Figure 9.11

9.7 Freezing Point Depression & Boiling Point Elevation

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

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

μ

$\mu_{solution}$ = 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:

$$\mu^*_{solid} - \mu^*_{solvent} = -\triangle G_{fusion,m}$$ (μ = 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. $x_{solvent}$,

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

(9.29)

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

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

(6.33)

Then

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

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

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

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

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

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

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

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

$$\ln x_{solvent} = \ln \frac{n_{solvent}}{n_{solvent} + m_{solute} M_{solvent}\ n_{solvent}}$$

$$= -\ln(1 + M_{solvent}\ m_{solute})$$

$$= -(M_{solvent}\ m_{solute})$$

(a)

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

Note Taylor series for ln(1+x)≃x for small x.

m = Molality=moles of solute/mass of solvent

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

(a), (b)→ (9.32)

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

– for Depression

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

Note 2: K_f depends only on the properties of the solvent and is primarily determined by the molecular mass and the enthalpy of fusion.

For most solvents

$1.5 \leq K_f \leq 10$ (See Table 9.2 for the constants of various materials)

<u>For boiling point elevation</u>

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

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

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

+ for elevation

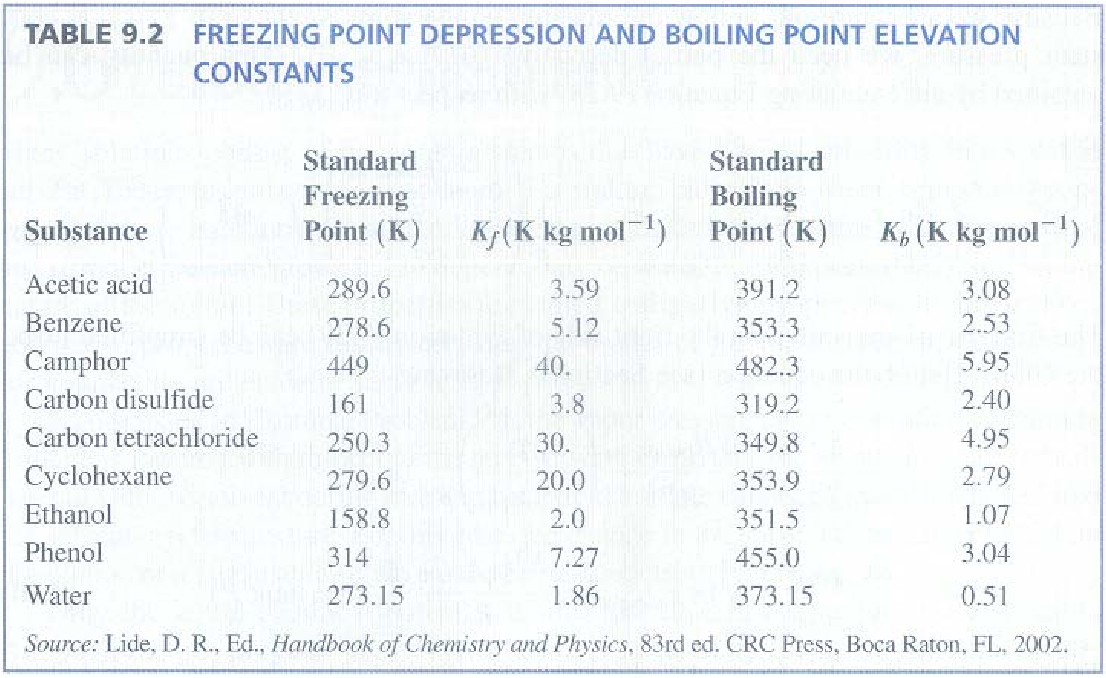


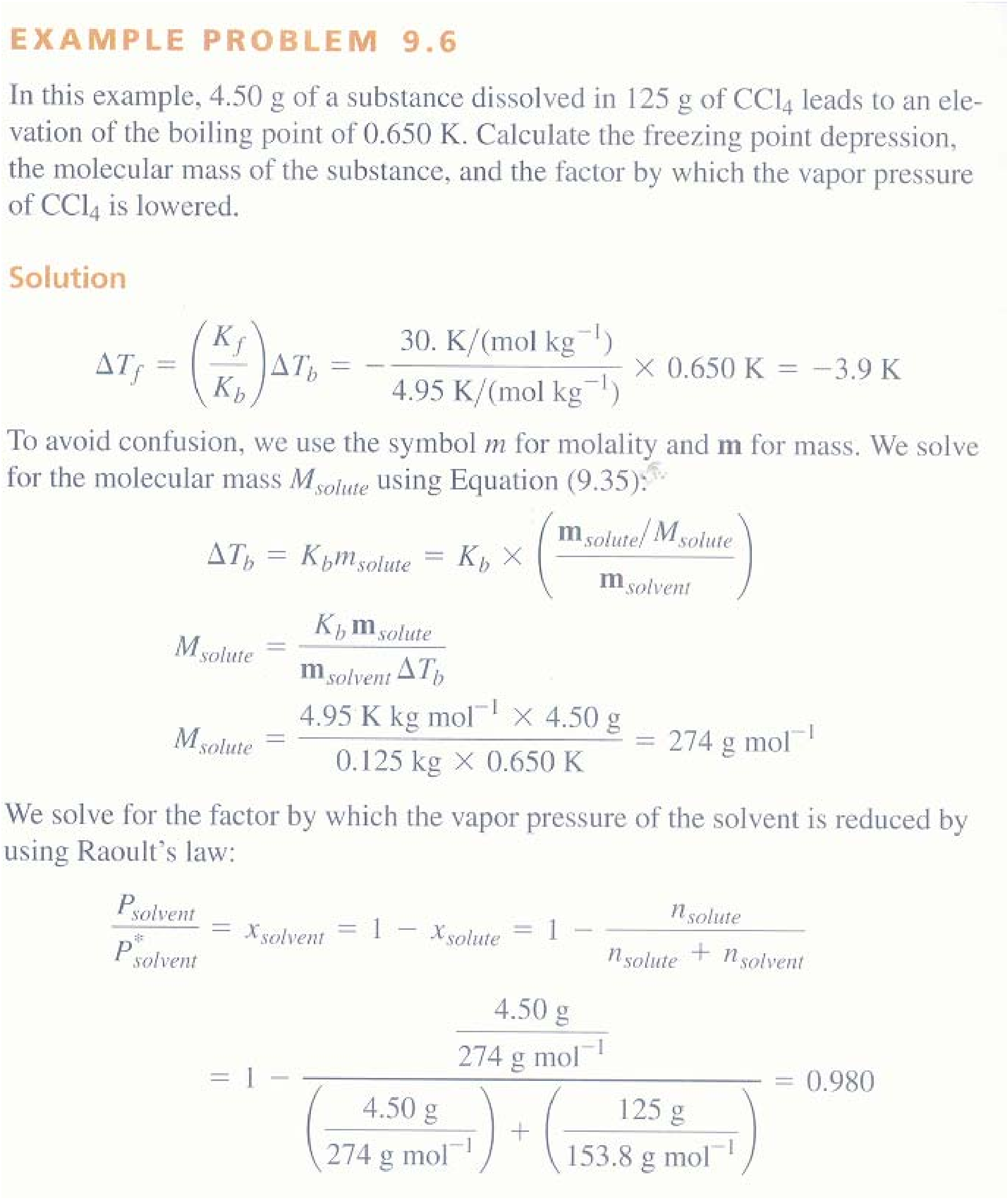
TABLE 9.2 FREEZING POINT DEPRESSION AND BOILING POINT ELEVATION CONSTANTS

Substance	Standard Freezing Point (K)	K_f (K kg mol^{-1})	Standard Boiling Point (K)	K_b (K kg mol^{-1})
Acetic acid	289.6	3.59	391.2	3.08
Benzene	278.6	5.12	353.3	2.53
Camphor	449	40.	482.3	5.95
Carbon disulfide	161	3.8	319.2	2.40
Carbon tetrachloride	250.3	30.	349.8	4.95
Cyclohexane	279.6	20.0	353.9	2.79
Ethanol	158.8	2.0	351.5	1.07
Phenol	314	7.27	455.0	3.04
Water	273.15	1.86	373.15	0.51

Source: Lide, D. R., Ed., *Handbook of Chemistry and Physics*, 83rd ed. CRC Press, Boca Raton, FL, 2002.

Table 9.2 here

Correct typeset error in 9.6



EXAMPLE PROBLEM 9.6

In this example, 4.50 g of a substance dissolved in 125 g of CCl_4 leads to an elevation of the boiling point of 0.650 K. Calculate the freezing point depression, the molecular mass of the substance, and the factor by which the vapor pressure of CCl_4 is lowered.

Solution

$$\Delta T_f = \left(\frac{K_f}{K_b}\right)\Delta T_b = -\frac{30.\ \mathrm{K/(mol\ kg^{-1})}}{4.95\ \mathrm{K/(mol\ kg^{-1})}} \times 0.650\ \mathrm{K} = -3.9\ \mathrm{K}$$

To avoid confusion, we use the symbol m for molality and $\mathbf{m}$ for mass. We solve for the molecular mass M_{solute} using Equation (9.35):

$$\Delta T_b = K_b m_{solute} = K_b \times \left(\frac{\mathbf{m}_{solute}/M_{solute}}{\mathbf{m}_{solvent}}\right)$$

$$M_{solute} = \frac{K_b\,\mathbf{m}_{solute}}{\mathbf{m}_{solvent}\,\Delta T_b}$$

$$M_{solute} = \frac{4.95\ \mathrm{K\ kg\ mol^{-1}} \times 4.50\ \mathrm{g}}{0.125\ \mathrm{kg} \times 0.650\ \mathrm{K}} = 274\ \mathrm{g\ mol^{-1}}$$

We solve for the factor by which the vapor pressure of the solvent is reduced by using Raoult's law:

$$\frac{P_{solvent}}{P^{*}_{solvent}} = x_{solvent} = 1 - x_{solute} = 1 - \frac{n_{solute}}{n_{solute} + n_{solvent}}$$

$$= 1 - \frac{\dfrac{4.50\ \mathrm{g}}{274\ \mathrm{g\ mol^{-1}}}}{\left(\dfrac{4.50\ \mathrm{g}}{274\ \mathrm{g\ mol^{-1}}}\right) + \left(\dfrac{125\ \mathrm{g}}{153.8\ \mathrm{g\ mol^{-1}}}\right)} = 0.980$$

Scan EX 9.6 here

Since

$$\triangle H_{vaporization} > \triangle H_{fusion} \Rightarrow K_f > K_b$$

BPE and FPD are used to determine the number average molecular weght (Mn) of polymer

m = moles of solute/g of solvent=(g of solute/Mn of solute)/ g of solvent =(1/Mn) (g of solute)/ (g of solvent)

$M_{solvent}$ * m = $M_{solvent}$ * (1/Mn) (g of solute)/ (g of solvent)

= (1/Mn) (g of solute)/ (g of solvent/$M_{solvent}$)

= (1/Mn) (g of solute)/ (mole of solvent)

= (1/Mn) (g of solute/vol of solvent)/ (mole of solvent/vol of solvent)

= (1/Mn) (g of solute/vol of solvent)*(vol of solvent)/mole of solvent)

= (1/Mn) c (molar volume of solvent=V_1)

→ (33) or (35) gives the following eq to determine Mn of polymer.

$$\triangle T_b = \frac{R M_{solvent} T^2_{vaporization}}{\triangle H_{vaporization,m}} m_{solute} = K_b\ m_{solute} \qquad (35)$$

- 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)

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

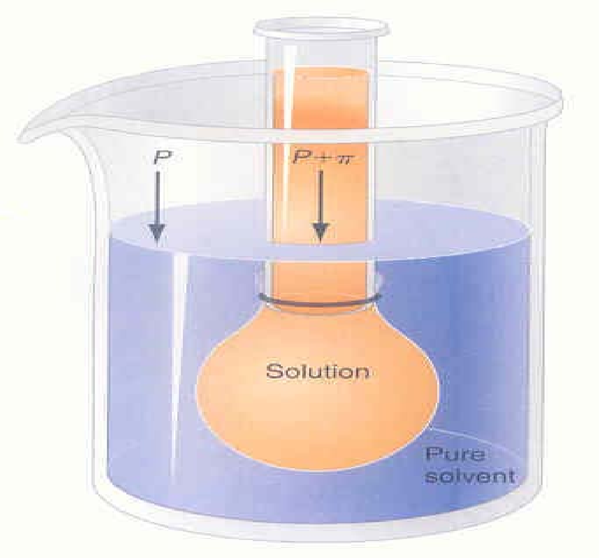


FIGURE 9.12

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

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

P (in sac) > P (solvent)

ΔP ≡ Osmotic pressure ≡ π

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

$$\mu^*_{solvent}(T,\ P+\pi) - \mu^*_{solvent}(T, P) = \int_P^{P+\pi} V^*_m dP' \quad = V^*_m \pi \quad (9.38)$$

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, $n_{solvent} \gg n_{solute}$ →

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

(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.

An important application of the selective diffusion of the components of a solution through a membrane is dialysis. In healthy individuals, the kidneys remove waste products from the bloodstream, whereas individuals with damaged kidneys use a dialysis machine for this purpose. Blood from the patient is shunted through tubes made of a selectively porous membrane surrounded by a flowing sterile solution made up of water, sugars, and other components. Blood cells and other vital components of blood are too large to fit through the pores in the membranes, but urea and salt flow out of the bloodstream through membranes into the sterile solution and are removed as waste.

Example Problem 9.7

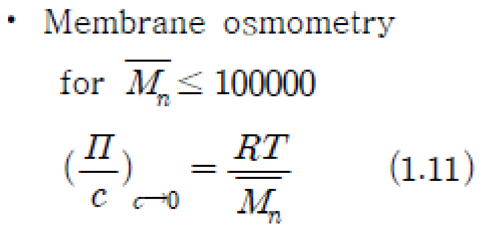
Calculate the osmotic pressure generated at 298K if a cell with a total solute concentration of 0.500 mol L^{-1} is immersed in pure water. The cell wall is permeable to water molecules, but not to the solute molecules.

Solution

$$\pi = \frac{n_{solute}RT}{V} = 0.500\,mol\,L^{-1} \times 8.206 \times 10^{-2} L\,atm\,K^{-1} mol^{-1} \times 298K$$
$$= 12.2\,atm$$

As this calculation shows, the osmotic pressure generated for moderate solute concentrations can be quite high. Hospital patients have died after pure water has accidentally been injected into their blood vessels, because the osmotic pressure is sufficient to burst the walls of blood cells.

Membrane osmometry is used to determine the Mn of polymer



- Membrane osmometry

  for $\overline{M}_n \leq 100000$

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

9.9 Real Solutions

For two volatile, miscible solution

A-B attraction is less (more) than A-A, B-B attraction

⇒ Positive (negative) deviation from the Rault's law (Real solution)

Ex. CS_2 - Acetone (Fig. 9.13)