

CHAPTER 13

PHYSICAL PROPERTIES OF SOLUTIONS

13.7 CsF is an ionic solid; the ion-ion attractions are too strong to be overcome in the dissolving process in benzene. The ion-induced dipole interaction is too weak to stabilize the ion. Nonpolar naphthalene molecules form a molecular solid in which the only interparticle forces are of the weak dispersion type. The same forces operate in liquid benzene causing naphthalene to dissolve with relative ease. Like dissolves like.

13.8 **Strategy:** In predicting solubility, remember the saying: Like dissolves like. A nonpolar solute will dissolve in a nonpolar solvent; ionic compounds will generally dissolve in polar solvents due to favorable ion-dipole interactions; solutes that can form hydrogen bonds with a solvent will have high solubility in the solvent.

Solution: Strong hydrogen bonding (dipole-dipole attraction) is the principal intermolecular attraction in liquid ethanol, but in liquid cyclohexane the intermolecular forces are dispersion forces because cyclohexane is nonpolar. Cyclohexane cannot form hydrogen bonds with ethanol, and therefore cannot attract ethanol molecules strongly enough to form a solution.

13.9 The order of increasing solubility is: $\text{O}_2 < \text{Br}_2 < \text{LiCl} < \text{CH}_3\text{OH}$. Methanol is miscible with water because of strong hydrogen bonding. LiCl is an ionic solid and is very soluble because of the high polarity of the water molecules. Both oxygen and bromine are nonpolar and exert only weak dispersion forces. Bromine is a larger molecule and is therefore more polarizable and susceptible to dipole-induced dipole attractions.

13.10 The longer the C–C chain, the more the molecule "looks like" a hydrocarbon and the less important the –OH group becomes. Hence, as the C–C chain length increases, the molecule becomes less polar. Since "like dissolves like", as the molecules become more nonpolar, the solubility in polar water decreases. The –OH group of the alcohols can form strong hydrogen bonds with water molecules, but this property decreases as the chain length increases.

13.13 Percent mass equals the mass of solute divided by the mass of the solution (that is, solute plus solvent) times 100 (to convert to percentage).

$$(a) \quad \frac{5.50 \text{ g NaBr}}{78.2 \text{ g soln}} \times 100\% = \mathbf{7.03\%}$$

$$(b) \quad \frac{31.0 \text{ g KCl}}{(31.0 + 152) \text{ g soln}} \times 100\% = \mathbf{16.9\%}$$

$$(c) \quad \frac{4.5 \text{ g toluene}}{(4.5 + 29) \text{ g soln}} \times 100\% = \mathbf{13\%}$$

13.14 **Strategy:** We are given the percent by mass of the solute and the mass of the solute. We can use Equation (13.2) of the text to solve for the mass of the solvent (water).

Solution:

(a) The percent by mass is defined as

$$\text{percent by mass of solute} = \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100\%$$

Substituting in the percent by mass of solute and the mass of solute, we can solve for the mass of solvent (water).

$$16.2\% = \frac{5.00 \text{ g urea}}{5.00 \text{ g urea} + \text{mass of water}} \times 100\%$$

$$(0.162)(\text{mass of water}) = 5.00 \text{ g} - (0.162)(5.00 \text{ g})$$

$$\text{mass of water} = 25.9 \text{ g}$$

(b) Similar to part (a),

$$1.5\% = \frac{26.2 \text{ g MgCl}_2}{26.2 \text{ g MgCl}_2 + \text{mass of water}} \times 100\%$$

$$\text{mass of water} = 1.72 \times 10^3 \text{ g}$$

13.15 (a) The molality is the number of moles of sucrose (molar mass 342.3 g/mol) divided by the mass of the solvent (water) in kg.

$$\text{mol sucrose} = 14.3 \text{ g sucrose} \times \frac{1 \text{ mol}}{342.3 \text{ g sucrose}} = 0.0418 \text{ mol}$$

$$\text{Molality} = \frac{0.0418 \text{ mol sucrose}}{0.676 \text{ kg H}_2\text{O}} = 0.0618 \text{ m}$$

(b) $\text{Molality} = \frac{7.20 \text{ mol ethylene glycol}}{3.546 \text{ kg H}_2\text{O}} = 2.03 \text{ m}$

13.16 molality = $\frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$

(a) mass of 1 L soln = $1000 \text{ mL} \times \frac{1.08 \text{ g}}{1 \text{ mL}} = 1080 \text{ g}$

$$\text{mass of water} = 1080 \text{ g} - \left(2.50 \text{ mol NaCl} \times \frac{58.44 \text{ g NaCl}}{1 \text{ mol NaCl}} \right) = 934 \text{ g} = 0.934 \text{ kg}$$

$$m = \frac{2.50 \text{ mol NaCl}}{0.934 \text{ kg H}_2\text{O}} = 2.68 \text{ m}$$

(b) 100 g of the solution contains 48.2 g KBr and 51.8 g H₂O.

$$\text{mol of KBr} = 48.2 \text{ g KBr} \times \frac{1 \text{ mol KBr}}{119.0 \text{ g KBr}} = 0.405 \text{ mol KBr}$$

$$\text{mass of H}_2\text{O (in kg)} = 51.8 \text{ g H}_2\text{O} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.0518 \text{ kg H}_2\text{O}$$

$$m = \frac{0.405 \text{ mol KBr}}{0.0518 \text{ kg H}_2\text{O}} = 7.82 \text{ m}$$

13.17 In each case we consider one liter of solution. mass of solution = volume \times density

$$(a) \text{ mass of sugar} = 1.22 \text{ mol sugar} \times \frac{342.3 \text{ g sugar}}{1 \text{ mol sugar}} = 418 \text{ g sugar} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.418 \text{ kg sugar}$$

$$\text{mass of soln} = 1000 \text{ mL} \times \frac{1.12 \text{ g}}{1 \text{ mL}} = 1120 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 1.120 \text{ kg}$$

$$\text{molality} = \frac{1.22 \text{ mol sugar}}{(1.120 - 0.418) \text{ kg H}_2\text{O}} = \mathbf{1.74 \text{ } m}$$

$$(b) \text{ mass of NaOH} = 0.87 \text{ mol NaOH} \times \frac{40.00 \text{ g NaOH}}{1 \text{ mol NaOH}} = 35 \text{ g NaOH}$$

$$\text{mass solvent (H}_2\text{O)} = 1040 \text{ g} - 35 \text{ g} = 1005 \text{ g} = 1.005 \text{ kg}$$

$$\text{molality} = \frac{0.87 \text{ mol NaOH}}{1.005 \text{ kg H}_2\text{O}} = \mathbf{0.87 \text{ } m}$$

$$(c) \text{ mass of NaHCO}_3 = 5.24 \text{ mol NaHCO}_3 \times \frac{84.01 \text{ g NaHCO}_3}{1 \text{ mol NaHCO}_3} = 440 \text{ g NaHCO}_3$$

$$\text{mass solvent (H}_2\text{O)} = 1190 \text{ g} - 440 \text{ g} = 750 \text{ g} = 0.750 \text{ kg}$$

$$\text{molality} = \frac{5.24 \text{ mol NaHCO}_3}{0.750 \text{ kg H}_2\text{O}} = \mathbf{6.99 \text{ } m}$$

13.18 Let's assume that we have 1.0 L of a 0.010 *M* solution.

Assuming a solution density of 1.0 g/mL, the mass of 1.0 L (1000 mL) of the solution is 1000 g or 1.0×10^3 g.

The mass of 0.010 mole of urea is:

$$0.010 \text{ mol urea} \times \frac{60.06 \text{ g urea}}{1 \text{ mol urea}} = 0.60 \text{ g urea}$$

The mass of the solvent is:

$$(\text{solution mass}) - (\text{solute mass}) = (1.0 \times 10^3 \text{ g}) - (0.60 \text{ g}) = 1.0 \times 10^3 \text{ g} = 1.0 \text{ kg}$$

$$m = \frac{\text{moles solute}}{\text{mass solvent}} = \frac{0.010 \text{ mol}}{1.0 \text{ kg}} = \mathbf{0.010 \text{ } m}$$

13.19 We find the volume of ethanol in 1.00 L of 75 proof gin. Note that 75 proof means $\left(\frac{75}{2}\right)\%$.

$$\text{Volume} = 1.00 \text{ L} \times \left(\frac{75}{2}\right)\% = 0.38 \text{ L} = 3.8 \times 10^2 \text{ mL}$$

$$\text{Ethanol mass} = (3.8 \times 10^2 \text{ mL}) \times \frac{0.798 \text{ g}}{1 \text{ mL}} = \mathbf{3.0 \times 10^2 \text{ g}}$$

13.20 (a) Converting mass percent to molality.

Strategy: In solving this type of problem, it is convenient to assume that we start with 100.0 grams of the solution. If the mass of sulfuric acid is 98.0% of 100.0 g, or 98.0 g, the percent by mass of water must be $100.0\% - 98.0\% = 2.0\%$. The mass of water in 100.0 g of solution would be 2.0 g. From the definition of molality, we need to find moles of solute (sulfuric acid) and kilograms of solvent (water).

Solution: Since the definition of molality is

$$\text{molality} = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$$

we first convert 98.0 g H_2SO_4 to moles of H_2SO_4 using its molar mass, then we convert 2.0 g of H_2O to units of kilograms.

$$98.0 \text{ g H}_2\text{SO}_4 \times \frac{1 \text{ mol H}_2\text{SO}_4}{98.09 \text{ g H}_2\text{SO}_4} = 0.999 \text{ mol H}_2\text{SO}_4$$

$$2.0 \text{ g H}_2\text{O} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 2.0 \times 10^{-3} \text{ kg H}_2\text{O}$$

Lastly, we divide moles of solute by mass of solvent in kg to calculate the molality of the solution.

$$m = \frac{\text{mol of solute}}{\text{kg of solvent}} = \frac{0.999 \text{ mol}}{2.0 \times 10^{-3} \text{ kg}} = 5.0 \times 10^2 \text{ m}$$

(b) Converting molality to molarity.

Strategy: From part (a), we know the moles of solute (0.999 mole H_2SO_4) and the mass of the solution (100.0 g). To solve for molarity, we need the volume of the solution, which we can calculate from its mass and density.

Solution: First, we use the solution density as a conversion factor to convert to volume of solution.

$$? \text{ volume of solution} = 100.0 \text{ g} \times \frac{1 \text{ mL}}{1.83 \text{ g}} = 54.6 \text{ mL} = 0.0546 \text{ L}$$

Since we already know moles of solute from part (a), 0.999 mole H_2SO_4 , we divide moles of solute by liters of solution to calculate the molarity of the solution.

$$M = \frac{\text{mol of solute}}{\text{L of soln}} = \frac{0.999 \text{ mol}}{0.0546 \text{ L}} = 18.3 \text{ M}$$

$$\mathbf{13.21} \quad \text{mol NH}_3 = 30.0 \text{ g NH}_3 \times \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} = 1.76 \text{ mol NH}_3$$

$$\text{Volume of the solution} = 100.0 \text{ g soln} \times \frac{1 \text{ mL}}{0.982 \text{ g}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.102 \text{ L}$$

$$\mathbf{\text{molarity}} = \frac{1.76 \text{ mol NH}_3}{0.102 \text{ L soln}} = 17.3 \text{ M}$$

$$\text{kg of solvent (H}_2\text{O)} = 70.0 \text{ g H}_2\text{O} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.0700 \text{ kg H}_2\text{O}$$

$$\text{molality} = \frac{1.76 \text{ mol NH}_3}{0.0700 \text{ kg H}_2\text{O}} = \mathbf{25.1 \text{ } m}$$

13.22 Assume 100.0 g of solution.

(a) The mass of ethanol in the solution is $0.100 \times 100.0 \text{ g} = 10.0 \text{ g}$. The mass of the water is $100.0 \text{ g} - 10.0 \text{ g} = 90.0 \text{ g} = 0.0900 \text{ kg}$. The amount of ethanol in moles is:

$$10.0 \text{ g ethanol} \times \frac{1 \text{ mol}}{46.07 \text{ g}} = 0.217 \text{ mol ethanol}$$

$$m = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{0.217 \text{ mol}}{0.0900 \text{ kg}} = \mathbf{2.41 \text{ } m}$$

(b) The volume of the solution is:

$$100.0 \text{ g} \times \frac{1 \text{ mL}}{0.984 \text{ g}} = 102 \text{ mL} = 0.102 \text{ L}$$

The amount of ethanol in moles is 0.217 mole [part (a)].

$$M = \frac{\text{mol solute}}{\text{liters of soln}} = \frac{0.217 \text{ mol}}{0.102 \text{ L}} = \mathbf{2.13 \text{ } M}$$

(c) **Solution volume** = $0.125 \text{ mol} \times \frac{1 \text{ L}}{2.13 \text{ mol}} = \mathbf{0.0587 \text{ L} = 58.7 \text{ mL}}$

13.25 The amount of salt dissolved in 100 g of water is:

$$\frac{3.20 \text{ g salt}}{9.10 \text{ g H}_2\text{O}} \times 100 \text{ g H}_2\text{O} = 35.2 \text{ g salt}$$

Therefore, the solubility of the salt is **35.2 g salt/100 g H₂O**.

13.26 At 75°C, 155 g of KNO₃ dissolves in 100 g of water to form 255 g of solution. When cooled to 25°C, only 38.0 g of KNO₃ remain dissolved. This means that $(155 - 38.0) \text{ g} = 117 \text{ g}$ of KNO₃ will crystallize.

The amount of KNO₃ formed when 100 g of saturated solution at 75°C is cooled to 25°C can be found by a simple unit conversion.

$$100 \text{ g saturated soln} \times \frac{117 \text{ g KNO}_3 \text{ crystallized}}{255 \text{ g saturated soln}} = \mathbf{45.9 \text{ g KNO}_3}$$

13.31 The solubility of gases in water usually decreases with increasing temperature (see Figure 13.4 of the text). When the water in the beaker is heated to 30°C, bubbles of air form because the air is less soluble in the water at the higher temperature. At 100°C, the normal boiling point of water, a phase transition is occurring from liquid water to water vapor. The bubbles will predominantly contain water vapor escaping from the liquid, although there will also be a small amount of air present in the bubbles at the higher temperature.

- 13.32** The solubility of gases in water usually decreases with increasing temperature. See Figure 13.4 of the text. Boiling the water decreased the oxygen content of the water. Cooling the water quickly did not allow enough time for oxygen gas from the atmosphere to re-dissolve in the water to reach the equilibrium concentration at the lower temperature. The oxygen concentration in the water was too low for the goldfish to survive.
- 13.33** When a dissolved gas is in dynamic equilibrium with its surroundings, the number of gas molecules entering the solution (dissolving) is equal to the number of dissolved gas molecules leaving and entering the gas phase. When the surrounding air is replaced by helium, the number of air molecules leaving the solution is greater than the number dissolving. As time passes the concentration of dissolved air becomes very small or zero, and the concentration of dissolved helium increases to a maximum.
- 13.34** According to Henry's law, the solubility of a gas in a liquid increases as the pressure increases ($c = kP$). The soft drink tastes flat at the bottom of the mine because the carbon dioxide pressure is greater and the dissolved gas is not released from the solution. As the miner goes up in the elevator, the atmospheric carbon dioxide pressure decreases and dissolved gas is released from his stomach.
- 13.35** We first find the value of k for Henry's law

$$k = \frac{c}{P} = \frac{0.034 \text{ mol/L}}{1 \text{ atm}} = 0.034 \text{ mol/L} \cdot \text{atm}$$

For atmospheric conditions we write:

$$c = kP = (0.034 \text{ mol/L} \cdot \text{atm})(0.00030 \text{ atm}) = \mathbf{1.0 \times 10^{-5} \text{ mol/L}}$$

- 13.36 Strategy:** The given solubility allows us to calculate Henry's law constant (k), which can then be used to determine the concentration of N_2 at 4.0 atm. We can then compare the solubilities of N_2 in blood under normal pressure (0.80 atm) and under a greater pressure that a deep-sea diver might experience (4.0 atm) to determine the moles of N_2 released when the diver returns to the surface. From the moles of N_2 released, we can calculate the volume of N_2 released.

Solution: First, calculate the Henry's law constant, k , using the concentration of N_2 in blood at 0.80 atm.

$$k = \frac{c}{P}$$

$$k = \frac{5.6 \times 10^{-4} \text{ mol/L}}{0.80 \text{ atm}} = 7.0 \times 10^{-4} \text{ mol/L} \cdot \text{atm}$$

Next, we can calculate the concentration of N_2 in blood at 4.0 atm using k calculated above.

$$c = kP$$

$$c = (7.0 \times 10^{-4} \text{ mol/L} \cdot \text{atm})(4.0 \text{ atm}) = 2.8 \times 10^{-3} \text{ mol/L}$$

From each of the concentrations of N_2 in blood, we can calculate the number of moles of N_2 dissolved by multiplying by the total blood volume of 5.0 L. Then, we can calculate the number of moles of N_2 released when the diver returns to the surface.

The number of moles of N_2 in 5.0 L of blood at 0.80 atm is:

$$(5.6 \times 10^{-4} \text{ mol/L})(5.0 \text{ L}) = 2.8 \times 10^{-3} \text{ mol}$$

The number of moles of N_2 in 5.0 L of blood at 4.0 atm is:

$$(2.8 \times 10^{-3} \text{ mol/L})(5.0 \text{ L}) = 1.4 \times 10^{-2} \text{ mol}$$

The amount of N_2 released in moles when the diver returns to the surface is:

$$(1.4 \times 10^{-2} \text{ mol}) - (2.8 \times 10^{-3} \text{ mol}) = 1.1 \times 10^{-2} \text{ mol}$$

Finally, we can now calculate the volume of N_2 released using the ideal gas equation. The total pressure pushing on the N_2 that is released is atmospheric pressure (1 atm).

The volume of N_2 released is:

$$V_{N_2} = \frac{nRT}{P}$$

$$V_{N_2} = \frac{(1.1 \times 10^{-2} \text{ mol})(273 + 37)\text{K}}{(1.0 \text{ atm})} \times \frac{0.0821 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} = \mathbf{0.28 \text{ L}}$$

13.49 The first step is to find the number of moles of sucrose and of water.

$$\text{Moles sucrose} = 396 \text{ g} \times \frac{1 \text{ mol}}{342.3 \text{ g}} = 1.16 \text{ mol sucrose}$$

$$\text{Moles water} = 624 \text{ g} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 34.6 \text{ mol water}$$

The mole fraction of water is:

$$X_{H_2O} = \frac{34.6 \text{ mol}}{34.6 \text{ mol} + 1.16 \text{ mol}} = 0.968$$

The vapor pressure of the solution is found as follows:

$$P_{\text{solution}} = X_{H_2O} \times P_{H_2O}^{\circ} = (0.968)(31.8 \text{ mmHg}) = \mathbf{30.8 \text{ mmHg}}$$

13.50 Strategy: From the vapor pressure of water at 20°C and the change in vapor pressure for the solution (2.0 mmHg), we can solve for the mole fraction of sucrose using Equation (13.7) of the text. From the mole fraction of sucrose, we can solve for moles of sucrose. Lastly, we convert from moles to grams of sucrose.

Solution: Using Equation (13.7) of the text, we can calculate the mole fraction of sucrose that causes a 2.0 mmHg drop in vapor pressure.

$$\Delta P = X_2 P_1^{\circ}$$

$$\Delta P = X_{\text{sucrose}} P_{\text{water}}^{\circ}$$

$$X_{\text{sucrose}} = \frac{\Delta P}{P_{\text{water}}^{\circ}} = \frac{2.0 \text{ mmHg}}{17.5 \text{ mmHg}} = 0.11$$

From the definition of mole fraction, we can calculate moles of sucrose.

$$X_{\text{sucrose}} = \frac{n_{\text{sucrose}}}{n_{\text{water}} + n_{\text{sucrose}}}$$

$$\text{moles of water} = 552 \text{ g} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 30.6 \text{ mol H}_2\text{O}$$

$$X_{\text{sucrose}} = 0.11 = \frac{n_{\text{sucrose}}}{30.6 + n_{\text{sucrose}}}$$

$$n_{\text{sucrose}} = 3.8 \text{ mol sucrose}$$

Using the molar mass of sucrose as a conversion factor, we can calculate the mass of sucrose.

$$\text{mass of sucrose} = 3.8 \text{ mol sucrose} \times \frac{342.3 \text{ g sucrose}}{1 \text{ mol sucrose}} = \mathbf{1.3 \times 10^3 \text{ g sucrose}}$$

13.51 Let us call benzene component 1 and camphor component 2.

$$P_1 = X_1 P_1^\circ = \left(\frac{n_1}{n_1 + n_2} \right) P_1^\circ$$

$$n_1 = 98.5 \text{ g benzene} \times \frac{1 \text{ mol}}{78.11 \text{ g}} = 1.26 \text{ mol benzene}$$

$$n_2 = 24.6 \text{ g camphor} \times \frac{1 \text{ mol}}{152.2 \text{ g}} = 0.162 \text{ mol camphor}$$

$$P_1 = \frac{1.26 \text{ mol}}{(1.26 + 0.162) \text{ mol}} \times 100.0 \text{ mmHg} = \mathbf{88.6 \text{ mmHg}}$$

13.52 For any solution the sum of the mole fractions of the components is always 1.00, so the mole fraction of 1-propanol is 0.700. The partial pressures are:

$$P_{\text{ethanol}} = X_{\text{ethanol}} \times P_{\text{ethanol}}^\circ = (0.300)(100 \text{ mmHg}) = \mathbf{30.0 \text{ mmHg}}$$

$$P_{1\text{-propanol}} = X_{1\text{-propanol}} \times P_{1\text{-propanol}}^\circ = (0.700)(37.6 \text{ mmHg}) = \mathbf{26.3 \text{ mmHg}}$$

Is the vapor phase richer in one of the components than the solution? Which component? Should this always be true for ideal solutions?

13.53 (a) First find the mole fractions of the solution components.

$$\text{Moles methanol} = 30.0 \text{ g} \times \frac{1 \text{ mol}}{32.04 \text{ g}} = 0.936 \text{ mol CH}_3\text{OH}$$

$$\text{Moles ethanol} = 45.0 \text{ g} \times \frac{1 \text{ mol}}{46.07 \text{ g}} = 0.977 \text{ mol C}_2\text{H}_5\text{OH}$$

$$X_{\text{methanol}} = \frac{0.936 \text{ mol}}{0.936 \text{ mol} + 0.977 \text{ mol}} = 0.489$$

$$X_{\text{ethanol}} = 1 - X_{\text{methanol}} = 0.511$$

The vapor pressures of the methanol and ethanol are:

$$P_{\text{methanol}} = (0.489)(94 \text{ mmHg}) = \mathbf{46 \text{ mmHg}}$$

$$P_{\text{ethanol}} = (0.511)(44 \text{ mmHg}) = \mathbf{22 \text{ mmHg}}$$

- (b) Since $n = PV/RT$ and V and T are the same for both vapors, the number of moles of each substance is proportional to the partial pressure. We can then write for the mole fractions:

$$X_{\text{methanol}} = \frac{P_{\text{methanol}}}{P_{\text{methanol}} + P_{\text{ethanol}}} = \frac{46 \text{ mmHg}}{46 \text{ mmHg} + 22 \text{ mmHg}} = \mathbf{0.68}$$

$$X_{\text{ethanol}} = 1 - X_{\text{methanol}} = \mathbf{0.32}$$

- 13.54** This problem is very similar to Problem 13.50.

$$\Delta P = X_{\text{urea}} P_{\text{water}}^{\circ}$$

$$2.50 \text{ mmHg} = X_{\text{urea}}(31.8 \text{ mmHg})$$

$$X_{\text{urea}} = 0.0786$$

The number of moles of water is:

$$n_{\text{water}} = 450 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 25.0 \text{ mol H}_2\text{O}$$

$$X_{\text{urea}} = \frac{n_{\text{urea}}}{n_{\text{water}} + n_{\text{urea}}}$$

$$0.0786 = \frac{n_{\text{urea}}}{25.0 + n_{\text{urea}}}$$

$$n_{\text{urea}} = 2.13 \text{ mol}$$

$$\mathbf{\text{mass of urea}} = 2.13 \text{ mol urea} \times \frac{60.06 \text{ g urea}}{1 \text{ mol urea}} = \mathbf{128 \text{ g of urea}}$$

13.55 $\Delta T_b = K_b m = (2.53^\circ\text{C}/m)(2.47 m) = 6.25^\circ\text{C}$

The new **boiling point** is $80.1^\circ\text{C} + 6.25^\circ\text{C} = \mathbf{86.4^\circ\text{C}}$

$$\Delta T_f = K_f m = (5.12^\circ\text{C}/m)(2.47 m) = 12.6^\circ\text{C}$$

The new **freezing point** is $5.5^\circ\text{C} - 12.6^\circ\text{C} = \mathbf{-7.1^\circ\text{C}}$

13.56 $m = \frac{\Delta T_f}{K_f} = \frac{1.1^\circ\text{C}}{1.86^\circ\text{C}/m} = \mathbf{0.59 m}$

- 13.57 METHOD 1:** The empirical formula can be found from the percent by mass data assuming a 100.0 g sample.

$$\text{Moles C} = 80.78 \text{ g} \times \frac{1 \text{ mol}}{12.01 \text{ g}} = 6.726 \text{ mol C}$$

$$\text{Moles H} = 13.56 \text{ g} \times \frac{1 \text{ mol}}{1.008 \text{ g}} = 13.45 \text{ mol H}$$

$$\text{Moles O} = 5.66 \text{ g} \times \frac{1 \text{ mol}}{16.00 \text{ g}} = 0.354 \text{ mol O}$$

This gives the formula: $C_{6.726}H_{13.45}O_{0.354}$. Dividing through by the smallest subscript (0.354) gives the empirical formula, $C_{19}H_{38}O$.

The freezing point depression is $\Delta T_f = 5.5^\circ\text{C} - 3.37^\circ\text{C} = 2.1^\circ\text{C}$. This implies a solution molality of:

$$m = \frac{\Delta T_f}{K_f} = \frac{2.1^\circ\text{C}}{5.12^\circ\text{C}/m} = 0.41 m$$

Since the solvent mass is 8.50 g or 0.00850 kg, the amount of solute is:

$$\frac{0.41 \text{ mol}}{1 \text{ kg benzene}} \times 0.00850 \text{ kg benzene} = 3.5 \times 10^{-3} \text{ mol}$$

Since 1.00 g of the sample represents 3.5×10^{-3} mol, the molar mass is:

$$\text{molar mass} = \frac{1.00 \text{ g}}{3.5 \times 10^{-3} \text{ mol}} = \mathbf{286 \text{ g/mol}}$$

The mass of the empirical formula is 282 g/mol, so the molecular formula is the same as the empirical formula, $C_{19}H_{38}O$.

METHOD 2: Use the freezing point data as above to determine the molar mass.

$$\text{molar mass} = \mathbf{286 \text{ g/mol}}$$

Multiply the mass % (converted to a decimal) of each element by the molar mass to convert to grams of each element. Then, use the molar mass to convert to moles of each element.

$$n_C = (0.8078) \times (286 \text{ g}) \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = \mathbf{19.2 \text{ mol C}}$$

$$n_H = (0.1356) \times (286 \text{ g}) \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = \mathbf{38.5 \text{ mol H}}$$

$$n_O = (0.0566) \times (286 \text{ g}) \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = \mathbf{1.01 \text{ mol O}}$$

Since we used the molar mass to calculate the moles of each element present in the compound, this method directly gives the molecular formula. The formula is $C_{19}H_{38}O$.

13.58 METHOD 1:

Strategy: First, we can determine the empirical formula from mass percent data. Then, we can determine the molar mass from the freezing-point depression. Finally, from the empirical formula and the molar mass, we can find the molecular formula.

Solution: If we assume that we have 100 g of the compound, then each percentage can be converted directly to grams. In this sample, there will be 40.0 g of C, 6.7 g of H, and 53.3 g of O. Because the subscripts in the formula represent a mole ratio, we need to convert the grams of each element to moles. The conversion factor needed is the molar mass of each element. Let n represent the number of moles of each element so that

$$n_C = 40.0 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 3.33 \text{ mol C}$$

$$n_H = 6.7 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 6.6 \text{ mol H}$$

$$n_{\text{O}} = 53.3 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 3.33 \text{ mol O}$$

Thus, we arrive at the formula $\text{C}_{3.33}\text{H}_{6.6}\text{O}_{3.3}$, which gives the identity and the ratios of atoms present. However, chemical formulas are written with whole numbers. Try to convert to whole numbers by dividing all the subscripts by the smallest subscript.

$$\text{C: } \frac{3.33}{3.33} = 1.00 \quad \text{H: } \frac{6.6}{3.33} = 2.0 \quad \text{O: } \frac{3.33}{3.33} = 1.00$$

This gives us the empirical, CH_2O .

Now, we can use the freezing point data to determine the molar mass. First, calculate the molality of the solution.

$$m = \frac{\Delta T_f}{K_f} = \frac{1.56^\circ\text{C}}{8.00^\circ\text{C}/m} = 0.195 \text{ m}$$

Multiplying the molality by the mass of solvent (in kg) gives moles of unknown solute. Then, dividing the mass of solute (in g) by the moles of solute, gives the molar mass of the unknown solute.

$$\begin{aligned} ? \text{ mol of unknown solute} &= \frac{0.195 \text{ mol solute}}{1 \text{ kg diphenyl}} \times 0.0278 \text{ kg diphenyl} \\ &= 0.00542 \text{ mol solute} \end{aligned}$$

$$\text{molar mass of unknown} = \frac{0.650 \text{ g}}{0.00542 \text{ mol}} = 1.20 \times 10^2 \text{ g/mol}$$

Finally, we compare the empirical molar mass to the molar mass above.

$$\text{empirical molar mass} = 12.01 \text{ g} + 2(1.008 \text{ g}) + 16.00 \text{ g} = 30.03 \text{ g/mol}$$

The number of (CH_2O) units present in the molecular formula is:

$$\frac{\text{molar mass}}{\text{empirical molar mass}} = \frac{1.20 \times 10^2 \text{ g}}{30.03 \text{ g}} = 4.00$$

Thus, there are four CH_2O units in each molecule of the compound, so the molecular formula is $(\text{CH}_2\text{O})_4$, or **$\text{C}_4\text{H}_8\text{O}_4$** .

METHOD 2:

Strategy: As in Method 1, we determine the molar mass of the unknown from the freezing point data. Once the molar mass is known, we can multiply the mass % of each element (converted to a decimal) by the molar mass to convert to grams of each element. From the grams of each element, the moles of each element can be determined and hence the mole ratio in which the elements combine.

Solution: We use the freezing point data to determine the molar mass. First, calculate the molality of the solution.

$$m = \frac{\Delta T_f}{K_f} = \frac{1.56^\circ\text{C}}{8.00^\circ\text{C}/m} = 0.195 \text{ m}$$

Multiplying the molality by the mass of solvent (in kg) gives moles of unknown solute. Then, dividing the mass of solute (in g) by the moles of solute, gives the molar mass of the unknown solute.

$$\begin{aligned} ? \text{ mol of unknown solute} &= \frac{0.195 \text{ mol solute}}{1 \text{ kg diphenyl}} \times 0.0278 \text{ kg diphenyl} \\ &= 0.00542 \text{ mol solute} \end{aligned}$$

$$\text{molar mass of unknown} = \frac{0.650 \text{ g}}{0.00542 \text{ mol}} = \mathbf{1.20 \times 10^2 \text{ g/mol}}$$

Next, we multiply the mass % (converted to a decimal) of each element by the molar mass to convert to grams of each element. Then, we use the molar mass to convert to moles of each element.

$$n_{\text{C}} = (0.400) \times (1.20 \times 10^2 \text{ g}) \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 4.00 \text{ mol C}$$

$$n_{\text{H}} = (0.067) \times (1.20 \times 10^2 \text{ g}) \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 7.98 \text{ mol H}$$

$$n_{\text{O}} = (0.533) \times (1.20 \times 10^2 \text{ g}) \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 4.00 \text{ mol O}$$

Since we used the molar mass to calculate the moles of each element present in the compound, this method directly gives the molecular formula. The formula is $\mathbf{C_4H_8O_4}$.

13.59 We want a freezing point depression of 20°C .

$$m = \frac{\Delta T_{\text{f}}}{K_{\text{f}}} = \frac{20^\circ\text{C}}{1.86^\circ\text{C}/m} = 10.8 \text{ } m$$

The mass of ethylene glycol (EG) in 6.5 L or 6.5 kg of water is:

$$\text{mass EG} = 6.50 \text{ kg H}_2\text{O} \times \frac{10.8 \text{ mol EG}}{1 \text{ kg H}_2\text{O}} \times \frac{62.07 \text{ g EG}}{1 \text{ mol EG}} = 4.36 \times 10^3 \text{ g EG}$$

The volume of EG needed is:

$$V = (4.36 \times 10^3 \text{ g EG}) \times \frac{1 \text{ mL EG}}{1.11 \text{ g EG}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = \mathbf{3.93 \text{ L}}$$

Finally, we calculate the boiling point:

$$\Delta T_{\text{b}} = mK_{\text{b}} = (10.8 \text{ } m)(0.52^\circ\text{C}/m) = 5.6^\circ\text{C}$$

The **boiling point** of the solution will be $100.0^\circ\text{C} + 5.6^\circ\text{C} = \mathbf{105.6^\circ\text{C}}$.

13.60 We first find the number of moles of gas using the ideal gas equation.

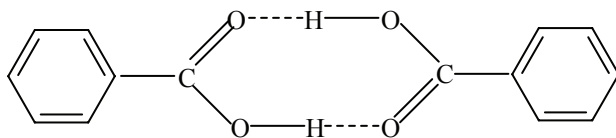
$$n = \frac{PV}{RT} = \frac{\left(748 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right)(4.00 \text{ L})}{(27 + 273) \text{ K}} \times \frac{\text{mol} \cdot \text{K}}{0.0821 \text{ L} \cdot \text{atm}} = 0.160 \text{ mol}$$

$$\text{molality} = \frac{0.160 \text{ mol}}{0.0580 \text{ kg benzene}} = 2.76 \text{ } m$$

$$\Delta T_f = K_f m = (5.12^\circ\text{C}/m)(2.76 m) = 14.1^\circ\text{C}$$

$$\text{freezing point} = 5.5^\circ\text{C} - 14.1^\circ\text{C} = \mathbf{-8.6^\circ\text{C}}$$

- 13.61** The experimental data indicate that the benzoic acid molecules are associated together in pairs in solution due to hydrogen bonding.



- 13.62** First, from the freezing point depression we can calculate the molality of the solution. See Table 13.2 of the text for the normal freezing point and K_f value for benzene.

$$\Delta T_f = (5.5 - 4.3)^\circ\text{C} = 1.2^\circ\text{C}$$

$$m = \frac{\Delta T_f}{K_f} = \frac{1.2^\circ\text{C}}{5.12^\circ\text{C}/m} = 0.23 m$$

Multiplying the molality by the mass of solvent (in kg) gives moles of unknown solute. Then, dividing the mass of solute (in g) by the moles of solute, gives the molar mass of the unknown solute.

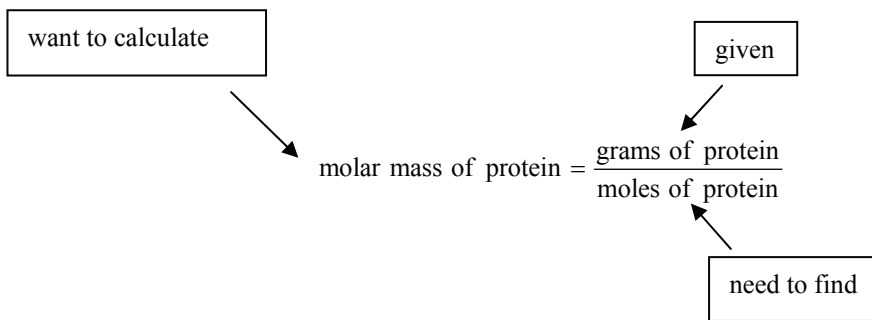
$$\begin{aligned} ? \text{ mol of unknown solute} &= \frac{0.23 \text{ mol solute}}{1 \text{ kg benzene}} \times 0.0250 \text{ kg benzene} \\ &= 0.0058 \text{ mol solute} \end{aligned}$$

$$\text{molar mass of unknown} = \frac{2.50 \text{ g}}{0.0058 \text{ mol}} = \mathbf{4.3 \times 10^2 \text{ g/mol}}$$

The empirical molar mass of $\text{C}_6\text{H}_5\text{P}$ is 108.1 g/mol. Therefore, the molecular formula is $(\text{C}_6\text{H}_5\text{P})_4$ or $\text{C}_{24}\text{H}_{20}\text{P}_4$.

- 13.63** $\pi = MRT = (12.36 \text{ mol/L})(0.0821 \text{ L}\cdot\text{atm}/\text{K}\cdot\text{mol})(22.0 + 273) \text{ K} = \mathbf{299 \text{ atm}}$

- 13.64 Strategy:** We are asked to calculate the molar mass of the protein. Grams of the protein are given in the problem, so we need to solve for moles of protein.



From the osmotic pressure of the solution, we can calculate the molarity of the solution. Then, from the molarity, we can determine the number of moles in 0.8330 g of the protein. What units should we use for π and temperature?

Solution: First, we calculate the molarity using Equation (13.10) of the text.

$$\pi = MRT$$

$$M = \frac{\pi}{RT} = \frac{\left(5.20 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right)}{298 \text{ K}} \times \frac{\text{mol} \cdot \text{K}}{0.0821 \text{ L} \cdot \text{atm}} = 2.80 \times 10^{-4} M$$

Multiplying the molarity by the volume of solution (in L) gives moles of solute (protein).

$$? \text{ mol of protein} = (2.80 \times 10^{-4} \text{ mol/L})(0.170 \text{ L}) = 4.76 \times 10^{-5} \text{ mol protein}$$

Lastly, dividing the mass of protein (in g) by the moles of protein, gives the molar mass of the protein.

$$\text{molar mass of protein} = \frac{0.8330 \text{ g protein}}{4.76 \times 10^{-5} \text{ mol protein}} = 1.75 \times 10^4 \text{ g/mol}$$

13.65 Method 1: First, find the concentration of the solution, then work out the molar mass. The concentration is:

$$\text{Molarity} = \frac{\pi}{RT} = \frac{1.43 \text{ atm}}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(300 \text{ K})} = 0.0581 \text{ mol/L}$$

The solution volume is 0.3000 L so the number of moles of solute is:

$$\frac{0.0581 \text{ mol}}{1 \text{ L}} \times 0.3000 \text{ L} = 0.0174 \text{ mol}$$

The molar mass is then:

$$\frac{7.480 \text{ g}}{0.0174 \text{ mol}} = 430 \text{ g/mol}$$

The empirical formula can be found most easily by assuming a 100.0 g sample of the substance.

$$\text{Moles C} = 41.8 \text{ g} \times \frac{1 \text{ mol}}{12.01 \text{ g}} = 3.48 \text{ mol C}$$

$$\text{Moles H} = 4.7 \text{ g} \times \frac{1 \text{ mol}}{1.008 \text{ g}} = 4.7 \text{ mol H}$$

$$\text{Moles O} = 37.3 \text{ g} \times \frac{1 \text{ mol}}{16.00 \text{ g}} = 2.33 \text{ mol O}$$

$$\text{Moles N} = 16.3 \text{ g} \times \frac{1 \text{ mol}}{14.01 \text{ g}} = 1.16 \text{ mol N}$$

This gives the formula: $\text{C}_{3.48}\text{H}_{4.7}\text{O}_{2.33}\text{N}_{1.16}$. Dividing through by the smallest subscript (1.16) gives the empirical formula, $\text{C}_3\text{H}_4\text{O}_2\text{N}$, which has a mass of 86.0 g per formula unit. The molar mass is five times this amount ($430 \div 86.0 = 5.0$), so the **molecular formula** is $(\text{C}_3\text{H}_4\text{O}_2\text{N})_5$ or **$\text{C}_{15}\text{H}_{20}\text{O}_{10}\text{N}_5$** .

METHOD 2: Use the molarity data as above to determine the molar mass.

$$\text{molar mass} = 430 \text{ g/mol}$$

Multiply the mass % (converted to a decimal) of each element by the molar mass to convert to grams of each element. Then, use the molar mass to convert to moles of each element.

$$n_{\text{C}} = (0.418) \times (430 \text{ g}) \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 15.0 \text{ mol C}$$

$$n_{\text{H}} = (0.047) \times (430 \text{ g}) \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 20 \text{ mol H}$$

$$n_{\text{O}} = (0.373) \times (430 \text{ g}) \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 10.0 \text{ mol O}$$

$$n_{\text{N}} = (0.163) \times (430 \text{ g}) \times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = 5.00 \text{ mol N}$$

Since we used the molar mass to calculate the moles of each element present in the compound, this method directly gives the molecular formula. The formula is $\text{C}_{15}\text{H}_{20}\text{O}_{10}\text{N}_5$.

13.66 We use the osmotic pressure data to determine the molarity.

$$M = \frac{\pi}{RT} = \frac{4.61 \text{ atm}}{(20 + 273) \text{ K}} \times \frac{\text{mol} \cdot \text{K}}{0.0821 \text{ L} \cdot \text{atm}} = 0.192 \text{ mol/L}$$

Next we use the density and the solution mass to find the volume of the solution.

$$\text{mass of soln} = 6.85 \text{ g} + 100.0 \text{ g} = 106.9 \text{ g soln}$$

$$\text{volume of soln} = 106.9 \text{ g soln} \times \frac{1 \text{ mL}}{1.024 \text{ g}} = 104.4 \text{ mL} = 0.1044 \text{ L}$$

Multiplying the molarity by the volume (in L) gives moles of solute (carbohydrate).

$$\text{mol of solute} = M \times L = (0.192 \text{ mol/L})(0.1044 \text{ L}) = 0.0200 \text{ mol solute}$$

Finally, dividing mass of carbohydrate by moles of carbohydrate gives the molar mass of the carbohydrate.

$$\text{molar mass} = \frac{6.85 \text{ g carbohydrate}}{0.0200 \text{ mol carbohydrate}} = 343 \text{ g/mol}$$

13.71 CaCl_2 is an ionic compound (why?) and is therefore an electrolyte in water. Assuming that CaCl_2 is a strong electrolyte and completely dissociates (no ion pairs, van't Hoff factor $i = 3$), the total ion concentration will be $3 \times 0.35 = 1.05 \text{ m}$, which is larger than the urea (nonelectrolyte) concentration of 0.90 m .

(a) The CaCl_2 solution will show a larger boiling point elevation.

(b) The CaCl_2 solution will show a larger freezing point depression. The freezing point of urea solution will be higher. Read the question carefully.

(c) The CaCl_2 solution will have a larger vapor pressure lowering.

13.72 Boiling point, vapor pressure, and osmotic pressure all depend on particle concentration. Therefore, these solutions also have the same boiling point, osmotic pressure, and vapor pressure.

13.73 Assume that all the salts are completely dissociated. Calculate the molality of the ions in the solutions.

- (a) $0.10\ m\ \text{Na}_3\text{PO}_4$: $0.10\ m \times 4\ \text{ions/unit} = 0.40\ m$
 (b) $0.35\ m\ \text{NaCl}$: $0.35\ m \times 2\ \text{ions/unit} = 0.70\ m$
 (c) $0.20\ m\ \text{MgCl}_2$: $0.20\ m \times 3\ \text{ions/unit} = 0.60\ m$
 (d) $0.15\ m\ \text{C}_6\text{H}_{12}\text{O}_6$: nonelectrolyte, $0.15\ m$
 (e) $0.15\ m\ \text{CH}_3\text{COOH}$: weak electrolyte, slightly greater than $0.15\ m$

The solution with the lowest molality will have the highest freezing point (smallest freezing point depression): **(d) > (e) > (a) > (c) > (b)**.

13.74 The freezing point will be depressed most by the solution that contains the most solute particles. You should try to classify each solute as a strong electrolyte, a weak electrolyte, or a nonelectrolyte. All three solutions have the same concentration, so comparing the solutions is straightforward. HCl is a strong electrolyte, so under ideal conditions it will completely dissociate into two particles per molecule. The concentration of particles will be $1.00\ m$. Acetic acid is a weak electrolyte, so it will only dissociate to a small extent. The concentration of particles will be greater than $0.50\ m$, but less than $1.00\ m$. Glucose is a nonelectrolyte, so glucose molecules remain as glucose molecules in solution. The concentration of particles will be $0.50\ m$. For these solutions, the order in which the freezing points become *lower* is:

$$0.50\ m\ \text{glucose} > 0.50\ m\ \text{acetic acid} > 0.50\ m\ \text{HCl}$$

In other words, the HCl solution will have the lowest freezing point (greatest freezing point depression).

13.75 (a) NaCl is a strong electrolyte. The concentration of particles (ions) is double the concentration of NaCl. Note that 135 mL of water has a mass of 135 g (why?).

The number of moles of NaCl is:

$$21.2\ \text{g NaCl} \times \frac{1\ \text{mol}}{58.44\ \text{g}} = 0.363\ \text{mol NaCl}$$

Next, we can find the changes in boiling and freezing points ($i = 2$)

$$m = \frac{0.363\ \text{mol}}{0.135\ \text{kg}} = 2.70\ m$$

$$\Delta T_b = iK_b m = 2(0.52^\circ\text{C}/m)(2.70\ m) = 2.8^\circ\text{C}$$

$$\Delta T_f = iK_f m = 2(1.86^\circ\text{C}/m)(2.70\ m) = 10.0^\circ\text{C}$$

The *boiling point* is **102.8°C** ; the *freezing point* is **-10.0°C** .

(b) Urea is a nonelectrolyte. The particle concentration is just equal to the urea concentration.

The molality of the urea solution is:

$$\text{moles urea} = 15.4\ \text{g urea} \times \frac{1\ \text{mol urea}}{60.06\ \text{g urea}} = 0.256\ \text{mol urea}$$

$$m = \frac{0.256\ \text{mol urea}}{0.0667\ \text{kg H}_2\text{O}} = 3.84\ m$$

$$\Delta T_b = iK_b m = 1(0.52^\circ\text{C}/m)(3.84 m) = 2.0^\circ\text{C}$$

$$\Delta T_f = iK_f m = 1(1.86^\circ\text{C}/m)(3.84 m) = 7.14^\circ\text{C}$$

The *boiling point* is **102.0°C**; the *freezing point* is **-7.14°C**.

- 13.76** Using Equation (13.7) of the text, we can find the mole fraction of the NaCl. We use subscript 1 for H₂O and subscript 2 for NaCl.

$$\Delta P = X_2 P_1^\circ$$

$$X_2 = \frac{\Delta P}{P_1^\circ}$$

$$X_2 = \frac{23.76 \text{ mmHg} - 22.98 \text{ mmHg}}{23.76 \text{ mmHg}} = 0.03283$$

Let's assume that we have 1000 g (1 kg) of water as the solvent, because the definition of molality is moles of solute per kg of solvent. We can find the number of moles of particles dissolved in the water using the definition of mole fraction.

$$X_2 = \frac{n_2}{n_1 + n_2}$$

$$n_1 = 1000 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 55.49 \text{ mol H}_2\text{O}$$

$$\frac{n_2}{55.49 + n_2} = 0.03283$$

$$n_2 = 1.884 \text{ mol}$$

Since NaCl dissociates to form two particles (ions), the number of moles of NaCl is half of the above result.

$$\text{Moles NaCl} = 1.884 \text{ mol particles} \times \frac{1 \text{ mol NaCl}}{2 \text{ mol particles}} = 0.9420 \text{ mol}$$

The molality of the solution is:

$$\frac{0.9420 \text{ mol}}{1.000 \text{ kg}} = \mathbf{0.9420 m}$$

- 13.77** Both NaCl and CaCl₂ are strong electrolytes. Urea and sucrose are nonelectrolytes. The NaCl or CaCl₂ will yield more particles per mole of the solid dissolved, resulting in greater freezing point depression. Also, sucrose and urea would make a mess when the ice melts.

- 13.78 Strategy:** We want to calculate the osmotic pressure of a NaCl solution. Since NaCl is a strong electrolyte, *i* in the van't Hoff equation is 2.

$$\pi = iMRT$$

Since, *R* is a constant and *T* is given, we need to first solve for the molarity of the solution in order to calculate the osmotic pressure (π). If we assume a given volume of solution, we can then use the density of

the solution to determine the mass of the solution. The solution is 0.86% by mass NaCl, so we can find grams of NaCl in the solution.

Solution: To calculate molarity, let's assume that we have 1.000 L of solution (1.000×10^3 mL). We can use the solution density as a conversion factor to calculate the mass of 1.000×10^3 mL of solution.

$$(1.000 \times 10^3 \text{ mL soln}) \times \frac{1.005 \text{ g soln}}{1 \text{ mL soln}} = 1005 \text{ g of soln}$$

Since the solution is 0.86% by mass NaCl, the mass of NaCl in the solution is:

$$1005 \text{ g} \times \frac{0.86\%}{100\%} = 8.6 \text{ g NaCl}$$

The molarity of the solution is:

$$\frac{8.6 \text{ g NaCl}}{1.000 \text{ L}} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} = 0.15 \text{ M}$$

Since NaCl is a strong electrolyte, we assume that the van't Hoff factor is 2. Substituting i , M , R , and T into the equation for osmotic pressure gives:

$$\pi = iMRT = (2) \left(\frac{0.15 \text{ mol}}{\text{L}} \right) \left(\frac{0.0821 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (310 \text{ K}) = \mathbf{7.6 \text{ atm}}$$

- 13.79** The temperature and molarity of the two solutions are the same. If we divide Equation (13.13) from the text for one solution by the same equation for the other, we can find the ratio of the van't Hoff factors in terms of the osmotic pressures:

$$\frac{\pi_{\text{CaCl}_2}}{\pi_{\text{urea}}} = \frac{iMRT}{MRT} = i = \frac{0.605 \text{ atm}}{0.245 \text{ atm}} = \mathbf{2.47}$$

- 13.80** From Table 13.3 of the text, $i = 1.3$

$$\pi = iMRT$$

$$\pi = (1.3) \left(\frac{0.0500 \text{ mol}}{\text{L}} \right) \left(\frac{0.0821 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (295 \text{ K})$$

$$\pi = \mathbf{1.6 \text{ atm}}$$

- 13.81** For this problem we must find the solution mole fractions, the molality, and the molarity. For molarity, we can assume the solution to be so dilute that its density is 1.00 g/mL. We first find the number of moles of lysozyme and of water.

$$n_{\text{lysozyme}} = 0.100 \text{ g} \times \frac{1 \text{ mol}}{13930 \text{ g}} = 7.18 \times 10^{-6} \text{ mol}$$

$$n_{\text{water}} = 150 \text{ g} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 8.32 \text{ mol}$$

Vapor pressure lowering: $\Delta P = X_{\text{lysozyme}} P_{\text{water}}^{\circ} = \frac{n_{\text{lysozyme}}}{n_{\text{lysozyme}} + n_{\text{water}}} (23.76 \text{ mmHg})$

$$\Delta P = \frac{7.18 \times 10^{-6} \text{ mol}}{[(7.18 \times 10^{-6}) + 8.32] \text{ mol}} (23.76 \text{ mmHg}) = \mathbf{2.05 \times 10^{-5} \text{ mmHg}}$$

Freezing point depression: $\Delta T_f = K_f m = (1.86^{\circ}\text{C}/m) \left(\frac{7.18 \times 10^{-6} \text{ mol}}{0.150 \text{ kg}} \right) = \mathbf{8.90 \times 10^{-5} ^{\circ}\text{C}}$

Boiling point elevation: $\Delta T_b = K_b m = (0.52^{\circ}\text{C}/m) \left(\frac{7.18 \times 10^{-6} \text{ mol}}{0.150 \text{ kg}} \right) = \mathbf{2.5 \times 10^{-5} ^{\circ}\text{C}}$

Osmotic pressure: As stated above, we assume the density of the solution is 1.00 g/mL. The volume of the solution will be 150 mL.

$$\pi = MRT = \left(\frac{7.18 \times 10^{-6} \text{ mol}}{0.150 \text{ L}} \right) (0.0821 \text{ L} \cdot \text{atm}/\text{mol} \cdot \text{K}) (298 \text{ K}) = \mathbf{1.17 \times 10^{-3} \text{ atm} = 0.889 \text{ mmHg}}$$

Note that only the osmotic pressure is large enough to measure.

- 13.82** At constant temperature, the osmotic pressure of a solution is proportional to the molarity. When equal volumes of the two solutions are mixed, the molarity will just be the mean of the molarities of the two solutions (assuming additive volumes). Since the osmotic pressure is proportional to the molarity, the osmotic pressure of the solution will be the mean of the osmotic pressure of the two solutions.

$$\pi = \frac{2.4 \text{ atm} + 4.6 \text{ atm}}{2} = \mathbf{3.5 \text{ atm}}$$

- 13.83** Water migrates through the semipermeable cell walls of the cucumber into the concentrated salt solution. When we go swimming in the ocean, why don't we shrivel up like a cucumber? When we swim in fresh water pool, why don't we swell up and burst?
- 13.84 (a)** We use Equation (13.6) of the text to calculate the vapor pressure of each component.

$$P_1 = X_1 P_1^{\circ}$$

First, you must calculate the mole fraction of each component.

$$X_A = \frac{n_A}{n_A + n_B} = \frac{1.00 \text{ mol}}{1.00 \text{ mol} + 1.00 \text{ mol}} = 0.500$$

Similarly,

$$X_B = 0.500$$

Substitute the mole fraction calculated above and the vapor pressure of the pure solvent into Equation (13.6) to calculate the vapor pressure of each component of the solution.

$$P_A = X_A P_A^{\circ} = (0.500)(76 \text{ mmHg}) = 38 \text{ mmHg}$$

$$P_B = X_B P_B^{\circ} = (0.500)(132 \text{ mmHg}) = 66 \text{ mmHg}$$

The total vapor pressure is the sum of the vapor pressures of the two components.

$$P_{\text{Total}} = P_A + P_B = 38 \text{ mmHg} + 66 \text{ mmHg} = \mathbf{104 \text{ mmHg}}$$

(b) This problem is solved similarly to part (a).

$$X_A = \frac{n_A}{n_A + n_B} = \frac{2.00 \text{ mol}}{2.00 \text{ mol} + 5.00 \text{ mol}} = 0.286$$

Similarly,

$$X_B = 0.714$$

$$P_A = X_A P_A^\circ = (0.286)(76 \text{ mmHg}) = 22 \text{ mmHg}$$

$$P_B = X_B P_B^\circ = (0.714)(132 \text{ mmHg}) = 94 \text{ mmHg}$$

$$P_{\text{Total}} = P_A + P_B = 22 \text{ mmHg} + 94 \text{ mmHg} = \mathbf{116 \text{ mmHg}}$$

13.85 $\Delta T_b = iK_b m$

$$i = \frac{\Delta T_b}{K_b m} = \frac{0.78}{(0.52)(0.40)} = \mathbf{3.8}$$

13.86 From the osmotic pressure, you can calculate the molarity of the solution.

$$M = \frac{\pi}{RT} = \frac{\left(30.3 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right)}{308 \text{ K}} \times \frac{\text{mol} \cdot \text{K}}{0.0821 \text{ L} \cdot \text{atm}} = 1.58 \times 10^{-3} \text{ mol/L}$$

Multiplying molarity by the volume of solution in liters gives the moles of solute.

$$(1.58 \times 10^{-3} \text{ mol solute/L soln}) \times (0.262 \text{ L soln}) = 4.14 \times 10^{-4} \text{ mol solute}$$

Divide the grams of solute by the moles of solute to calculate the molar mass.

$$\mathbf{\text{molar mass of solute}} = \frac{1.22 \text{ g}}{4.14 \times 10^{-4} \text{ mol}} = \mathbf{2.95 \times 10^3 \text{ g/mol}}$$

13.87 One manometer has pure water over the mercury, one manometer has a 1.0 M solution of NaCl and the other manometer has a 1.0 M solution of urea. The pure water will have the highest vapor pressure and will thus force the mercury column down the most; column X. Both the salt and the urea will lower the overall pressure of the water. However, the salt dissociates into sodium and chloride ions (van't Hoff factor $i = 2$), whereas urea is a molecular compound with a van't Hoff factor of 1. Therefore the urea solution will lower the pressure only half as much as the salt solution. Y is the NaCl solution and Z is the urea solution.

Assuming that you knew the temperature, could you actually calculate the distance from the top of the solution to the top of the manometer?

13.88 Solve Equation (13.9) of the text algebraically for molality (m), then substitute ΔT_f and K_f into the equation to calculate the molality. You can find the normal freezing point for benzene and K_f for benzene in Table 13.2 of the text.

$$\Delta T_f = 5.5^\circ\text{C} - 3.9^\circ\text{C} = 1.6^\circ\text{C}$$

$$m = \frac{\Delta T_f}{K_f} = \frac{1.6^\circ\text{C}}{5.12^\circ\text{C}/m} = 0.31 m$$

Multiplying the molality by the mass of solvent (in kg) gives moles of unknown solute. Then, dividing the mass of solute (in g) by the moles of solute, gives the molar mass of the unknown solute.

$$\begin{aligned} ? \text{ mol of unknown solute} &= \frac{0.31 \text{ mol solute}}{1 \text{ kg benzene}} \times (8.0 \times 10^{-3} \text{ kg benzene}) \\ &= 2.5 \times 10^{-3} \text{ mol solute} \\ \text{molar mass of unknown} &= \frac{0.50 \text{ g}}{2.5 \times 10^{-3} \text{ mol}} = 2.0 \times 10^2 \text{ g/mol} \end{aligned}$$

The molar mass of cocaine $\text{C}_{17}\text{H}_{21}\text{NO}_4 = 303 \text{ g/mol}$, so the compound is not cocaine. We assume in our analysis that the compound is a pure, monomeric, nonelectrolyte.

13.89 The pill is in a hypotonic solution. Consequently, by osmosis, water moves across the semipermeable membrane into the pill. The increase in pressure pushes the elastic membrane to the right, causing the drug to exit through the small holes at a constant rate.

13.90 First, we calculate the number of moles of HCl in 100 g of solution.

$$n_{\text{HCl}} = 100 \text{ g soln} \times \frac{37.7 \text{ g HCl}}{100 \text{ g soln}} \times \frac{1 \text{ mol HCl}}{36.46 \text{ g HCl}} = 1.03 \text{ mol HCl}$$

Next, we calculate the volume of 100 g of solution.

$$V = 100 \text{ g} \times \frac{1 \text{ mL}}{1.19 \text{ g}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.0840 \text{ L}$$

Finally, the molarity of the solution is:

$$\frac{1.03 \text{ mol}}{0.0840 \text{ L}} = \mathbf{12.3 M}$$

13.91 (a) Using Equation (13.10) of the text, we find the molarity of the solution.

$$M = \frac{\pi}{RT} = \frac{0.257 \text{ atm}}{(0.0821 \text{ L} \cdot \text{atm}/\text{mol} \cdot \text{K})(298 \text{ K})} = 0.0105 \text{ mol/L}$$

This is the combined concentrations of all the ions. The amount dissolved in 10.0 mL (0.01000 L) is

$$? \text{ moles} = \frac{0.0105 \text{ mol}}{1 \text{ L}} \times 0.0100 \text{ L} = 1.05 \times 10^{-4} \text{ mol}$$

Since the mass of this amount of protein is 0.225 g, the apparent molar mass is

$$\frac{0.225 \text{ g}}{1.05 \times 10^{-4} \text{ mol}} = \mathbf{2.14 \times 10^3 \text{ g/mol}}$$

- (b) We need to use a van't Hoff factor to take into account the fact that the protein is a strong electrolyte. The van't Hoff factor will be $i = 21$ (why?).

$$M = \frac{\pi}{iRT} = \frac{0.257 \text{ atm}}{(21)(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(298 \text{ K})} = 5.00 \times 10^{-4} \text{ mol/L}$$

This is the actual concentration of the protein. The amount in 10.0 mL (0.0100 L) is

$$\frac{5.00 \times 10^{-4} \text{ mol}}{1 \text{ L}} \times 0.0100 \text{ L} = 5.00 \times 10^{-6} \text{ mol}$$

Therefore the actual molar mass is:

$$\frac{0.225 \text{ g}}{5.00 \times 10^{-6} \text{ mol}} = \mathbf{4.50 \times 10^4 \text{ g/mol}}$$

- 13.92** Solution A: Let molar mass be \mathcal{M} .

$$\Delta P = X_A P_A^\circ$$

$$(760 - 754.5) = X_A(760)$$

$$X_A = 7.237 \times 10^{-3}$$

$$n = \frac{\text{mass}}{\text{molar mass}}$$

$$X_A = \frac{n_A}{n_A + n_{\text{water}}} = \frac{5.00/\mathcal{M}}{5.00/\mathcal{M} + 100/18.02} = 7.237 \times 10^{-3}$$

$$\mathbf{\mathcal{M} = 124 \text{ g/mol}}$$

- Solution B: Let molar mass be \mathcal{M}

$$\Delta P = X_B P_B^\circ$$

$$X_B = 7.237 \times 10^{-3}$$

$$n = \frac{\text{mass}}{\text{molar mass}}$$

$$X_B = \frac{n_B}{n_B + n_{\text{benzene}}} = \frac{2.31/\mathcal{M}}{2.31/\mathcal{M} + 100/78.11} = 7.237 \times 10^{-3}$$

$$\mathbf{\mathcal{M} = 248 \text{ g/mol}}$$

The molar mass in benzene is about twice that in water. This suggests some sort of dimerization is occurring in a nonpolar solvent such as benzene.

- 13.93** $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$

$$10 \text{ mL} \times \frac{3.0 \text{ g H}_2\text{O}_2}{100 \text{ mL}} \times \frac{1 \text{ mol H}_2\text{O}_2}{34.02 \text{ g H}_2\text{O}_2} \times \frac{1 \text{ mol O}_2}{2 \text{ mol H}_2\text{O}_2} = 4.4 \times 10^{-3} \text{ mol O}_2$$

- (a) Using the ideal gas law:

$$V = \frac{nRT}{P} = \frac{(4.4 \times 10^{-3} \text{ mol O}_2)(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(273 \text{ K})}{1.0 \text{ atm}} = \mathbf{99 \text{ mL}}$$

- (b) The ratio of the volumes: $\frac{99 \text{ mL}}{10 \text{ mL}} = \mathbf{9.9}$

Could we have made the calculation in part (a) simpler if we used the fact that 1 mole of all ideal gases at STP occupies a volume of 22.4 L?

- 13.94** (a) Boiling under reduced pressure.

- (b) CO₂ boils off, expands and cools, condensing water vapor to form fog.

- 13.95** Let the 1.0 M solution be solution 1 and the 2.0 M solution be solution 2. Due to the higher vapor pressure of solution 1, there will be a net transfer of water from beaker 1 to beaker 2 until the vapor pressures of the two solutions are equal. In other words, at equilibrium, the concentration in the two beakers is equal.

At equilibrium,

$$M_1 = M_2$$

Initially, there is 0.050 mole glucose in solution 1 and 0.10 mole glucose in solution 2, and the volume of both solutions is 0.050 L. The volume of solution 1 will decrease, and the volume of solution 2 will increase by the same volume. Let x be the change in volume.

$$\frac{0.050 \text{ mol}}{(0.050 - x) \text{ L}} = \frac{0.10 \text{ mol}}{(0.050 + x) \text{ L}}$$

$$0.0025 + 0.050x = 0.0050 - 0.10x$$

$$0.15x = 0.0025$$

$$x = 0.0167 \text{ L} = 16.7 \text{ mL}$$

The final volumes are:

$$\text{solution 1: } (50 - 16.7) \text{ mL} = \mathbf{33.3 \text{ mL}}$$

$$\text{solution 2: } (50 + 16.7) \text{ mL} = \mathbf{66.7 \text{ mL}}$$

- 13.96** (a) Seawater has a larger number of ionic compounds dissolved in it; thus the boiling point is elevated.
- (b) Carbon dioxide escapes from an opened soft drink bottle because gases are less soluble in liquids at lower pressure (Henry's law).
- (c) As you proved in Problem 13.18, at dilute concentrations molality and molarity are almost the same because the density of the solution is almost equal to that of the pure solvent.
- (d) For colligative properties we are concerned with the number of solute particles in solution relative to the number of solvent particles. Since in colligative particle measurements we frequently are dealing with changes in temperature (and since density varies with temperature), we need a concentration unit that is temperature invariant. We use units of moles per kilogram of mass (molality) rather than moles per liter of solution (molarity).
- (e) Methanol is very water soluble (why?) and effectively lowers the freezing point of water. However in the summer, the temperatures are sufficiently high so that most of the methanol would be lost to vaporization.

13.97 We can calculate the molality of the solution from the freezing point depression.

$$\begin{aligned}\Delta T_f &= K_f m \\ 0.203 &= 1.86 m \\ m &= \frac{0.203}{1.86} = 0.109 m\end{aligned}$$

The molality of the original solution was 0.106 *m*. Some of the solution has ionized to H⁺ and CH₃COO⁻.

	$\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$		
Initial	0.106 <i>m</i>	0	0
Change	- <i>x</i>	+ <i>x</i>	+ <i>x</i>
Equil.	0.106 <i>m</i> - <i>x</i>	<i>x</i>	<i>x</i>

At equilibrium, the total concentration of species in solution is 0.109 *m*.

$$\begin{aligned}(0.106 - x) + 2x &= 0.109 m \\ x &= 0.003 m\end{aligned}$$

The percentage of acid that has undergone ionization is:

$$\frac{0.003 m}{0.106 m} \times 100\% = \mathbf{3\%}$$

13.98 $\Delta T_f = 5.5 - 2.2 = 3.3^\circ\text{C}$ C₁₀H₈: 128.2 g/mol

$$m = \frac{\Delta T_f}{K_f} = \frac{3.3}{5.12} = 0.645 m$$
C₆H₁₂: 84.16 g/mol

Let *x* = mass of C₆H₁₂ (in grams).

Using,

$$m = \frac{\text{mol solute}}{\text{kg solvent}} \quad \text{and} \quad \text{mol} = \frac{\text{mass}}{\text{molar mass}}$$

$$0.645 = \frac{\frac{x}{84.16} + \frac{1.32 - x}{128.2}}{0.0189 \text{ kg}}$$

$$0.0122 = \frac{128.2x + 111.1 - 84.16x}{84.16 \times 128.2}$$

$$x = 0.47 \text{ g}$$

$$\% \text{C}_6\text{H}_{12} = \frac{0.47}{1.32} \times 100\% = \mathbf{36\%}$$

$$\% \text{C}_{10}\text{H}_8 = \frac{0.86}{1.32} \times 100\% = \mathbf{65\%}$$

The percentages don't add up to 100% because of rounding procedures.

- 13.99** (a) Solubility decreases with increasing lattice energy.
 (b) Ionic compounds are more soluble in a polar solvent.
 (c) Solubility increases with enthalpy of hydration of the cation and anion.

13.100 The completed table is shown below:

Attractive Forces	Deviation from Raoult's	$\Delta H_{\text{solution}}$
$A \leftrightarrow A, B \leftrightarrow B > A \leftrightarrow B$	Positive	Positive (endothermic)
$A \leftrightarrow A, B \leftrightarrow B < A \leftrightarrow B$	Negative	Negative (exothermic)
$A \leftrightarrow A, B \leftrightarrow B = A \leftrightarrow B$	Zero	Zero

The first row represents a Case 1 situation in which A's attract A's and B's attract B's more strongly than A's attract B's. As described in Section 13.6 of the text, this results in positive deviation from Raoult's law (higher vapor pressure than calculated) and positive heat of solution (endothermic).

In the second row a negative deviation from Raoult's law (lower than calculated vapor pressure) means A's attract B's better than A's attract A's and B's attract B's. This causes a negative (exothermic) heat of solution.

In the third row a zero heat of solution means that A–A, B–B, and A–B interparticle attractions are all the same. This corresponds to an ideal solution which obeys Raoult's law exactly.

What sorts of substances form ideal solutions with each other?

13.101 $P_A = X_A P_A^\circ$

$$P_{\text{ethanol}} = (0.62)(108 \text{ mmHg}) = 67.0 \text{ mmHg}$$

$$P_{1\text{-propanol}} = (0.38)(40.0 \text{ mmHg}) = 15.2 \text{ mmHg}$$

In the vapor phase:

$$X_{\text{ethanol}} = \frac{67.0}{67.0 + 15.2} = \mathbf{0.815}$$

13.102 Since the total volume is less than the sum of the two volumes, the ethanol and water must have an intermolecular attraction that results in an overall smaller volume.

13.103 First, we can calculate the molality of the solution from the freezing point depression.

$$\Delta T_f = (5.12)m$$

$$(5.5 - 3.5) = 5.12m$$

$$m = 0.39$$

Next, from the definition of molality, we can calculate the moles of solute.

$$m = \frac{\text{mol solute}}{\text{kg solvent}}$$

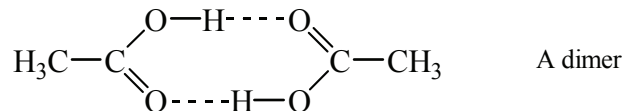
$$0.39 \text{ m} = \frac{\text{mol solute}}{80 \times 10^{-3} \text{ kg benzene}}$$

$$\text{mol solute} = 0.031 \text{ mol}$$

The molar mass (\mathcal{M}) of the solute is:

$$\frac{3.8 \text{ g}}{0.031 \text{ mol}} = 1.2 \times 10^2 \text{ g/mol}$$

The molar mass of CH_3COOH is 60.05 g/mol. Since the molar mass of the solute calculated from the freezing point depression is twice this value, the structure of the solute most likely is a dimer that is held together by hydrogen bonds.



13.104 Let the mass of NaCl be x g. Then, the mass of sucrose is $(10.2 - x)$ g.

We know that the equation representing the osmotic pressure is:

$$\pi = MRT$$

π , R , and T are given. Using this equation and the definition of molarity, we can calculate the percentage of NaCl in the mixture.

$$\text{molarity} = \frac{\text{mol solute}}{\text{L soln}}$$

Remember that NaCl dissociates into two ions in solution; therefore, we multiply the moles of NaCl by two.

$$\text{mol solute} = 2 \left(x \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} \right) + \left((10.2 - x) \text{ g sucrose} \times \frac{1 \text{ mol sucrose}}{342.3 \text{ g sucrose}} \right)$$

$$\text{mol solute} = 0.03422x + 0.02980 - 0.002921x$$

$$\text{mol solute} = 0.03130x + 0.02980$$

$$\text{Molarity of solution} = \frac{\text{mol solute}}{\text{L soln}} = \frac{0.03130x + 0.02980}{0.250 \text{ L}}$$

Substitute molarity into the equation for osmotic pressure to solve for x .

$$\pi = MRT$$

$$7.32 \text{ atm} = \left(\frac{(0.03130x + 0.02980) \text{ mol}}{0.250 \text{ L}} \right) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (296 \text{ K})$$

$$0.0753 = 0.03130x + 0.02980$$

$$x = 1.45 \text{ g} = \text{mass of NaCl}$$

$$\text{Mass \% NaCl} = \frac{1.45 \text{ g}}{10.2 \text{ g}} \times 100\% = 14.2\%$$

- 13.105 (a)** Looking at Figure 13.8(b) of the text, you would have to apply a pressure greater than the osmotic pressure to the right compartment to force pure solvent (water) through to the left compartment.
- (b)** Reverse osmosis uses high pressure to force water from a more concentrated solution to a less concentrated one through a semipermeable membrane. Desalination by reverse osmosis is considerably cheaper than by distillation and avoids the technical difficulties associated with desalination by freezing. Reverse osmosis does *not* involve a phase transition.
- (c)** To reverse the osmotic migration of water across a semipermeable membrane, an external pressure exceeding the osmotic pressure must be applied. To find the osmotic pressure of 0.70 M NaCl solution, we must use the van't Hoff factor because NaCl is a strong electrolyte (see Table 13.3 of the text).

The osmotic pressure of sea water is:

$$\pi = iMRT = 1.9(0.70 \text{ mol/L})(0.0821 \text{ L}\cdot\text{atm/K}\cdot\text{mol})(298 \text{ K}) = \mathbf{33 \text{ atm}}$$

To cause reverse osmosis a pressure in excess of 33 atm must be applied.

- 13.106 (a)** The solution is prepared by mixing equal masses of A and B. Let's assume that we have 100 grams of each component. We can convert to moles of each substance and then solve for the mole fraction of each component.

Since the molar mass of A is 100 g/mol, we have 1.00 mole of A. The moles of B are:

$$100 \text{ g B} \times \frac{1 \text{ mol B}}{110 \text{ g B}} = 0.909 \text{ mol B}$$

The mole fraction of A is:

$$X_A = \frac{n_A}{n_A + n_B} = \frac{1}{1 + 0.909} = \mathbf{0.524}$$

Since this is a two component solution, the mole fraction of B is: $X_B = 1 - 0.524 = \mathbf{0.476}$

- (b)** We can use Equation (13.6) of the text and the mole fractions calculated in part (a) to calculate the partial pressures of A and B over the solution.

$$P_A = X_A P_A^\circ = (0.524)(95 \text{ mmHg}) = \mathbf{50 \text{ mmHg}}$$

$$P_B = X_B P_B^\circ = (0.476)(42 \text{ mmHg}) = \mathbf{20 \text{ mmHg}}$$

- (c)** Recall that pressure of a gas is directly proportional to moles of gas ($P \propto n$). The ratio of the partial pressures calculated in part (b) is 50 : 20, and therefore the ratio of moles will also be 50 : 20. Let's assume that we have 50 moles of A and 20 moles of B. We can solve for the mole fraction of each component and then solve for the vapor pressures using Equation (13.6) of the text.

The mole fraction of A is:

$$X_A = \frac{n_A}{n_A + n_B} = \frac{50}{50 + 20} = \mathbf{0.71}$$

Since this is a two component solution, the mole fraction of B is: $X_B = 1 - 0.71 = \mathbf{0.29}$

The vapor pressures of each component above the solution are:

$$P_A = X_A P_A^\circ = (0.71)(95 \text{ mmHg}) = \mathbf{67 \text{ mmHg}}$$

$$P_B = X_B P_B^\circ = (0.29)(42 \text{ mmHg}) = \mathbf{12 \text{ mmHg}}$$

- 13.107** The desired process is for (fresh) water to move from a more concentrated solution (seawater) to pure solvent. This is an example of reverse osmosis, and external pressure must be provided to overcome the osmotic pressure of the seawater. The source of the pressure here is the water pressure, which increases with increasing depth. The osmotic pressure of the seawater is:

$$\begin{aligned}\pi &= MRT \\ \pi &= (0.70 M)(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(293 \text{ K}) \\ \pi &= 16.8 \text{ atm}\end{aligned}$$

The water pressure at the membrane depends on the height of the sea above it, *i.e.* the depth. $P = \rho gh$, and fresh water will begin to pass through the membrane when $P = \pi$. Substituting $\pi = P$ into the equation gives:

$$\pi = \rho gh$$

and

$$h = \frac{\pi}{g\rho}$$

Before substituting into the equation to solve for h , we need to convert atm to pascals, and the density to units of kg/m^3 . These conversions will give a height in units of meters.

$$16.8 \text{ atm} \times \frac{1.01325 \times 10^5 \text{ Pa}}{1 \text{ atm}} = 1.70 \times 10^6 \text{ Pa}$$

$1 \text{ Pa} = 1 \text{ N/m}^2$ and $1 \text{ N} = 1 \text{ kg}\cdot\text{m/s}^2$. Therefore, we can write $1.70 \times 10^6 \text{ Pa}$ as $1.70 \times 10^6 \text{ kg/m}\cdot\text{s}^2$

$$\frac{1.03 \text{ g}}{1 \text{ cm}^3} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \left(\frac{100 \text{ cm}}{1 \text{ m}}\right)^3 = 1.03 \times 10^3 \text{ kg/m}^3$$

$$h = \frac{\pi}{g\rho} = \frac{1.70 \times 10^6 \frac{\text{kg}}{\text{m}\cdot\text{s}^2}}{\left(9.81 \frac{\text{m}}{\text{s}^2}\right)\left(1.03 \times 10^3 \frac{\text{kg}}{\text{m}^3}\right)} = \mathbf{168 \text{ m}}$$

- 13.108** The total vapor pressure depends on the vapor pressures of A and B in the mixture, which in turn depends on the vapor pressures of pure A and B. With the total vapor pressure of the two mixtures known, a pair of simultaneous equations can be written in terms of the vapor pressures of pure A and B. We carry 2 extra significant figures throughout this calculation to avoid rounding errors.

For the solution containing 1.2 moles of A and 2.3 moles of B,

$$X_A = \frac{1.2 \text{ mol}}{1.2 \text{ mol} + 2.3 \text{ mol}} = 0.3429$$

$$X_B = 1 - 0.3429 = 0.6571$$

$$P_{\text{total}} = P_A + P_B = X_A P_A^\circ + X_B P_B^\circ$$

Substituting in P_{total} and the mole fractions calculated gives:

$$331 \text{ mmHg} = 0.3429 P_A^\circ + 0.6571 P_B^\circ$$

Solving for P_A° ,

$$P_A^\circ = \frac{331 \text{ mmHg} - 0.6571P_B^\circ}{0.3429} = 965.3 \text{ mmHg} - 1.916P_B^\circ \quad (1)$$

Now, consider the solution with the additional mole of B.

$$X_A = \frac{1.2 \text{ mol}}{1.2 \text{ mol} + 3.3 \text{ mol}} = 0.2667$$

$$X_B = 1 - 0.2667 = 0.7333$$

$$P_{\text{total}} = P_A + P_B = X_A P_A^\circ + X_B P_B^\circ$$

Substituting in P_{total} and the mole fractions calculated gives:

$$347 \text{ mmHg} = 0.2667P_A^\circ + 0.7333P_B^\circ \quad (2)$$

Substituting Equation (1) into Equation (2) gives:

$$347 \text{ mmHg} = 0.2667(965.3 \text{ mmHg} - 1.916P_B^\circ) + 0.7333P_B^\circ$$

$$0.2223P_B^\circ = 89.55 \text{ mmHg}$$

$$P_B^\circ = 402.8 \text{ mmHg} = \mathbf{4.0 \times 10^2 \text{ mmHg}}$$

Substitute the value of P_B° into Equation (1) to solve for P_A° .

$$P_A^\circ = 965.3 \text{ mmHg} - 1.916(402.8 \text{ mmHg}) = 193.5 \text{ mmHg} = \mathbf{1.9 \times 10^2 \text{ mmHg}}$$

13.109 Starting with $n = kP$ and substituting into the ideal gas equation ($PV = nRT$), we find:

$$PV = (kP)RT$$

$$V = kRT$$

This equation shows that the volume of a gas that dissolves in a given amount of solvent is dependent on the *temperature*, not the pressure of the gas.

13.110 To calculate the freezing point of the solution, we need the solution molality and the freezing-point depression constant for water (see Table 13.2 of the text). We can first calculate the molarity of the solution using Equation (13.10) of the text: $\pi = MRT$. The solution molality can then be determined from the molarity.

$$M = \frac{\pi}{RT} = \frac{10.50 \text{ atm}}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(298 \text{ K})} = 0.429 \text{ M}$$

Let's assume that we have 1 L (1000 mL) of solution. The mass of 1000 mL of solution is:

$$\frac{1.16 \text{ g}}{1 \text{ mL}} \times 1000 \text{ mL} = 1160 \text{ g soln}$$

The mass of the solvent (H₂O) is:

$$\text{mass H}_2\text{O} = \text{mass soln} - \text{mass solute}$$

$$\text{mass H}_2\text{O} = 1160 \text{ g} - \left(0.429 \text{ mol glucose} \times \frac{180.2 \text{ g glucose}}{1 \text{ mol glucose}} \right) = 1083 \text{ g} = 1.083 \text{ kg}$$

The molality of the solution is:

$$\text{molality} = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{0.429 \text{ mol}}{1.083 \text{ kg}} = 0.396 \text{ m}$$

The freezing point depression is:

$$\Delta T_f = K_f m = (1.86^\circ\text{C}/m)(0.396 \text{ m}) = 0.737^\circ\text{C}$$

The solution will freeze at $0^\circ\text{C} - 0.737^\circ\text{C} = \mathbf{-0.737^\circ\text{C}}$