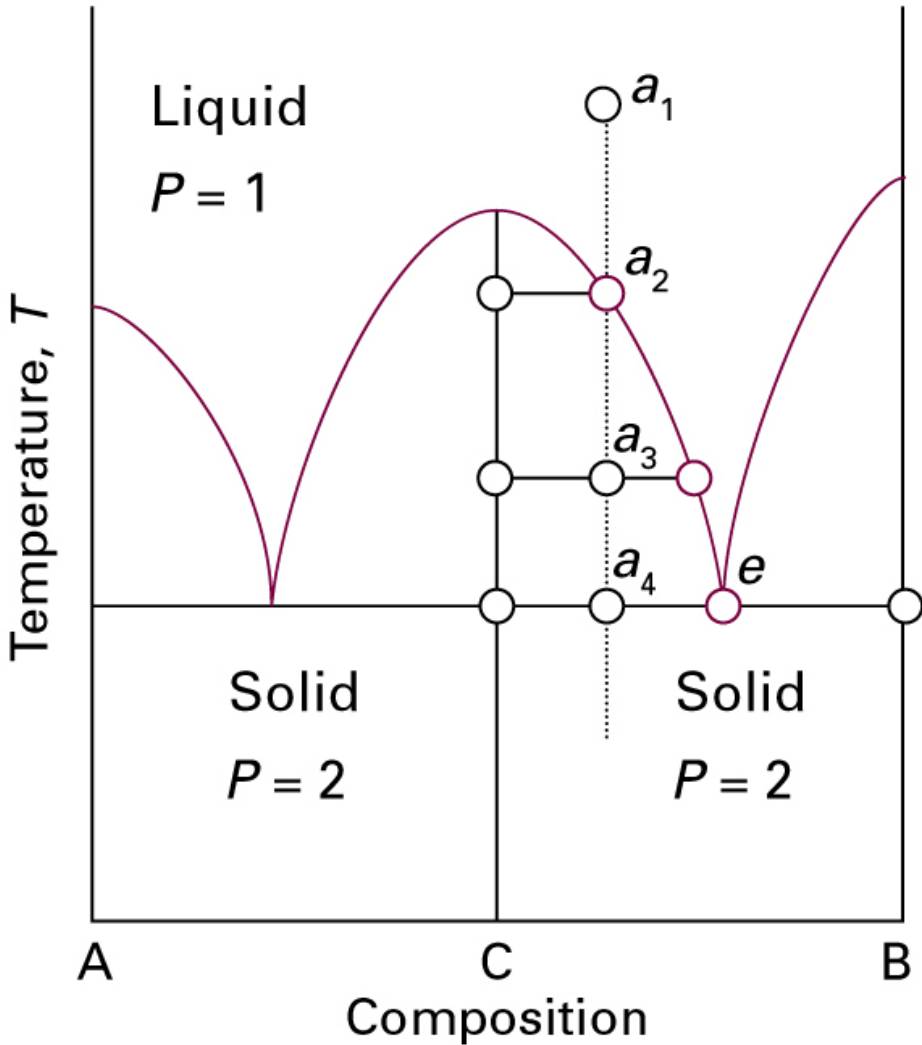
5C.4(b) Reacting System
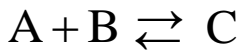
$A + B \rightleftarrows C$

Figure 5C.30
The phase diagram for a system in which A and B react to form a compound C = AB.

The constituent C is a true compound (phase), not just an equimolar mixture.

The pure compound C melts

congruently, that is, the composition of the liquid it forms is the same as that of the solid compound.
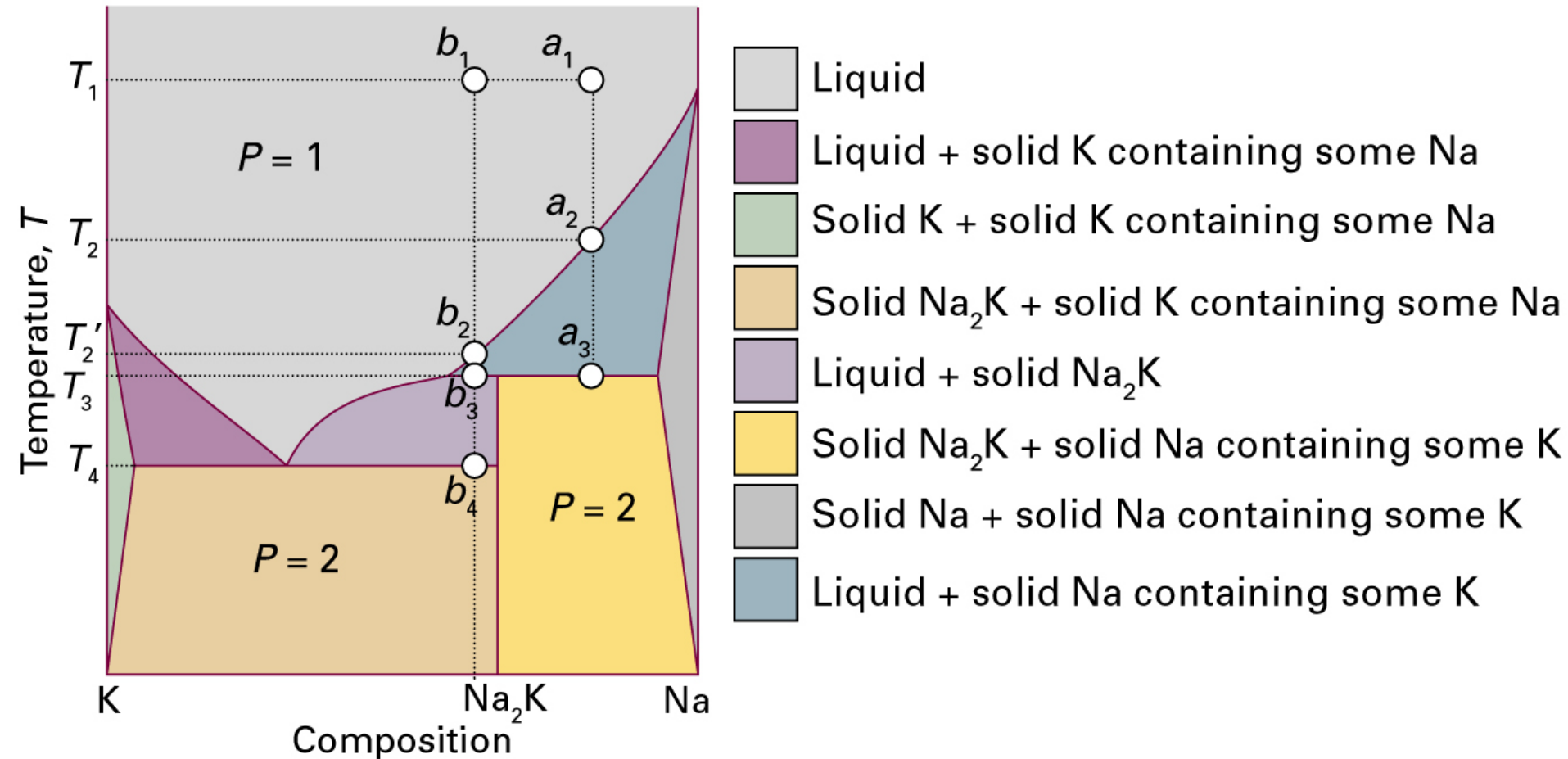
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Figure 5C.31

The phase diagram for an actual system (sodium and potassium) like that shown in Figure 5C.30, but with two differences. One is that the compound is Na_2K, corresponding to A_2B and not AB as in that illustration. The second is that the compound exists only as the solid, not as the liquid. The transformation of the compound at its melting point is an example of **incongruent** melting.

1. $a_1 \to a_2$. A solid solution rich in Na is deposited, and the remaining liquid is richer in K.

2. $a_2 \to$ just below a_3. The sample is now entirely solid, and consists of a solid solution rich in Na and a solid Na_2K.

Consider the isopleth through b_1:

1. $b_1 \to b_2$. No obvious change occurs until the phase boundary is reached at b_2 when a solid solution rich in Na begins to deposit.

2. $b_2 \to b_3$. A solid solution rich in Na deposits, but at b_3 a reaction occurs to form Na_2K: this compound is formed by the K atoms diffusing into the solid Na.

3. b_3. At b_3, three phases are in mutual equilibrium: the liquid, the compound Na_2K, and a solid solution rich in Na. The horizontal line representing this three-phase equilibrium is called a

<u>peritectic</u> line.

4. $b_3 \to b_4$. As cooling continues, the amount of solid compound increases until at b_4 the liquid reaches its eutectic composition. It then solidifies to give a two phase solid consisting of a solid solution rich in K and solid Na_2K.

No liquid Na_2K forms at any stage because it is too unstable to exist as a liquid.

This is an example of incongruent melting, in which a compound melts into its component and does not itself form a liquid phase.
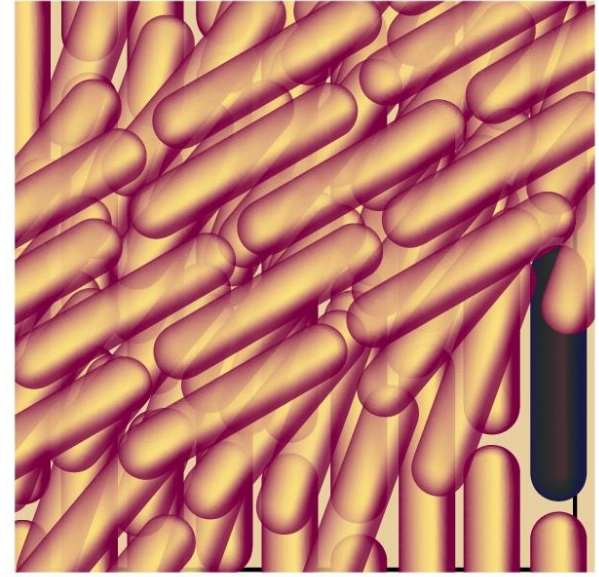
Liquid Crystals   (p. 188)

A *mesophase* is a phase intermediate between solid and liquid. When the solids melts, some aspects of the long-range order characteristic of the solid may be retained and the new phase may be a *liquid crystal*, a substance having liquid-like imperfect long-range order in at least one direction in space but positional or orientational order in at least one other direction.
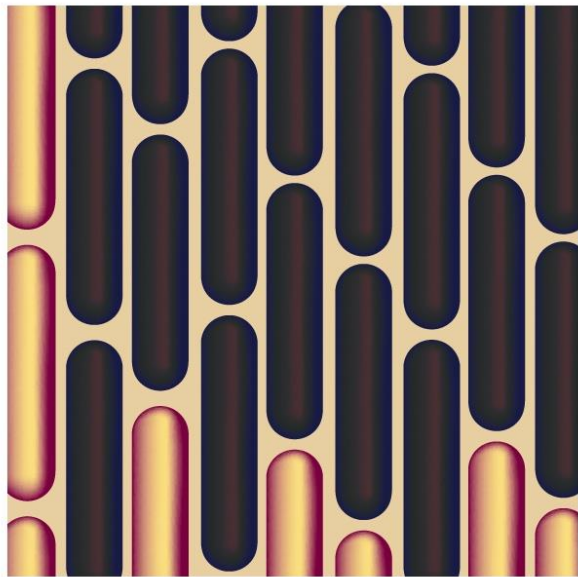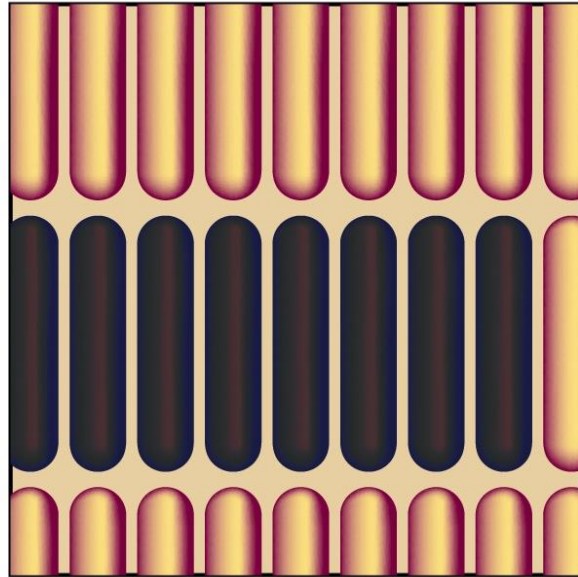

(a)   (b)   (c)

The arrangement of molecules in (a) the nematic phase, (b) the semectic phase, and (c) the cholesteric phase of liquid crystals. In the cholesteric phase, the stacking of layers continues to give a helical arrangement of molecules.

5E Real Solutions and Activities (p. 220)

Raoult's Law: $p_A = p_A^* x_A$ **Ideal Solution**

Henry's Law: **Dilute Solution**

The vapor pressure of the solute depends linearly on the amount of solute present at low concentrations.
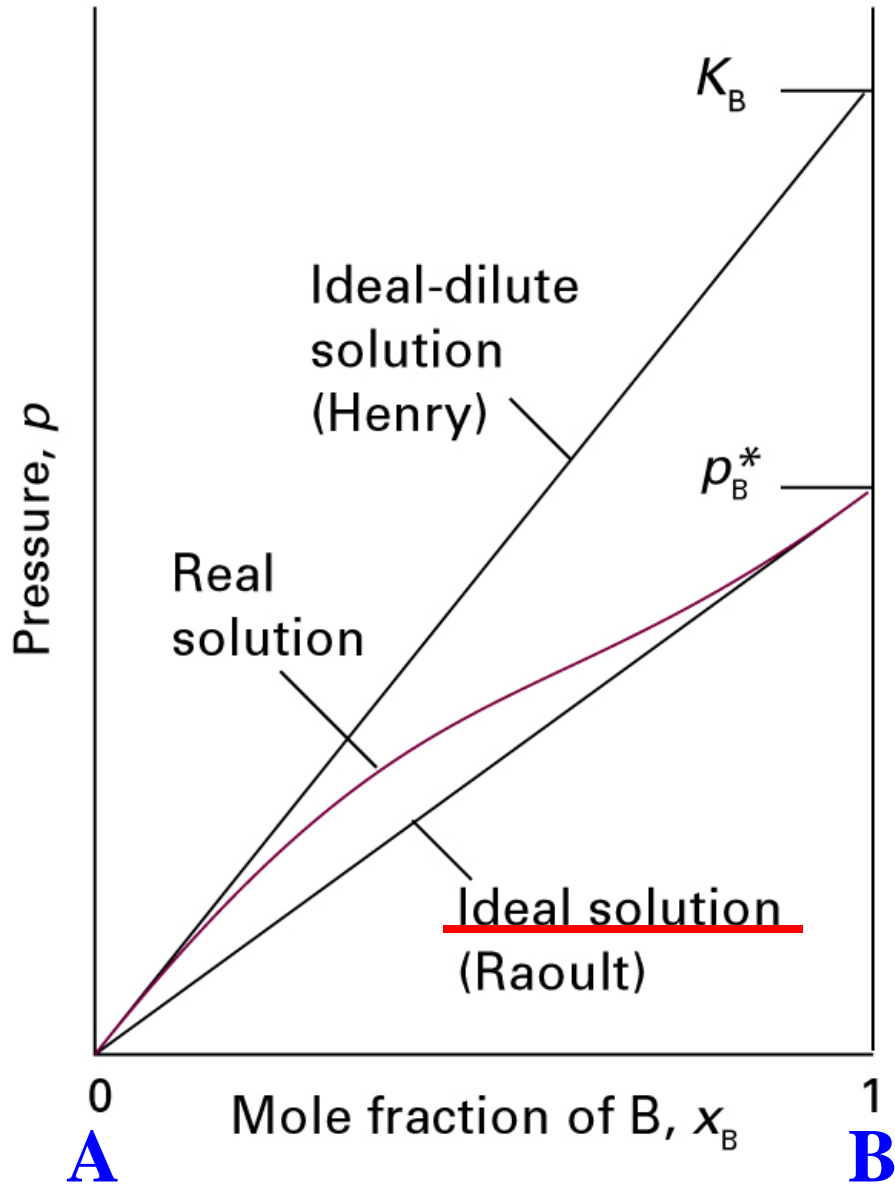
When a component (the solvent) is nearly pure, it has a **<u>vapor pressure</u>** that is proportional to the mole fraction with a slope p_{B^*} (Raoult's law).

When it is the minor component (the solute), its vapor pressure is still proportional to the mole fraction (Henry's law).
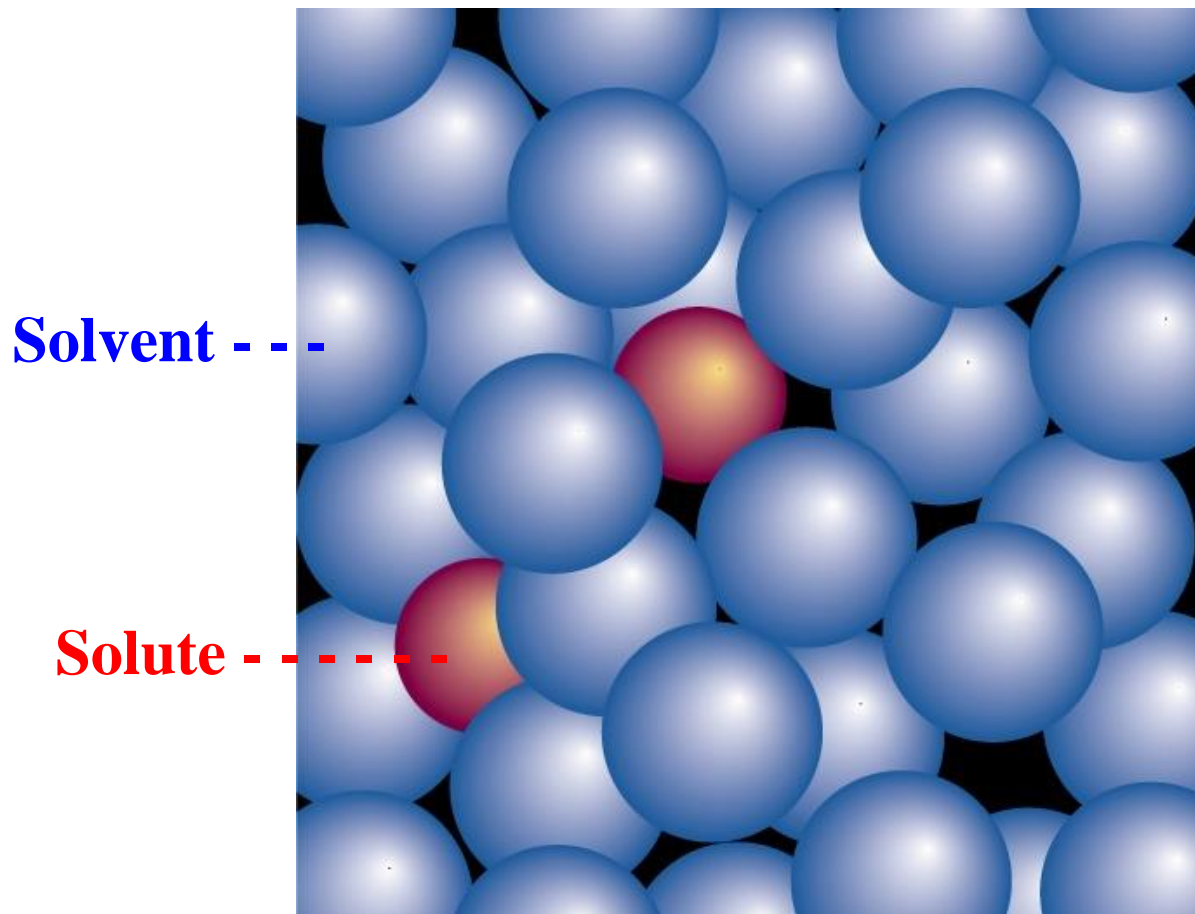
Solvent - - -

Solute - - - - - -

In a dilute solution, **the <u>solvent</u> molecules (the blue spheres)** are in an environment that **<u>differs only slightly from that of the pure solvent</u>**.

The **<u>solute</u>** particles (**red** spheres), however, are in an environment totally unlike that of the pure solute.

5E.3 (p. 223)

In the case of an ideal solution, the solution obeys the Raoult's law.

$$\mu_B(p, T, n_A, n_B, n_C, ...) = \mu_B^0(p, T) + RT \ln x_B$$

The standard state is the pure liquid.

In the <u>case of a non-ideal solution</u>,

$$\mu_i(p, T, n_A, n_B, n_C, ...) \equiv \mu_i^0(p, T) + RT \ln a_i \quad \text{(5E.9)}$$

Definition of Activity

where a_A is the activity of A.

$$a_i(T, p, x_A, x_B, x_C, ...)$$

$$\Delta G'_{mix} = nRT\{x_A \ln a_A + x_B \ln a_B\}$$

5E.3 (p. 223)

As is the case of real gases, a convenient way of expressing this convergence is to introduce the activity coefficient, γ, by the definition:

$$a_A = \gamma_A x_A$$

where γ_A is the **activity coefficient (definition)**

(5E.18)

$$x_A \to 1 \Rightarrow \gamma_A \to 1$$

The chemical potential of the solvent

$$\mu_A = \mu_A^* + RT \ln a_A = \mu_A^* + RT \ln x_A + RT \ln \gamma_A$$

Problems from Chap. 5

5A.1(b) 5A3.(b)   5A.4(b)

5B.5(b)

5B.6 5B.8 5B.12

5C.3(b) 5C.4(b)