Students are encouraged to drill the chapter end problems.

Supplementary

Review of Ideal Dilute Solutions (Engel & Reid, Ch 9)

Ideal solution

Interactions between like and unlike molecules are the same like Benzene-toluene solution.

A-A = A-B = B-B

Ideal solution follows Rault's law (Definition of ideal solution)

$P_i = x_i P_i^*$ $i=1,2$ (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.

At equilibrium

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

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

μ_i^o = For pure i at P^o = 1 bar.

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

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

For pure liquid i **in equilibrium** with its vapor, $\mu_i^*(\text{liquid})=\mu_i^*(\text{vapor})=\mu_i^*$.

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

If vapor pressure is measured, chemical potential is calculated.

(9.4)-(9.5) gives

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

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

(9.1)→(9.6)

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

→ Central equation for ideal solutions.

9.3 Equations for Ideal Solution

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

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

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

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

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).

▶Chemical potential of solid and gas do not change with the addition of solute.

▶Only chemical potential of solvent is decreased by adding solute. See Figure 9.11a ($\mu_i^{solution} = \mu_i^{*} + RT\ln x$). Then Tm decrease lowers triple point and solid-gas coexistence curve (Figure 9.11b).

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

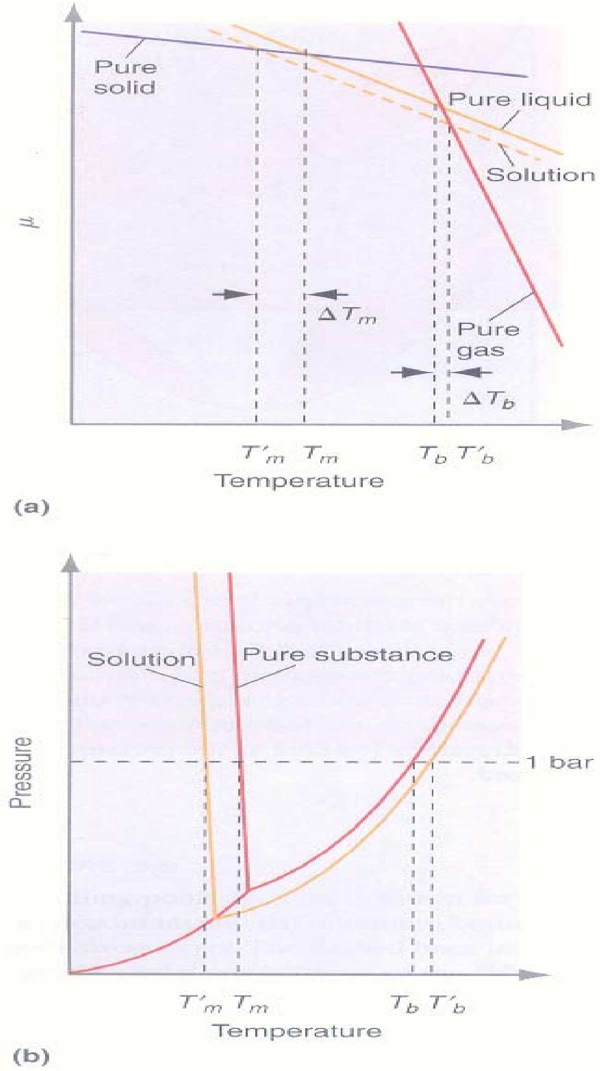

FIGURE 9.11

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.

9.7 Freezing Point Depression & Boiling Point Elevation

If the solution is in equilibrium with the pure solid solvent,

$$\mu_{solution} = \mu^*_{solid} \qquad (9.25)$$

$\mu_{solution}$ = chemical potential of the solvent in the solution

μ^*_{solid} = chemical potential of the pure solvent in the solid form

Imagine ice in (water + salt) solution!

We know (General form for component i)

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

Then (9.25) can be rewritten as (i=solvent):

$$\mu^*_{solvent} + RT\ln x_{solvent} = \mu^*_{solid} \qquad (9.26)$$

Rewriting gives:

$$\ln x_{solvent} = \frac{\mu^*_{solid} - \mu^*_{solvent}}{RT} \qquad (9.27)$$

Also by definition:

$\mu^*_{solid} - \mu^*_{solvent} = -\triangle G_{fusion,}$ ($\mu = G_m$ for pure component)

Plug this into (27):

$$\ln x_{solvent} = \frac{-\triangle G_{fusion,m}}{RT} \qquad (9.28)$$

We need ΔT_f vs $x_{solvent}$ relationship @ constant P

To get this, differentiate (9.28) w.r.t. $x_{solvent}$,

$$\left(\frac{\partial \ln x_{solvent}}{\partial x_{solvent}}\right)_P = \frac{1}{x_{solvent}} = -\frac{1}{R}\left(\frac{\partial \frac{\Delta G_{fusion,m}}{T}}{\partial T}\right)_P \left(\frac{\partial T}{\partial x_{solvent}}\right)_P \qquad (9.29)$$

The first partial derivative on the RHS can be simplified using Gibbs-Helmholtz eq (see 6.3)

$$\left(\frac{\partial \frac{G}{T}}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2} = -\frac{S}{T} - \frac{G}{T^2} = -\frac{G+TS}{T^2} = -\frac{H}{T^2} \qquad (6.33)$$

Then

$$\frac{1}{x_{solvent}} = \frac{\Delta H_{fusion,m}}{RT^2}\left(\frac{\partial T}{\partial x_{solvent}}\right)_P$$

or

$$\frac{dx_{solvent}}{x_{solvent}} = d\ln x_{solvent} = \frac{\Delta H_{fusion,m}}{R}\frac{dT}{T^2}(\text{constant} \qquad (9.30)$$

Integrate this eq from pure solvent ($x_{solvent} = 1$, $T = T_{fusion}$) to an arbitrary small solute concentration ($x_{solvent}$, $T = T$) :

$$\int_1^{x_{solvent}} \frac{dx}{x} = \int_{T_{fusion}}^{T} \frac{\Delta H_{fusion,m}}{R}\frac{dT'}{T'^2} \qquad (9.31)$$

For $x_{solvent} \simeq 1$, $\Delta H_{fusion,m}$ is independent of T, and (9.31) becomes,

$$\frac{1}{T} = \frac{1}{T_{fusion}} - \frac{R\ln x_{solvent}}{\Delta H_{fusion,m}} \qquad (9.32)$$

So, $T<T_{fusion}$ (since $x<1$)

▶ Molar concentration→Molality (More convenient in dilute solution)

$$\begin{aligned}\ln x_{solvent} &= \ln \frac{n_{solvent}}{n_{solvent} + m_{solute} M_{solvent}\ n_{solvent}} \\ &= -\ln(1 + M_{solvent}\ m_{solute}) \\ &= -(M_{solvent}\ m_{solute})\end{aligned}$$

(a)

$$\frac{1}{T} - \frac{1}{T_{fusion}} \simeq -\frac{\Delta T_f}{T_{fusion}^2} \qquad \text{(b)}$$

Note Taylor series for $\ln(1+x) \simeq x$ for small x.

m = Molality=moles of solute/mass of solvent

$M_{solvent}$ = Molar mass of solvent (Mol wt)

(a), (b)→ (9.32)

$$\Delta T_f = -\frac{RM_{solvent} T_{fusion}^2}{\Delta H_{fusion,m}} m_{solute} = -K_f\ m_{solute} \qquad (9.33)$$

- for Depression

Note 1: $\triangle T \propto m_{solute}$ (Colligative property)

<u>For boiling point elevation</u>

$\Delta H_{fusion} \rightarrow \Delta H_{vaporization}$, $T_{fusion} \rightarrow T_{vaporization}$ in (33)

$$\left(\frac{\partial T}{\partial m_{solute}}\right)_{P,m\rightarrow 0} = \frac{{}_{solvent} T_{vaporication}^2}{\Delta H_{vaporication,m}} \qquad (9.34)$$

$$\triangle T_b = \frac{R M_{solvent} T^2_{vaporization}}{\triangle H_{vaporization,m}} m_{solute} = K_b \, m_{solute} \qquad (9.35)$$

BPE and FPD are used to determine the Mn of polymer

$$m = \frac{moles\ of\ solute}{g\ of\ solvent} = \left(\frac{g\ of\ solute}{Mn\ of\ solute}\right)\left(\frac{1}{g\ of\ solvent}\right)$$

$$M_{solvent}\, m = M_{solvent}\left(\frac{1}{M_n}\right)\left(\frac{g\ of\ solute}{g\ of\ solvent}\right)$$

$$= \left(\frac{1}{M_n}\right)\left(\frac{g\ of\ solute}{g\ of\ solvent / M_{solvent}}\right) \equiv \left(\frac{1}{M_n}\right)\left(\frac{g\ of\ solute}{moles\ of\ solvent}\right)$$

$$= \left(\frac{1}{M_n}\right)\left(\frac{g\ of\ solute / vol\ of\ solvent}{moles\ of\ solvent / vol\ of\ solvent}\right)$$

$$= \left(\frac{1}{M_n}\right)(g\ of\ solute/vol\ of\ solvent)(vol\ of\ solvent/molees\ of\ solvent)$$

$$= \left(\frac{1}{M_n}\right) c\,(molar\ volume\ of\ solvent = V_1) \rightarrow (33)\ \text{or}\ (35) \rightarrow M_n\,(Spering\ Eqs\ 35, 36)$$
or $1-10$

- Boiling point elevation (ebulliometry)/ freezing point depression (cryoscopy) for $\overline{M}_n < 10000$

$$\left(\frac{\Delta T_x}{c}\right)_{c \to 0} = \frac{V_1 R T_0{}^2}{\Delta H_x} \times \frac{1}{\overline{M}_n} \qquad (1.10)$$

V_1=Molar volume of solvent (See more in LN #189)

T_o= Boiling (freezing) point of pure solvent

M_n=Number average molecular weight of polymer

ΔH=Latent heat of boiling or freezing

9.8 Osmotic Pressure

Suppose a sac of semipermeable membrane is immersed in solvent (Figure 9.12)

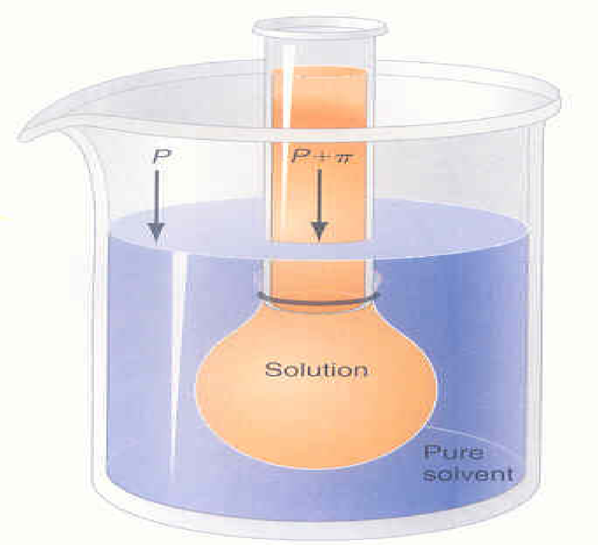

FIGURE 9.12

An osmotic pressure arises if a solution containing a solute that cannot pass through the membrane boundary is immersed in the pure solvent.

@t=0, pressure on both sides = P (Atmospheric pressure)

As time goes, solvent diffuses into the sac until equilibrium →

P (in sac) > P (solvent)

$\Delta P \equiv$ Osmotic pressure $\equiv \pi$

Origin of osmotic pressure

@ equilibrium

$$\mu_{solvent}^{solution}(T,\ P+\pi,\ x_{solvent}) = \mu^{*}_{solvent}(T,\ P) \qquad (9.36)$$

Since $\mu_{solvent}^{solution} < \mu^{*}_{solvent}$, only an increased pressure in the solution can raise its μ equal to the pure solvent.

Using Raoult's law, LHS is expressed as (See Eq 9.7)

$$\mu_{solvent}^{solution}(T,\ P+\pi,\ x_{solvent}) = \mu_{solvent}^{*}(T,\ P+\pi) + RT\ln x_{solvent} \quad (9.37)$$

(37)→(36)

$$\mu_{solvent}^{*}(T,\ P+\pi) + RT\ln x_{solvent} \ = \mu_{solvent}^{*}(T,\ P) \qquad (37)'$$

Now effect of T and P on μ is given by

$$d\mu = dG_m = V_m dP - S_m dT$$

@ T = Constant

$$\mu_{solvent}^{*}(T,\ P+\pi) - \mu_{solvent}^{*}(T,P) = \int_{P}^{P+\pi} V_m^{*}\, dP' \ = V_m^{*}\pi \qquad (9.38)$$

V_m^{*} = Molar volume of pure solvent ≠ f (P) for liquid

P = Pressure in the solvent

Then (38)→(37)'

$$\pi V_m^{*} + RT\ln x_{solvent} = 0 \qquad (9.39)$$

For a dilute solution, $n_{solvent} \gg n_{solute} \longrightarrow$

$$\ln x_{solvent} = \ln(1 - x_{solute}) \approx -x_{solute} = -\frac{n_{solute}}{n_{solute} + n_{solvent}} \approx -\frac{n_{solute}}{n_{solvent}} \qquad (9.40)$$

Also, for dilute solution

$$V \approx n_{solvent} V_m^{*} \qquad (40)'$$

Then (40), (40)' → (39) becomes

$$\pi = \frac{n_{solute}RT}{V} \qquad \text{(van't Hoff eq.)} \qquad (9.41)$$

See the similarity of van't Hoff with I. G. law.

$$n_{solute} = \frac{g\ of\ solute}{M_{solute}} \qquad (9.41a)$$

(9.41a)→(9.41)→ M_n (Eq 3.38 Spering, (1.11) below)

- Membrane osmometry

  for $\overline{M_n} \leq 100000$

  $$\left(\frac{\Pi}{c}\right)_{c \to 0} = \frac{RT}{\overline{\overline{M_n}}} \qquad (1.11)$$

Membrane osmometry is used to determine the Mn of polymer