CHAPTER 13
SOLUTIONS AND THEIR PHYSICAL PROPERTIES
PRACTICE EXAMPLES

1A To determine mass percent, we need both the mass of ethanol and the mass of solution. From volume percent, we know that 100.0 mL of solution contains 20.0 mL pure ethanol. The density of pure ethanol is 0.789 g/mL. We now can determine the mass of solute (ethanol) and solution. We perform the calculation in one step.

$$\text{mass percent ethanol} = \frac{20.0\text{ mL ethanol} \times \dfrac{0.789\text{ g}}{1\text{ mL ethanol}}}{100.0\text{ mL soln} \times \dfrac{0.977\text{ g}}{1\text{ mL soln}}} \times 100\% = 16.2\%\text{ ethanol by mass}$$

1B In each case, we use the definition of the concentration unit, making sure that the numerator and denominator are converted to the correct units.

(a) We first determine the mass in grams of the solute and of the solution.

$$\text{mass CH}_3\text{OH} = 11.3\text{ mL CH}_3\text{OH} \times \frac{0.793\text{ g}}{1\text{ mL}} = 8.96\text{ g CH}_3\text{OH}$$

$$\text{mass soln} = 75.0\text{ mL soln} \times \frac{0.980\text{ g}}{1\text{ mL}} = 73.5\text{ g soln}$$

$$\text{amount of H}_2\text{O} = (73.5\text{ g soln} - 8.96\text{ g CH}_3\text{OH}) \times \frac{1\text{ mol H}_2\text{O}}{18.02\text{ g H}_2\text{O}}$$

$$\text{amount of H}_2\text{O} = 3.58\text{ mol H}_2\text{O}$$

$$\text{amount of CH}_3\text{OH} = 8.96\text{ g CH}_3\text{OH} \times \frac{1\text{ mol CH}_3\text{OH}}{32.04\text{ g CH}_3\text{OH}} = 0.280\text{ mol CH}_3\text{OH}$$

$$\begin{matrix}\text{H}_2\text{O mole}\\ \text{fraction}\end{matrix} = \frac{\text{amount of H}_2\text{O in moles}}{\text{amount of soln in moles}} = \frac{3.58\text{ mol H}_2\text{O}}{3.58\text{ mol H}_2\text{O} + 0.280\text{ mol CH}_3\text{OH}} = 0.927$$

(b) $$[\text{CH}_3\text{OH}] = \frac{\text{amount of CH}_3\text{OH in moles}}{\text{volume of soln in L}} = \frac{0.280\text{ mol CH}_3\text{OH}}{75.0\text{ mL soln} \times \dfrac{1\text{ L}}{1000\text{ mL}}} = 3.73\text{ M}$$

$$\text{mass of H}_2\text{O} = 7.35 - 8.96 = 64.5\text{ g H}_2\text{O}$$

(c) $$\text{molality of CH}_3\text{OH} = \frac{\text{amount of CH}_3\text{OH in moles}}{\text{mass of H}_2\text{O in kg}} = \frac{0.280\text{ mol CH}_3\text{OH}}{64.5\text{ g H}_2\text{O} \times \dfrac{1\text{ kg}}{1000\text{ g}}} = 4.34\text{ m}$$

2A First we need to find the amount of each component in solution. Let us consider a 100.00-g sample of solution, in which there are 16.00 g glycerol and 84.00 g water.

The shorthand notation for glycerol, $HOCH_2CH(OH)CH_2OH$, is $C_3H_5(OH)_3$

$$\text{amount of glycerol} = 16.00 \text{ g } C_3H_5(OH)_3 \times \frac{1 \text{ mol } C_3H_5(OH)_3}{92.10 \text{ g } C_3H_5(OH)_3} = 0.1737 \text{ mol } C_3H_5(OH)_3$$

$$\text{amount of water} = 84.00 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 4.661 \text{ mol } H_2O$$

$$\text{mole fraction of } C_3H_5(OH)_3 = \frac{n_{C_3H_5(OH)_3}}{n_{[C_3H_5(OH)_3 + H_2O]}} = \frac{0.1737 \text{ mol } C_3H_5(OH)_3}{0.1737 \text{ mol } C_3H_5(OH)_3 + 4.661 \text{ mol } H_2O}$$

$$\text{mole fraction of } C_3H_5(OH)_3 = 0.03593$$

2B First we need the amount of sucrose in solution. We use a 100.00-g sample of solution, in which there are 10.00 g sucrose and 90.00 g water.

$$\text{amount } C_{12}H_{22}O_{11} = 10.00 \text{ g } C_{12}H_{22}O_{11} \times \frac{1 \text{ mol } C_{12}H_{22}O_{11}}{342.30 \text{ g } C_{12}H_{22}O_{11}} = 0.02921 \text{ mol } C_{12}H_{22}O_{11}$$

(a) Molarity is amount of solute in moles per liter of solution. Convert the 100.00 g of solution to L with density as a conversion factor.

$$C_{12}H_{22}O_{11} \text{ molarity} = \frac{0.02921 \text{ mol } C_{12}H_{22}O_{11}}{1000. \text{ g soln}} \times \frac{1.040 \text{ g soln}}{1 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.3038 \text{ M}$$

(b) Molality is amount of solute in moles per kilogram of solvent.
Convert 90.00 g of solvent to kg.

$$C_{12}H_{22}O_{11} \text{ molality} = \frac{0.02921 \text{ mol } C_{12}H_{22}O_{11}}{90.00 \text{ g } H_2O} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 0.3246 m$$

(c) Mole fraction is the moles of solute per moles of solution. First compute the moles in 90.00 g H_2O.

$$n_{H_2O} = 90.00 \text{ g} \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 4.994 \text{ mol } H_2O$$

$$\text{mole fraction } C_{12}H_{22}O_{11} = \frac{0.02921 \text{ mol } C_{12}H_{22}O_{11}}{0.02921 \text{ mol } C_{12}H_{22}O_{11} + 4.994 \text{ mol } H_2O} = 0.005815$$

3A Water is a highly polar compound. In fact, water molecules bond to each other through hydrogen bonds, which are unusually strong dipole–dipole interactions. Thus, water should mix well with other polar, hydrogen bonding compounds. (a) Toluene is nonpolar and should not be very soluble in water. (c) Benzaldehyde can form hydrogen bonds to water through its O atom. However, most of the molecule is nonpolar and, as a result, it has limited solubility in water. (b) Oxalic acid is polar and can form hydrogen bonds. Of these three compounds, oxalic acid should be the most readily soluble in water. Actual solubilities (w/w%) are: toluene (0.067%) < benzaldehyde (0.28%) < oxalic acid (14%).

3B Both I_2 and CCl_4 are nonpolar molecules. It does not take much energy to break the attractions among I_2 molecules, or among CCl_4 molecules. Also, there is not a strong I_2-CCl_4 attraction created when a solution forms. Thus, I_2 should dissolve well in CCl_4 by simple mixing. H_2O is extensively hydrogen bonded with strong intermolecular forces that are difficult to break, but there is not a strong I_2-H_2O attraction created when a solution forms. Thus, we expect I_2 to dissolve poorly in water. Actual solubilities are: $2.603\text{ g } I_2/100\text{ g } CCl_4$ and $0.033\text{ g } I_2/100\text{ g } H_2O$.

4A The two suggestions are quoted first, followed by the means for achieving each one.

(1) Dissolve the 95 g NH_4Cl in just enough water to produce a saturated solution $(55\text{ g } NH_4Cl/100\text{ g } H_2O)$ at $60^\circ C$.

$$\text{mass of water needed} = 95\text{ g } NH_4Cl \times \frac{100\text{ g } H_2O}{55\text{ g } NH_4Cl} = 173\text{ g } H_2O$$

The mass of NH_4Cl in the saturated solution at $20^\circ C$ will be smaller.

$$\text{mass } NH_4Cl \text{ dissolved} = 173\text{ g } H_2O \times \frac{37\text{ g } NH_4Cl}{100\text{ g } H_2O} = 64\text{ g } NH_4Cl \text{ dissolved}$$

$$\begin{aligned}\text{crystallized mass } NH_4Cl &= 95\text{ g } NH_4Cl \text{ total} - 64\text{ g } NH_4Cl \text{ dissolved at } 20^\circ C \\ &= 31\text{ g } NH_4Cl \text{ crystallized}\end{aligned}$$

(2) Lower the final temperature to 0° C, rather than 20° C. From Figure 13-8, at 0° C, the solubility of NH_4Cl is 28.5 g NH_4Cl/100 g H_2O. From this (and knowing that there are 173 g H_2O present in the solution) we calculate the mass of NH_4Cl dissolved at this lower temperature.

$$\text{mass dissolved } NH_4Cl = 173\text{ g } H_2O \times \frac{28.5\text{ g } NH_4Cl}{100\text{ g } H_2O} = 49.3\text{ g } NH_4Cl \text{ dissolved}$$

The mass of NH_4Cl recrystallized is $95\text{ g} - 49.3\text{ g} = 46\text{ g}$

$$\text{yield} = \left(\frac{46\text{ g}}{95\text{ g}}\right) \times 100\% = 48\%$$

4B Percent yield for the recrystallization can be defined as:

$$\%\text{ yield} = \frac{\text{mass crystallized}}{\text{mass dissolved}(40^\circ C)} \times 100\%$$

$$\%\text{ yield} = \frac{\text{mass dissolved}(\text{at } 40^\circ C) - \text{mass dissolved}(\text{at } 20^\circ C)}{\text{mass dissolved}(\text{at } 40^\circ C)} \times 100\%$$

Figure 13-8 solubilities per 100 g H_2O are followed by percent yield calculations.

Solubility of $KClO_4$: 4.84 g at 40°C and 3.0 g at 20° C

$$\text{Percent yield of } KClO_4 = \frac{4.84\text{ g} - 3.0\text{ g}}{4.84\text{ g}} \times 100\% = 38\%\ KClO_4$$

Solubility of KNO_3: 60.7 g at 40°C and 32.3 g at 20°C

$$\text{Percent Yield of } KNO_3 = \frac{60.7\text{ g} - 32.3\text{ g}}{60.7\text{ g}} \times 100\% = 47\%\ KNO_3$$

Solubility of K_2SO_4: 15.1 g at 40°C and 11.9 g at 20° C

$$\text{Percent yield of } K_2SO_4 = \frac{15.1\text{ g} - 11.9\text{ g}}{15.1\text{ g}} \times 100\% = 21\%\ K_2SO_4$$

Ranked in order of decreasing percent yield we have:
$KNO_3(47\%) > KClO_4(38\%) > K_2SO_4(21\%)$

5A From Example 13-5, we know that the Henry's law constant for O_2 dissolved in water is $k = 2.18 \times 10^{-3}\text{ M atm}^{-1}$. Consequently,

$$P_{\text{gas}} = \frac{C}{k} = \frac{\dfrac{5.00 \times 10^{-3}\text{ g} \times \dfrac{1\text{ mol } O_2}{32.00\text{ g } O_2}}{0.100\text{ L}}}{2.18 \times 10^{-3}\text{ M atm}^{-1}} = 0.717\text{ atm } O_2 \text{ pressure}$$

5B We note the relationship between gas partial pressure over a liquid and its dissolved concentration is given by Henry's Law: C = k_H P, where C is the concentration (given in dimensionless "volume parts" unit, akin to ppm), k_H is the Henry's Law constant, and P is the partial pressure of CO, which is given by: $\chi_{P_{CO}} = P_{CO}/P_{\text{total}}$. Assuming a CO partial pressure of 1.0 (100% at 1 atm), the k_H value is 0.0354 $\text{mL}\cdot\text{mL}^{-1}\cdot\text{atm}^{-1}$.

First, since the concentration of CO is 0.0100 mol CO/1.000 L of H_2O, we have to find the volume of CO at 273 K and 1.0 atm. That is,

$$V = \frac{nRT}{P} = \frac{(0.0100\text{ mol})(0.08206\text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(273\text{ K})}{1.0\text{ atm}} = 0.224\text{ L}$$

Therefore, the concentration of CO may be expressed as follows:

$$\text{v/v concentration of CO} = \frac{0.224\text{ L CO}}{1.000\text{ L } H_2O} = 0.224\text{ L/L or } 0.224\text{ mL/mL}$$

$$P_{CO} = \frac{C}{k} = \frac{0.224\text{ mL}\cdot\text{mL}^{-1}}{0.0354\text{ mL}\cdot\text{mL}^{-1}\cdot\text{atm}^{-1}} = 6.328\text{ atm}$$

6A Raoult's law enables us to determine the vapor pressure of each component.
$P_{\text{hex}} = \chi_{\text{hex}} P°_{\text{hex}} = 0.750 \times 149.1\text{ mmHg} = 112\text{ mmHg}$
$P_{\text{pen}} = \chi_{\text{pen}} P°_{\text{pen}} = 0.250 \times 508.5\text{ mmHg} = 127\text{ mmHg}.$
We use Dalton's law to determine the total vapor pressure:
$P_{\text{total}} = P_{\text{hex}} + P_{\text{pen}} = 112\text{ mmHg} + 127\text{ mmHg} = 239\text{ mmHg}$

6B The masses of solution components need to be converted to amounts in moles through the use of molar masses. Let us choose as our amount precisely 1.0000 mole of $C_6H_6 = 78.11\text{ g } C_6H_6$ and an equal mass of toluene.

$$\text{amount of toluene} = 78.11\text{ g } C_7H_8 \times \frac{1\text{ mol } C_7H_8}{92.14\text{ g } C_7H_8} = 0.8477\text{ mol } C_7H_8$$

$$\text{mole fraction toluene} = \chi_{\text{tol}} = \frac{0.8477\text{ mol } C_7H_8}{0.8477\text{ mol } C_7H_8 + 1.0000\text{ mol } C_6H_6} = 0.4588$$

$$\text{toluene vapor pressure} = \chi_{\text{tol}} P°_{\text{tol}} = 0.4588 \times 28.4\text{ mmHg} = 13.0\text{ mmHg}$$

$$\text{benzene vapor pressure} = \chi_{\text{benz}} P°_{\text{benz}} = (1.0000 - 0.4588) \times 95.1\text{ mmHg} = 51.5\text{ mmHg.}$$

$$\text{total vapor pressure} = 13.0\text{ mmHg} + 51.5\text{ mmHg} = 64.5\text{ mmHg}$$

7A The vapor pressure composition of each component is that component's partial pressure divided by the total pressure. Again, we note that the vapor is richer in the more volatile component.

$$y_{\text{hexane}} = \frac{P_{\text{hexane}}}{P_{\text{total}}} = \frac{112\text{ mmHg hexane}}{239\text{ mmHg total}} = 0.469 \quad y_{\text{pentane}} = \frac{P_{\text{pentane}}}{P_{\text{total}}} = \frac{127\text{ mmHg pentane}}{239\text{ mmHg total}} = 0.531 \text{ or}$$

simply $1.000 - 0.469 = 0.531$

7B The vapor pressure composition of each component is that component's partial pressure divided by the total pressure. Again we note that the vapor is richer in the more volatile component.

$$y_t = \frac{P_{\text{toluene}}}{P_{\text{total}}} = \frac{13.0\text{ mmHg toluene}}{64.5\text{ mmHg total}} = 0.202 \qquad y_b = \frac{P_{\text{benzene}}}{P_{\text{total}}} = \frac{51.5\text{ mmHg benzene}}{64.5\text{ mmHg total}} = 0.798$$

or simply 1.000-0.202 = 0.798

8A We use the osmotic pressure equation, converting the mass of solute to amount in moles, the temperature to Kelvin, and the solution volume to liters.

$$\pi = \frac{nRT}{V} = \frac{\left(1.50\text{ g } C_{12}H_{22}O_{11} \times \frac{1\text{ mol } C_{12}H_{22}O_{11}}{342.3\text{ g } C_{12}H_{22}O_{11}}\right) \times 0.08206 \frac{\text{L atm}}{\text{mol K}} \times 298\text{ K}}{125\text{ mL} \times \frac{1\text{ L}}{1000\text{ mL}}} = 0.857\text{ atm}$$

8B We use the osmotic pressure equation to determine the molarity of the solution.

$$\frac{n}{V} = \frac{\pi}{RT} = \frac{0.015\text{ atm}}{0.08206\text{ L atm mol}^{-1}\text{ K}^{-1} \times 298\text{ K}} = 6.1 \times 10^{-4}\text{ M}$$

Now, we can calculate the mass of urea.

$$\text{urea mass} = 0.225\text{ L} \times \frac{6.1 \times 10^{-4}\text{ mol urea}}{1\text{ L soln}} \times \frac{60.06\text{ g } CO(NH_2)_2}{1\text{ mol } CO(NH_2)_2} = 8.2\underline{4} \times 10^{-3}\text{ g}$$

9A We could substitute directly into the equation for molar mass derived in Example 13-9, but let us rather think our way through each step of the process. First, we find the concentration of the solution, by rearranging $\pi = \frac{n}{V}RT$. We need to convert the osmotic pressure to atmospheres.

$$\frac{n}{V} = \frac{\pi}{RT} = \frac{8.73 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}}{0.08206 \frac{\text{L atm}}{\text{mol K}} \times 298 \text{ K}} = 4.70 \times 10^{-4} \text{ M}$$

Next we determine the amount in moles of dissolved solute.

$$\text{amount of solute} = 100.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{4.70 \times 10^{-4} \text{ mol solute}}{1 \text{ L solution}} = 4.70 \times 10^{-5} \text{ mol solute}$$

We use the mass of solute, 4.04 g, to determine the molar mass. → $M = \frac{4.04 \text{ g}}{4.70 \times 10^{-5} \text{ mol}} = 8.60 \times 10^{4} \text{ g/mol}$

9B We use the osmotic pressure equation along with the molarity of the solution.

$$\pi = \frac{n}{V}RT = \frac{2.12 \text{ g} \times \frac{1 \text{ mol}}{6.86 \times 10^{4} \text{ g}}}{75.00 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}} \times \frac{0.08206 \text{ L atm}}{\text{mol K}} \times (310.2)\text{K} = 0.0105 \text{ atm} = 7.97 \text{ mmHg}$$

10A **(a)** The freezing point depression constant for water is $K_f = 1.86\,°\text{C}\,m^{-1}$.

$$\text{molality} = \frac{\Delta T_f}{-K_f} = \frac{-0.227\,°\text{C}}{-1.86\,°\text{C}\,m^{-1}} = 0.122\ m$$

(b) We will use the definition of molality to determine the number of moles of riboflavin in 0.833 g of dissolved riboflavin.

$$\text{amount of riboflavin} = 18.1 \text{ g solvent H}_2\text{O} \times \frac{1 \text{ kg solvent}}{1000 \text{ g}} \times \frac{0.122 \text{ mol solute}}{1 \text{ kg solvent}}$$

$$\text{amount of riboflavin} = 2.21 \times 10^{-3} \text{ mol riboflavin}$$

$$\text{molar mass} = \frac{0.833 \text{ g riboflavin}}{2.21 \times 10^{-3} \text{ mol}} = 377 \text{ g/mol}$$

(c) We use the method of Chapter 3 to find riboflavin's empirical formula, starting with a 100.00-g sample.

$$54.25\text{ g C}\times\frac{1\text{ mol C}}{12.01\text{ g C}}=4.517\text{ mol C}\ \div 1.063 \quad\rightarrow\ =4.249\text{ mol C}$$

$$5.36\text{ g H}\times\frac{1\text{ mol H}}{1.008\text{ g H}}=5.32\text{ mol H}\quad \div 1.063 \quad\rightarrow\ =5.00\text{ mol H}$$

$$25.51\text{ g O}\times\frac{1\text{ mol O}}{16.00\text{ g O}}=1.594\text{ mol O}\ \div 1.063 \quad\rightarrow\ =1.500\text{ mol O}$$

$$14.89\text{ g N}\times\frac{1\text{ mol N}}{14.01\text{ g N}}=1.063\text{ mol N}\div 1.063\rightarrow\ =1.000\text{ mol N}$$

If we multiply each of these amounts by 4 (because 4.249 is almost equal to $4\frac{1}{4}$), the empirical formula is found to be $C_{17}H_{20}O_6N_4$ with a molar mass of 376 g/mol. The molecular formula is $C_{17}H_{20}O_6N_4$.

10B The boiling point of pure water at 760.0 mmHg is 100.000°C. For higher pressures, the boiling point occurs at a higher temperature; for lower pressures, a lower boiling point is observed. The boiling point elevation for the urea solution is calculated as follows.

$\Delta T_b = K_b \times m = 0.512\ ^\circ\text{C}m^{-1}\times 0.205m = 0.105\ ^\circ\text{C}$

We would expect this urea solution to boil at $(100.00+0.105=)100.105\ ^\circ\text{C}$ under 760.0 mmHg atmospheric pressure. Since it boils at a lower temperature, the atmospheric pressure must be lower than 760.0 mmHg.

11A We assume a van't Hoff factor of $i = 3.00$ and convert the temperature to Kelvin, 298 K.

$$\pi = iMRT = \frac{3.00\text{ mol ions}}{1\text{ mol MgCl}_2}\times\frac{0.0530\text{ mol MgCl}_2}{1\text{ L soln}}\times 0.08206\frac{\text{L atm}}{\text{mol K}}\times 298\text{ K} = 3.89\text{ atm}$$

11B We first determine the molality of the solution, and assume a van't Hoff factor of $i = 2.00$.

$$m=\frac{\Delta T_f}{-K_f\times i}=\frac{-0.100\ ^\circ\text{C}}{-1.86\ ^\circ\text{C}m^{-1}\times 2.00}=0.0269\,m\approx 0.0269\text{ M}$$

$$\text{volume of HCl(aq)} = 250.0\text{ mL final soln}\times\frac{0.0269\text{ mmol HCl}}{1\text{ mL soln}}\times\frac{1\text{ mL conc soln}}{12.0\text{ mmol HCl}}$$

$$\text{volume of HCl(aq)} = 0.560\text{ mL conc soln}$$

INTEGRATIVE EXAMPLE

A. We determine the mass of each component in the water-rich phase.

$$\text{mass H}_2\text{O} = 32.8\text{ g phase}\times\frac{92.50\text{ g H}_2\text{O}}{100.00\text{ g phase}} = 30.3\text{ g H}_2\text{O}$$

mass phenol = 32.8 g phase – 30.3 g H_2O = 2.5 g phenol

Then we determine the mass of each component in the other phase.

mass phenol = 50.0 g – 2.5 g = 47.5 g phenol mass H_2O = 50.0 g – 30.3 g = 19.7 g H_2O

$$\%\,H_2O = \frac{19.7\text{ g } H_2O}{19.7\text{ g } H_2O + 47.5\text{ g phenol}} \times 100\% = 29.3\%\ H_2O$$

Above 66.8 °C phenol and water are completely miscible. Consequently, for temperatures above 66.8 °C, the mixture will be a homogeneous solution consisting of 50.0 g of H_2O and 50.0 g of phenol. To calculate the mole fraction of phenol in the mixture, we must first determine the number of moles of each component.

number of moles of H_2O = 50.0 g H_2O × $\frac{1\text{ mol } H_2O}{18.016\text{ g } H_2O}$ = 2.77$\underline{5}$ mol H_2O

number of moles of H_2O = 50.0 g phenol × $\frac{1\text{ mol phenol}}{94.11\text{ g phenol}}$ = 0.531 mol phenol

Thus χ_{phenol}(mol fraction) = $\frac{0.531\text{ mol phenol}}{2.775\text{ mol phenol} + 0.531\text{ mol } H_2O}$ = 0.161

B. **(a)** Rearrange Raoult's law (Equation 13.3) to the form $\frac{P_A^\circ - P_A}{P_A^\circ} = x_B$. The mass of H_2O absorbed by D_1 is proportional to P_A°; the mass of H_2O absorbed by D_2 is proportional to P_A. Hence,

$$\frac{11.7458 - 11.5057}{11.7458} = x_B = 0.0204.\ \ X_A = 0.9796,$$

P_A = 0.9796 × 23.76 mmHg = 23.28 mmHg.

The observed vapor pressure lowering = 23.76 mmHg – 23.28 mmHg = 0.48 mmHg.

(b) Calculate x_B for a 1.00 *m* solution. x_B = 0.0177; x_A = 0.9823. Calculate P_A using Raoult's law. P_A = 23.34 mmHg. The expected vapor pressure lowering = (23.76 – 23.34) mmHg = 0.42 mmHg.

EXERCISES

Homogeneous and Heterogeneous Mixtures

1. $NH_2OH(s)$ should be the most soluble in water. Both $C_6H_6(l)$ and $C_{10}H_8(s)$ are composed of essentially nonpolar molecules, which are barely (if at all) soluble in water. Both $NH_2OH(s)$ and $CaCO_3(s)$ should be able to interact with water molecules. But $CaCO_3(s)$ contains ions of high charge, and thus it dissolves with great difficulty because of the high lattice energy. (Recall the solubility rules of Chapter 5: most carbonates are insoluble in water.)

3. (b) Salicyl alcohol probably is moderately soluble in both benzene and water. The reason for this assertion is that salicyl alcohol contains a benzene ring, which would make it soluble in benzene, and also can use its $-\mathrm{OH}$ groups to hydrogen bond to water molecules. On the other hand, (c) diphenyl contains only nonpolar benzene rings; it should be soluble in benzene but not in water. (a) *para*-dichlorobenzene contains a benzene ring, making it soluble in benzene, and two polar $\mathrm{C-Cl}$ bonds, which oppose each other, producing a nonpolar—and thus water-insoluble—molecule. (d) Hydroxyacetic acid is a very polar molecule with many opportunities for hydrogen bonding. Its polar nature would make it insoluble in benzene, while the prospective hydrogen bonding will enhance aqueous solubility.

5. (c) Formic acid and (f) propylene glycol are soluble in water. They both can form hydrogen bonds with water, and they both have small nonpolar portions. (b) Benzoic acid and (d) 1-Butanol are only slightly soluble in water. Although they both can form hydrogen bonds with water, both molecules contain reasonably large nonpolar portions, which will not interact strongly with water. (a) Iodoform and (e) chlorobenzene are insoluble in water. Although both molecules have polar groups, their influence is too small to enable the molecules to disrupt the hydrogen bonds in water and form a homogeneous liquid mixture.

7. We expect small, highly charged ions to form crystals with large lattice energies, which tends to decrease their solubility in water. Based on this information, we would expect $\mathrm{MgF_2}$ to be insoluble and KF to be soluble. It is also probable that $\mathrm{CaF_2}$ is insoluble due to its high lattice energy, but that NaF, with smaller lattice energy, is soluble. Of all of the fluorides listed, KF is probably the most water soluble. The actual solubilities at $25^\circ\mathrm{C}$ are: 0.00020 M $\mathrm{CaF_2}$ < 0.0021 M $\mathrm{MgF_2}$ < 0.95 M NaF < 16 M KF.

Percent Concentration

9. $$\%\ \mathrm{NaBr} = \frac{116\ \mathrm{g\ NaBr}}{116\ \mathrm{g\ NaBr} + 100\ \mathrm{g\ H_2O}} \times 100\% = 53.7\% = 53.7\ \mathrm{g\ NaBr/100\ g\ solution}$$

11. $$\text{soln. volume} = 725\ \mathrm{kg\ NaCl} \times \frac{1000\ \mathrm{g\ NaCl}}{1\ \mathrm{kg\ NaCl}} \times \frac{100.00\ \mathrm{g\ soln}}{3.87\ \mathrm{g\ NaCl}} \times \frac{75.0\ \mathrm{mL\ soln}}{76.9\ \mathrm{g\ soln}} \times \frac{1\ \mathrm{L\ soln}}{1000\ \mathrm{mL\ soln}}$$
$$= 1.83 \times 10^4\ \mathrm{L\ sol'n}$$

13. For water, the mass in grams and the volume in mL are about equal; the density of water is close to 1.0 g/mL. For ethanol, on the other hand, the density is about 0.8 g/mL. As long as the final solution volume after mixing is close to the sum of the volumes for the two pure liquids, the percent by volume of ethanol will have to be larger than its percent by mass. This would not necessarily be true of other ethanol solutions. It would only be true in those cases where the density of the other component is greater than the density of ethanol.

15. $$\text{mass } HC_2H_3O_2 = 355 \text{ mL vinegar} \times \frac{1.01 \text{ g vinegar}}{1 \text{ mL}} \times \frac{6.02 \text{ g } HC_2H_3O_2}{100.00 \text{ g vinegar}} = 21.6 \text{ g } HC_2H_3O_2$$

17. $46.1 \text{ ppm} = \dfrac{46.1 \text{ mg} SO_4^{2-}}{1 \text{ L solution}}$ (Assumes density of water ~1.00 g mL^{-1})

$$[SO_4^{2-}] = \frac{46.1 \text{ mg} SO_4^{2-}}{1 \text{ L solution}} \times \frac{1 \text{ g} SO_4^{2-}}{1000 \text{ mg } SO_4^{2-}} \times \frac{1 \text{ mol } SO_4^{2-}}{96.06 \text{ g} SO_4^{2-}} = 4.80 \times 10^{-4} \text{ M}$$

Molarity

19.

$$\text{molarity} = \frac{6.00 \text{ g } CH_3OH \times \dfrac{1 \text{ mol } CH_3OH}{32.04 \text{ g } CH_3OH}}{100.00 \text{ g soln} \times \dfrac{1 \text{ mL}}{0.988 \text{ g}} \times \dfrac{1 \text{ L}}{1000 \text{ mL}}} = 1.85 \text{ M} = [CH_3OH]$$

21. The solution of Example 13-1 is 1.71 M C_2H_5OH, or 1.71 mmol C_2H_5OH in each mL of solution.

$$\text{volume conc. soln} = 825 \text{ mL} \times \frac{0.235 \text{ mmol } C_2H_5OH}{1 \text{ mL soln}} \times \frac{1 \text{ mL conc. soln}}{1.71 \text{ mmol } C_2H_5OH}$$
$$= 113 \text{ mL conc. soln}$$

23. The easiest way to work with ppm is to think of it in terms of mg of a substance in a kg of solvent. The molarity of CO_2 is calculated as follows:

$$\text{molarity of } CO_2 = \frac{280 \text{ mg } CO_2}{1 \text{ kg } H_2O} \times \frac{1 \text{ g } CO_2}{1000 \text{ mg } CO_2} \times \frac{1 \text{ mol } CO_2}{44.0 \text{ g } CO_2} \times \frac{1027 \text{ kg } H_2O}{1000 \text{ L } H_2O}$$
$$= 0.00654 \text{ M}$$

Molality

25.

$$\text{molality} = \frac{2.65 \text{ g } C_6H_4Cl_2 \times \dfrac{1 \text{ mol } C_6H_4Cl_2}{147.0 \text{ g } C_6H_4Cl_2}}{50.0 \text{ mL} \times \dfrac{0.879 \text{ g}}{1 \text{ mL}} \times \dfrac{1 \text{ kg}}{1000 \text{ g}}} = 0.410\ m$$

27. The mass of solvent in kg multiplied by the molality gives the amount in moles of the solute.

$$\text{mass } I_2 = \left(725.0 \text{ mL } CS_2 \times \frac{1.261 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ kg}}{1000 \text{ g}}\right) \times \frac{0.236 \text{ mol } I_2}{1 \text{ kg } CS_2} \times \frac{253.8 \text{ g } I_2}{1 \text{ mol } I_2} = 54.8 \text{ g } I_2$$

29.

$$H_3PO_4 \text{ molarity} = \frac{34.0 \text{ g } H_3PO_4 \times \dfrac{1 \text{ mol } H_3PO_4}{98.00 \text{ g } H_3PO_4}}{100.0 \text{ g soln} \times \dfrac{1 \text{ mL}}{1.209 \text{ g}} \times \dfrac{1 \text{ L}}{1000 \text{ mL}}} = 4.19 \text{ M}$$

$$H_3PO_4 \text{ molality} = \frac{34.0 \text{ g } H_3PO_4 \times \dfrac{1 \text{ mol } H_3PO_4}{98.00 \text{ g } H_3PO_4}}{66.0 \text{ g solvent} \times \dfrac{1 \text{ kg}}{1000 \text{ g}}} = 5.26 \ m$$

Mole Fraction, Mole Percent

31. The total number of moles $= 1.28 \text{ mol } C_7H_{16} + 2.92 \text{ mol } C_8H_{18} + 2.64 \text{ mol } C_9H_{20} = 6.84$ moles

(a) $\chi_{C_7H_{16}} = \dfrac{1.28 \text{ mol } C_7H_{16}}{6.84 \text{ moles total}} = 0.187$ **(b)** $\times 100\% = 18.7 \text{ mol\% } C_7H_{16}$

$\chi_{C_8H_{18}} = \dfrac{2.92 \text{ mol } C_8H_{18}}{6.84 \text{ moles total}} = 0.427$ $\times 100\% = 42.7 \text{ mol\% } C_8H_{18}$

$\chi_{C_9H_{20}} = \dfrac{2.64 \text{ mol } C_9H_{20}}{6.84 \text{ moles total}} = 0.386$ $\times 100\% = 38.6 \text{ mol\% } C_9H_{20}$

or 1.00-0.187-0.427 = 0.386 or 100-18.7-42.7 = 38.6 %

33. **(a)** The amount of solvent is found after the solute's mass is subtracted from the total mass of the solution.

$$\begin{aligned}\text{solvent amount} &= \left(\left(1 \text{ L soln} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1.006 \text{ g}}{1 \text{ mL}}\right) - \left(0.112 \text{ mol } C_6H_{12}O_6 \times \frac{180.2 \text{ g } C_6H_{12}O_6}{1 \text{ mol } C_6H_{12}O_6}\right)\right) \\ &= [1006 \text{ g solution} - 20.2 \text{ g } C_6H_{12}O_6] \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 54.7 \text{ mol } H_2O\end{aligned}$$

$$\chi_{\text{solute}} = \frac{0.112 \text{ mol } C_6H_{12}O_6}{0.112 \text{ mol } C_6H_{12}O_6 + 54.7 \text{ mol } H_2O} = 0.00204$$

(b) First we must determine the mass and the number of moles of ethanol. The number of moles of solvent is calculated after the ethanol's mass is subtracted from the solution's mass. Use a 100.00-mL sample of solution for computation. This 100 mL sample would contain 3.20 mL of C_2H_5OH. We calculate the mass of ethanol first, followed by the number of moles:

$$\text{mass}_{C_2H_5OH} = 3.20 \text{ mL } C_2H_5OH \times \frac{0.789 \text{ g}}{1 \text{ mL } C_2H_5OH} = 2.52 \text{ g } C_2H_5OH$$

$$\text{moles } C_2H_5OH = 2.52 \text{ g } C_2H_5OH \times \frac{1 \text{ mol } C_2H_5OH}{46.07 \text{ g } C_2H_5OH} = 0.0547 \text{ mol } C_2H_5OH$$

$$\text{mass of } H_2O = \left(\left(100.0 \text{ mL soln} \times \frac{0.993 \text{ g}}{1 \text{ mL}} \right) - 2.52 \text{ g } C_2H_5OH \right) = 96.8 \text{ g } H_2O$$

$$\text{amount of } H_2O = 96.8 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 5.37 \text{ mol } H_2O$$

$$\chi_{\text{solute}} = \frac{0.0547 \text{ mol } C_2H_5OH}{0.0547 \text{ mol } C_2H_5OH + 5.37 \text{ mol } H_2O} = 0.0101$$

35. The amount of water present in 1 kg is $n_{\text{water}} = 1000 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 55.49 \text{ mol } H_2O$. Now, solve the following expression for n_{gly}, the amount of glycerol. 4.85% = 0.0485 mole fraction.

$$\chi_{\text{gly}} = 0.0485 = \frac{n_{\text{gly}}}{n_{\text{gly}} + 55.49} \qquad n_{\text{gly}} = 0.0485 \;\; n_{\text{gly}} + 2.69$$

$$n_{\text{gly}} = \frac{2.69}{(1.0000 - 0.0485)} = 2.83 \text{ mol glycerol}$$

$$\text{volume glycerol} = 2.83 \text{ mol } C_3H_8O_3 \times \frac{92.09 \text{ g } C_3H_8O_3}{1 \text{ mol } C_3H_8O_3} \times \frac{1 \text{ mL}}{1.26 \text{ g}} = 207 \text{ mL glycerol}$$

37. We assume that density of water is 1.000 g/mL, so 1.000 mL of water has a mass of 1.000 g. First, determine the number of moles of Pb, and then the number of moles of water:

$$\text{mol Pb} = \frac{15 \; \mu\text{g Pb}}{1.000 \text{ g } H_2O} \times \frac{1 \text{ g}}{10^6 \; \mu\text{g}} \times \frac{1 \text{ mol Pb}}{207.19 \text{ g Pb}} = 7.24 \times 10^{-8} \text{mol}$$

$$\# \text{ Pb atoms} = 7.24 \times 10^{-8} \text{mol Pb} \times \frac{6.022 \times 10^{23} \text{atoms}}{1 \text{ mol Pb}} = 4.36 \times 10^{16} \text{atoms}$$

$$\text{mol } H_2O = 1.000 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.0 \text{ g } H_2O} = 0.05556 \text{ mol}$$

$$\chi_{\text{Pb}} = \frac{7.24 \times 10^{-8}}{0.05556 + 7.24 \times 10^{-8}} = 1.303 \times 10^{-6}$$

Solubility Equilibrium

39. At 40 °C the solubility of NH_4Cl is 46.3 g per 100 g of H_2O. To determine molality, we calculate amount in moles of the solute and the solvent mass in kg.

$$\text{molarity} = \frac{46.3 \text{ g} \times \frac{1 \text{ mol } NH_4Cl}{53.49 \text{ g } NH_4Cl}}{100 \text{ g } H_2O \times \frac{1 \text{ kg}}{1000 \text{ g}}} = 8.66 \;\; m$$

41. **(a)** The concentration for $KClO_4$ in this mixture is calculated first.

$$\frac{\text{mass solute}}{100\text{ g H}_2\text{O}} = 100\text{ g H}_2\text{O} \times \frac{20.0\text{ g KClO}_4}{500.0\text{ g water}} = 4.00\text{ g KClO}_4$$

At 40 °C a saturated $KClO_4$ solution has a concentration of about 4.6 g $KClO_4$ dissolved in 100 g water. Thus, the solution is unsaturated.

(b) The mass of $KClO_4$ that must be added is the difference between the mass now present in the mixture and the mass that is dissolved in 500 g H_2O to produce a saturated solution.

$$\text{mass to be added} = \left(500.0\text{ g H}_2\text{O} \times \frac{4.6\text{ g KClO}_4}{100\text{ g H}_2\text{O}}\right) - 20.0\text{ g KClO}_4 = 3.0\text{ g KClO}_4$$

Solubility of Gases

43. We first determine the number of moles of O_2 that have dissolved.

$$\text{moles of O}_2 = \frac{PV}{RT} = \frac{1.00\text{ atm} \times 0.02831\text{ L}}{0.08206\text{ L atm mol}^{-1}\text{ K}^{-1} \times 298\text{ K}} = 1.16 \times 10^{-3}\text{ mol O}_2$$

$$[\text{O}_2] = \frac{1.16 \times 10^{-3}\text{ mol O}_2}{1.00\text{ L soln}} = 1.16 \times 10^{-3}\text{ M}$$

The oxygen concentration now is computed at the higher pressure.

$$[\text{O}_2] = \frac{1.16 \times 10^{-3}\text{ M}}{1\text{ atm O}_2} \times 3.86\text{ atm O}_2 = 4.48 \times 10^{-3}\text{ M}$$

45. $\text{mass of CH}_4 = 1.00 \times 10^3\text{ kg H}_2\text{O} \times \dfrac{0.02\text{ g CH}_4}{1\text{ kg H}_2\text{O} \cdot \text{atm}} \times 20\text{ atm} = 4 \times 10^2\text{ g CH}_4$ (natural gas)

47. We use the STP molar volume $(22.414\text{ L} = 22{,}414\text{ mL})$ to determine the molarity of Ar under 1 atmosphere of pressure and then use Henry's law.

$$k_{\text{Ar}} = \frac{C}{P_{\text{Ar}}} = \frac{\dfrac{33.7\text{ mL Ar}}{1\text{ L soln}} \times \dfrac{1\text{ mol Ar}}{22{,}414\text{ mL at STP}}}{1\text{ atm pressure}} = \frac{0.00150\text{ M}}{\text{atm}}$$

In the atmosphere, the partial pressure of argon is $P_{\text{Ar}} = 0.00934$ atm. (Recall that pressure fractions equal volume fractions for ideal gases.) We now compute the concentration of argon in aqueous solution.

$$C = k_{\text{Ar}} P_{\text{Ar}} = \frac{0.00150\text{ M}}{\text{atm}} \times 0.00934\text{ atm} = 1.40 \times 10^{-5}\text{ M Ar}$$

49. Because of the low density of molecules in the gaseous state, the solution volume remains essentially constant as a gas dissolves in a liquid. Changes in concentrations in the solution result from changes in the number of dissolved gas molecules (recall Figure 13-11). This number is directly proportional to the mass of dissolved gas.

Raoult's Law and Liquid–Vapor Equilibrium

51. First we determine the number of moles of each component, its mole fraction in the solution, the partial pressure due to that component above the solution, and finally the total pressure.

$$\text{amount benzene} = n_\text{b} = 35.8\text{ g }C_6H_6 \times \frac{1\text{ mol }C_6H_6}{78.11\text{ g }C_6H_6} = 0.458\text{ mol }C_6H_6$$

$$\text{amount toluene} = n_t = 56.7\text{ g }C_7H_8 \times \frac{1\text{ mol }C_7H_8}{92.14\text{ g }C_7H_8} = 0.615\text{ mol }C_7H_8$$

$$\chi_\text{b} = \frac{0.458\text{ mol }C_6H_6}{(0.458+0.615)\text{ total moles}} = 0.427 \qquad \chi_\text{t} = \frac{0.615\text{ mol }C_7H_8}{(0.458+0.615)\text{ total moles}} = 0.573$$

$$P_\text{b} = 0.427 \times 95.1\text{ mmHg} = 40.6\text{ mmHg} \qquad P_\text{t} = 0.573 \times 28.4\text{ mmHg} = 16.3\text{ mmHg}$$

$$\text{total pressure} = 40.6\text{ mmHg} + 16.3\text{ mmHg} = 56.9\text{ mmHg}$$

53. We need to determine the mole fraction of water in this solution.

$$n_\text{glucose} = 165\text{ g }C_6H_{12}O_6 \times \frac{1\text{ mol }C_6H_{12}O_6}{180.2\text{ g }C_6H_{12}O_6} = 0.916\text{ mol }C_6H_{12}O_6$$

$$n_\text{water} = 685\text{ g }H_2O \times \frac{1\text{ mol }H_2O}{18.02\text{ g }H_2O} = 38.0\text{ mol }H_2O \qquad \chi_\text{water} = \frac{38.0\text{ mol }H_2O}{(38.0+0.916)\text{ total moles}} = 0.976$$

$$P_\text{sol'n} = \chi_\text{water} P^*_\text{water} = 0.976 \times 23.8\text{ mmHg} = 23.2\text{ mmHg}$$

55. We consider a sample of 100.0 g of the solution and determine the number of moles of each component in this sample. From this information and the given vapor pressures, we determine the vapor pressure of each component. Note that styrene, $C_6H_5C{=}CH_2$, is represented by the simplified molecular formula C_8H_8 in this problem.

$$\text{amount of styrene} = n_\text{s} = 38\text{ g styrene} \times \frac{1\text{ mol }C_8H_8}{104\text{ g }C_8H_8} = 0.37\text{ mol }C_8H_8$$

$$\text{amount of ethylbenzene} = n_e = 62\text{ g ethylbenzene} \times \frac{1\text{ mol }C_8H_{10}}{106\text{ g }C_8H_{10}} = 0.58\text{ mol }C_8H_{10}$$

$$\chi_\text{s} = \frac{n_\text{s}}{n_\text{s}+n_\text{e}} = \frac{0.37\text{ mol styrene}}{(0.37+0.58)\text{ total moles}} = 0.39;\ P_\text{s} = 0.39 \times 134\text{ mmHg} = 52\text{ mmHg for }C_8H_8$$

$$\chi_\text{e} = \frac{n_\text{e}}{n_\text{s}+n_\text{e}} = \frac{0.58\text{ mol ethylbenzene}}{(0.37+0.58)\text{ total moles}} = 0.61;\ P_\text{e} = 0.61 \times 182\text{ mmHg} = 111\text{ mmHg for }C_8H_{10}$$

Then the mole fraction in the vapor can be determined.

$$y_\text{e} = \frac{P_\text{e}}{P_\text{e}+P_\text{s}} = \frac{111\text{ mmHg}}{(111+52)\text{ mmHg}} = 0.68 \qquad y_\text{s} = 1.00 - 0.68 = 0.32$$

57. The total vapor pressure above the solution at its normal boiling point is 760 mm Hg. The vapor pressure due to toluene is given by the following equation.
$P_{\text{toluene}} = \chi_{\text{toluene}} \cdot P^{\circ}_{\text{toluene}} = 0.700 \times 533 \text{ mm Hg} = 373 \text{ mm Hg}$. Next, the vapor pressure due to benzene is determined, followed by the vapor pressure for pure benzene.
$P_{\text{benzene}} = P_{\text{total}} - P_{\text{toluene}} = 760 \text{ mm Hg} - 373 \text{ mm Hg} = 387 \text{ mm Hg} = \chi_{\text{benzene}} \cdot P^{\circ}_{\text{benzene}}$
$387 \text{ mm Hg} = 0.300 \times P^{\circ}_{\text{benzene}}$ and hence, $P^{\circ}_{\text{benzene}} = 1.29 \times 10^3 \text{ mm Hg}$

Osmotic Pressure

59. We first compute the concentration of the solution. Then, assuming that the solution volume is the same as that of the solvent (0.2500 L), we determine the amount of solute dissolved, and finally the molar mass.

$$\frac{n}{V} = \frac{\pi}{RT} = \frac{1.67 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298.2 \text{ K}} = 8.98 \times 10^{-5} \text{ M}$$

$$\text{solute amount} = 0.2500 \text{ L} \times \frac{8.98 \times 10^{-5} \text{ mol}}{1 \text{ L}} = 2.25 \times 10^{-5} \text{ mol} \qquad M = \frac{0.72 \text{ g}}{2.25 \times 10^{-5} \text{ mol}} = 3.2 \times 10^4 \text{ g/mol}$$

61. Both the flowers and the cucumber contain ionic solutions (plant sap), but both of these solutions are less concentrated than the salt solution. Thus, the solution in the plant material moves across the semipermeable membrane in an attempt to dilute the salt solution, leaving behind wilted flowers and shriveled pickles (wilted/shriveled plants have less water in their tissues).

63. We first determine the molarity of the solution. Let's work the problem out with three significant figures.

$$\frac{n}{V} = \frac{\pi}{RT} = \frac{1.00 \text{ atm}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 273 \text{ K}} = 0.0446 \text{ M}$$

$$\text{volume} = 1 \text{ mol} \times \frac{1 \text{ L}}{0.0446 \text{ mol solute}} = 22.4 \text{ L solution} \approx 22.4 \text{ L solvent}$$

We have assumed that the solution is so dilute that its volume closely approximates the volume of the solvent constituting it. Note that this volume corresponds to the STP molar volume of an ideal gas. The osmotic pressure equation also resembles the ideal gas equation.

65. First we determine the concentration of the solution from the osmotic pressure, then the amount of solute dissolved, and finally the molar mass of that solute.

$$\pi = 5.1 \text{ mm soln} \times \frac{0.88 \text{ mmHg}}{13.6 \text{ mm soln}} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 4.3 \times 10^{-4} \text{ atm}$$

$$\frac{n}{V} = \frac{\pi}{RT} = \frac{4.3 \times 10^{-4} \text{ atm}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 1.8 \times 10^{-5} \text{ M}$$

$$\text{amount solute} = 100.0\text{ mL} \times \frac{1\text{ L}}{1000\text{ mL}} \times 1.8 \times 10^{-5}\text{ M} = 1.8 \times 10^{-6}\text{ mol solute}$$

$$\text{molar mass} = \frac{0.50\text{ g}}{1.8 \times 10^{-6}\text{ mol}} = 2.8 \times 10^{5}\text{ g/mol}$$

<u>67</u>. The reverse osmosis process requires a pressure equal to or slightly greater than the osmotic pressure of the solution. We assume that this solution has a density of 1.00 g/mL. First, we determine the molar concentration of ions in the solution.

$$[\text{ions}] = \frac{2.5\text{ g NaCl} \times \frac{1\text{ mol NaCl}}{58.4\text{ g NaCl}} \times \frac{2\text{ mol ions}}{1\text{ mol NaCl}}}{100.0\text{ mL soln} \times \frac{1\text{ mL soln}}{1.00\text{ g}} \times \frac{1\text{ L soln}}{1000\text{ mL}}} = 0.86\text{ M}$$

$$\pi = \frac{n}{V}RT = 0.86\frac{\text{mol}}{\text{L}} \times 0.08206\text{ L atm mol}^{-1}\text{ K}^{-1} \times (25 + 273.2)\text{ K} = 21\text{ atm}$$

Freezing-Point Depression and Boiling-Point Elevation

<u>69</u>. First we compute the molality of the benzene solution, then the number of moles of solute dissolved, and finally the molar mass of the unknown compound.

$$m = \frac{\Delta T_f}{-K_f} = \frac{4.92°\text{C} - 5.53°\text{C}}{-5.12^\circ\text{C}/m} = 0.12\, m$$

$$\text{amount solute} = 0.07522\text{ kg benzene} \times \frac{0.12\text{ mol solute}}{1\text{ kg benzene}} = 9.0 \times 10^{-3}\text{ mol solute}$$

$$\text{molecular weight} = \frac{1.10\text{ g unknown compound}}{9.0 \times 10^{-3}\text{ mol}} = 1.2 \times 10^{2}\text{ g/mol}$$

<u>71</u>. **(a)** First we determine the molality of the solution, then the value of the freezing-point depression constant.

$$m = \frac{1.00\text{ g C}_6\text{H}_6 \times \frac{1\text{ mol C}_6\text{H}_6}{78.11\text{ g C}_6\text{H}_6}}{80.00\text{ g solvent} \times \frac{1\text{ kg}}{1000\text{ g}}} = 0.160\, m \qquad K_\text{f} = \frac{\Delta T_\text{f}}{-m} = \frac{3.3°\text{C} - 6.5°\text{C}}{-0.160\, m} = 20.°\text{C}/m$$

(b) For benzene, $K_\text{f} = 5.12\ ^\circ\text{C}m^{-1}$. Cyclohexane is the better solvent for freezing-point depression determinations of molar mass, because a less concentrated solution will still give a substantial freezing-point depression. For the same concentration, cyclohexane solutions will show a freezing-point depression approximately four times that of benzene. Also, one should steer clear of benzene because it is a known carcinogen.

<u>73</u>. Here we determine the molality of the solution, then the number of moles of solute present, and the molar mass of the solute to start things off. Then we determine the compound's empirical formula, and combine this with the molar mass to determine the molecular formula.

$$m = \frac{\Delta T_\text{f}}{-K_\text{f}} = \frac{1.37\ ^\circ\text{C} - 5.53\ ^\circ\text{C}}{-5.12^\circ\text{C}/m} = 0.813\ m$$

$$\text{amount} = \left(50.0\text{ mL C}_6\text{H}_6 \times \frac{0.879\text{ g}}{1\text{ mL}} \times \frac{1\text{ kg}}{1000\text{ g}}\right) \times \frac{0.813\text{ mol solute}}{1\text{ kg C}_6\text{H}_6} = 3.57\times10^{-2}\text{ mol}$$

$$\text{molecular weight} = \frac{6.45\text{ g}}{3.57\times10^{-2}\text{ mol}} = 181\text{ g/mol}$$

Now, calculate the empirical formula from the provided mass percents for C, H, N, and O.

$$42.9\text{ g C}\times\frac{1\text{ mol C}}{12.01\text{ g C}} = 3.57\text{ mol C} \quad \div 1.19 \rightarrow 3.00\text{ mol C}$$

$$2.4\text{ g H}\times\frac{1\text{ mol H}}{1.01\text{ g H}} = 2.4\text{ mol H} \quad \div 1.19 \rightarrow 2.0\text{ mol H}$$

$$16.7\text{ g N}\times\frac{1\text{ mol N}}{14.01\text{ g N}} = 1.19\text{ mol N} \quad \div 1.19 \rightarrow 1.00\text{ mol N}$$

$$38.1\text{ g O}\times\frac{1\text{ mol O}}{16.00\text{ g O}} = 2.38\text{ mol O} \quad \div 1.19 \rightarrow 2.00\text{ mol O}$$

The empirical formula is $C_3H_2NO_2$, with a formula mass of 84.0 g/mol. This is one-half the experimentally determined molar mass. Thus, the molecular formula is $C_6H_4N_2O_4$.

75. We determine the molality of the benzene solution first, then the molar mass of the solute.

$$m = \frac{\Delta T_f}{-K_f} = \frac{-1.183^\circ\text{C}}{-5.12^\circ\text{C}/m} = 0.231 m$$

$$\text{amount solute} = 0.04456\text{ kg benzene}\times\frac{0.231\text{ mol solute}}{1\text{ kg benzene}} = 0.0103\text{ mol solute}$$

$$\text{molar mass} = \frac{0.867\text{ g thiophene}}{0.0103\text{ mol thiophene}} = 84.2\text{ g/mol}$$

Next, we determine the empirical formula from the masses of the combustion products.

$$\text{amount C} = 4.913\text{ g CO}_2\times\frac{1\text{ mol CO}_2}{44.010\text{ g CO}_2}\times\frac{1\text{ mol C}}{1\text{ mol CO}_2} = 0.1116\text{ mol C} \div 0.02791 \rightarrow 4.000\text{ mol C}$$

$$\text{amount H} = 1.005\text{ g H}_2\text{O}\times\frac{1\text{ mol H}_2\text{O}}{18.015\text{ g H}_2\text{O}}\times\frac{2\text{ mol H}}{1\text{ mol H}_2\text{O}} = 0.1116\text{ mol H} \div 0.02791 \rightarrow 4.000\text{ mol H}$$

$$\text{amount S} = 1.788\text{ g SO}_2\times\frac{1\text{ mol SO}_2}{64.065\text{ g SO}_2}\times\frac{1\text{ mol S}}{1\text{ mol SO}_2} = 0.02791\text{ mol S} \div 0.02791 \rightarrow 1.000\text{ mol S}$$

A reasonable empirical formula is C_4H_4S, which has an empirical mass of 84.1 g/mol. Since this is the same as the experimentally determined molar mass, the molecular formula of thiophene is C_4H_4S.

77. The boiling point must go up by 2 °C, so $\Delta T_b = 2$ °C. We know that $K_b = 0.512$ °C/m for water. We assume that the mass of a liter of water is 1.000 kg and the van't Hoff factor for NaCl is $i = 2$. We first determine the molality of the saltwater solution and then the mass of solute needed.

$$m = \frac{\Delta T_b}{i\ K_b} = \frac{2^\circ\text{C}}{2.00\times0.512\ ^\circ\text{C/m}} = 2\ m$$

$$\text{solute mass} = 1.00\ \text{L H}_2\text{O} \times \frac{1\ \text{kg}\ \ \text{H}_2\text{O}}{1\ \ \text{L}\ \ \text{H}_2\text{O}} \times \frac{2\ \text{mol NaCl}}{1\ \ \text{kg}\ \ \text{H}_2\text{O}} \times \frac{58.4\ \text{g NaCl}}{1\ \text{mol NaCl}} = 12\underline{0}\ \text{g NaCl}$$

This is at least ten times the amount of salt one would typically add to a liter of water for cooking purposes!

79. Assume that 1 L of ocean water has a mass of 1 kg.

$\Delta T_f = -K_f \cdot m$

$-1.94\ ^\circ C = \left(-1.86\ ^\circ C \cdot m^{-1}\right) \cdot m$

$m = 1.04$

Strong Electrolytes, Weak Electrolytes, and Nonelectrolytes

81. The freezing-point depression is given by $\Delta T_f = -iK_f m$. Since $K_f = 1.86^\circ C/m$ for water, $\Delta T_f = -i0.186^\circ C$ for this group of $0.10\,m$ solutions.

(a) $T_f = -0.186°$ C. Urea is a nonelectrolyte, and $i = 1$.

(b) $T_f = -0.372°$ C. NH_4NO_3 is a strong electrolyte, composed of two ions per formula unit; $i = 2$.

(c) $T_f = -0.372°$ C. HCl is a strong electrolyte, composed of two ions per formula unit; $i = 2$.

(d) $T_f = -0.558°$ C. $CaCl_2$ is a strong electrolyte, composed of three ions per formula unit; $i = 3$.

(e) $T_f = -0.372°$ C. $MgSO_4$ is a strong electrolyte, composed of two ions per formula unit; $i = 2$.

(f) $T_f = -0.186°$ C. Ethanol is a nonelectrolyte; $i = 1$.

(g) $T_f < -0.186°$ C. $HC_2H_3O_2$ is a weak electrolyte; i is somewhat larger than 1.

83. The combination of NH_3(aq) with $HC_2H_3O_2$(aq), results in the formation of $NH_4C_2H_3O_2$(aq), which is a solution of the ions NH_4^+ and CH_3COO^-.

$$NH_3(aq) + HC_2H_3O_2(aq) \rightarrow NH_4C_2H_3O_2(aq) \rightarrow NH_4^+(aq) + C_2H_3O_2^-(aq)$$

This solution of ions or strong electrolytes conducts a current very well.

85. The answer is (d). The other options describe (a) a gas dissolved in water, (b) a gas which when dissolved in water fully dissociates and is a strong electrolyte, and (c) a non-electrolytic molecule in water.

INTEGRATIVE AND ADVANCED EXERCISES

88. The molarity of the original solution is computed first.

$$\text{KOH molarity} = \frac{109.2\text{ g KOH} \times \frac{1\text{ mol KOH}}{56.010\text{ g KOH}}}{1\text{ L soln}} = 1.950\text{ M}$$

A 1.950 M solution is more concentrated than a 0.250 *m* solution. Thus, we must dilute the original solution. First we determine the mass of water produced in the final solution, and the mass of water present in the original solution, and finally the mass of water we must add.

$$\text{mass } H_2O \text{ in final soln} = 0.1000\text{ L orig. soln} \times \frac{1.950\text{ mol KOH}}{1\text{ L soln}} \times \frac{1\text{ kg } H_2O}{0.250\text{ mol KOH}} = 0.780\text{ kg } H_2O$$

$$\text{mass original solution} = 100.0\text{ mL} \times \frac{1.09\text{ g}}{1\text{ mL}} = 109\text{ g original solution}$$

$$\text{mass KOH} = 100.0\text{ mL} \times \frac{1\text{ L}}{1000\text{ mL}} \times \frac{109.2\text{ g KOH}}{1\text{ L soln}} = 10.92\text{ g KOH}$$

$$\text{original mass of water} = 109\text{ g soln} - 10.92\text{ g KOH} = 98\text{ g } H_2O$$

$$\text{mass added } H_2O = 780.\text{g } H_2O - 98\text{ g } H_2O = 682\text{ g } H_2O$$

92. First determine the molality of the solution with the desired freezing point and compare it to the molality of the supplied solution to determine if ethanol or water needs to be added.

$$m = \frac{\Delta T_f}{-K_f} = \frac{-2.0\text{ °C}}{-1.86\text{ °C}/m} = 1.1\ m\ \text{(desired)}$$

$$\text{mass solution} = 2.50\text{ L} \times \frac{1000\text{ mL}}{1\text{ L}} \times \frac{0.9767\text{ g}}{1\text{ mL}} = 2.44 \times 10^3\text{ g solution}$$

$$\text{mass solute} = 2.44 \times 10^3\text{ g soln} \times \frac{13.8\text{ g } C_2H_5OH}{100.0\text{ g soln}} = 337\text{ g } C_2H_5OH$$

$$\text{mass } H_2O = (2.44 \times 10^3\text{ g} - 337\text{ g } C_2H_5OH) \times \frac{1\text{ kg}}{1000\text{ g}} = 2.10\text{ kg } H_2O$$

$$m = \frac{337\text{ g } C_2H_5OH \times \frac{1\text{ mol } C_2H_5OH}{46.07\text{ g } C_2H_5OH}}{2.10\text{ kg } H_2O} = 3.48\ m\ \text{(available)}$$

Thus we need to dilute the solution with water. We must find the mass of water needed in the final solution, then the mass of water that must be added.

$$\text{final mass of water} = 337\text{ g } C_2H_5OH \times \frac{1\text{ mol } C_2H_5OH}{46.07\text{ g } C_2H_5OH} \times \frac{1\text{ kg } H_2O}{1.1\text{ mol } C_2H_5OH} = 6.6\text{ kg } H_2O$$

$$\text{mass } H_2O \text{ needed} = 6.6\text{ kg total} - 2.10\text{ kg already present} = 4.5\text{ kg } H_2O$$

95. First we determine the molality of the benzene solution, and then the number of moles of solute in the sample.

$$\text{molality}=\frac{\Delta T_{\text{f}}}{-K_{\text{f}}}=\frac{5.072\,^{\circ}\text{C}-5.533\,^{\circ}\text{C}}{-5.12\,^{\circ}\text{C}/m}=0.0900\,m$$

$$\text{amount of solute}=50.00\text{ mL}\times\frac{0.879\text{ g}}{1\text{ mL}}\times\frac{1\text{ kg}}{1000\text{ g}}\times\frac{0.0900\text{ mol solute}}{1\text{ kg solvent}}=0.00396\text{ mol solute}$$

We use this amount to determine the amount of each acid in the solute, with the added data of the molar masses of stearic acid, $C_{18}H_{36}O_2$, 284.5 g/mol, and palmitic acid, $C_{18}H_{36}O_2$, 256.4 g/mol. We let *x* represent the amount in moles of palmitic acid.

$$1.115\text{ g sample}=(0.00396\ -x)\text{ mol}\times 284.5\text{ g/mol}+x\text{ mol}\times 256.4\text{ g/mol}$$

$$=1.12\underline{7}-284.5\,x+256.4\,x=1.12\underline{7}-28.1\,x$$

$$x=\frac{1.12\underline{7}-1.115}{28.1}=0.0004\underline{3}\text{ mol palmitic acid}$$

$$0.00396-0.0004\underline{3}=0.0035\underline{3}\text{ mol stearic acid}$$

mass palmitic acid = 0.00043 mol × 256.4 g/mol = 0.11 g palmitic acid

$$\%\text{ palmitic acid }=\frac{0.11\text{ g palmitic acid}}{1.115\text{ g sample}}\times 100\%=1\times 10^{1}\ \%\text{ palmitic acid (about 10\%)}$$

97. We first determine the amount in moles of each substance.

$$\text{amount }CO(NH_2)_2=0.515\text{ g }CO(NH_2)_2\times\frac{1\text{ mol }CO(NH_2)_2}{60.06\text{ g }CO(NH_2)_2}=0.00858\text{ mol }CO(NH_2)_2$$

$$\text{amount }H_2O\text{ with urea}=92.5\text{ g }H_2O\times\frac{1\text{ mol }H_2O}{18.015\text{ g }H_2O}=5.13\text{ mol }H_2O$$

$$\text{amount }C_{12}H_{22}O_{11}=2.50\text{ g }C_{12}H_{22}O_{11}\times\frac{1\text{ mol }C_{12}H_{22}O_{11}}{342.3\text{ g }C_{12}H_{22}O_{11}}=0.00730\text{ mol }C_{12}H_{22}O_{11}$$

$$\text{amount }H_2O\text{ with sucrose}=85.0\text{ g }H_2O\times\frac{1\text{ mol }H_2O}{18.015\text{ g }H_2O}=4.72\text{ mol }H_2O$$

The vapor pressure of water will be the same above both solutions when their mole fractions are equal. We assume that the amount of water present as water vapor is negligible. The total amount of water in the two solutions is (4.72 + 5.13 =) 9.85 mol H_2O. We let n_{water} designate the amount of water in the urea solution. The amount of water in the sucrose solution is then 9.85 mole – n_{water}. Note that we can compute the mole fraction of solute for comparison, since when the two solute mole fractions are equal, the mole fractions of solvent will also be equal ($\chi_{\text{solvent}} = 1.0000 - \chi_{\text{solute}}$).

$$\frac{0.00857\ \text{mol urea}}{0.00858\ \text{mol urea} + n_{\text{water}}} = \chi_{\text{urea}} = \chi_{\text{sucrose}} = \frac{0.00730\ \text{mol sucrose}}{0.00730\ \text{mol sucrose} + (9.85 - n_{\text{water}})}$$

We "cross multiply'' to begin the solution for n_{water}.

$$0.00857\,(0.00730 + 9.85 - n_{\text{water}}) = 0.00730\,(0.00858 + n_{\text{water}})$$

$$0.0845 - 0.00857\,n_{\text{water}} = 0.0000626 + 0.00730\,n_{\text{water}} \quad n_{\text{water}} = \frac{0.0845 - 0.0000626}{0.00730 + 0.00857} = 5.32\ \text{mol}$$

We check the answer by substitution into the mole fraction equation.

$$\frac{0.00857\ \text{mol urea}}{0.00857\ \text{mol} + 5.32\underline{4}} = 0.00161 = \chi_{\text{urea}} = \chi_{\text{sucrose}} = 0.00161 = \frac{0.00730\ \text{mol sucrose}}{0.00730\ \text{mol} + (9.85 - 5.32\underline{4})\text{mol}}$$

The mole fraction of water in each solution is (1.00000 – 0.00161 =) 0.99839, or 99.839 mol%

100.

(a) Surface area of a particle = $4\pi r^2$ = $4(3.1416)(1\text{x}10^{-7}\text{m})^2$ = $1.26\text{x}10^{-13}$ m^2/particle. We need to find the number of particles present (not atoms!)

$$\text{particle volume} = \frac{4\pi r^3}{3} = \frac{4\pi(1\times10^{-7}\text{m})^3}{3} = 4.19\times10^{-21}\,m^3$$

$$\text{particle mass} = \text{density} \times \text{volume} = \frac{19.3\ \text{g}}{\text{cm}^3}\frac{(100cm)^3}{(1m)^3} \times 4.19\times10^{-21}\,m^3 = 8.09\times10^{-14}\,\text{g/particle}$$

$$\text{number of Au particles} = \frac{\text{mass of Au}}{\text{particle mass}} = \frac{1.00\times10^{-3}\text{g Au}}{8.09\times10^{-14}\text{g/particle}} = 1.24\times10^{10}\,\text{particles}$$

$$\text{total surface area} = (1.26\times10^{-13}\ \text{m}^2/\text{particle})(1.24\times10^{10}\,\text{particles}) = 1.56\times10^{-3}\,\text{m}^2$$

(b) For 1.00 mg Au the volume of Au is: (1.00 mg)(1 g/1000 mg)/(19.3 g/cm^3) = 5.18 × 10^{-5} cm^3

Volume of a cube is L^3, where L is the edge length, so

$$L = \sqrt[3]{5.18\times10^{-5}\ \text{cm}^3} = 3.73\times10^{-2}\ \text{cm}$$

area = 6×L^2 = 6×(3.73×10^{-2} cm)^2 × (1m/100cm)^2 = 8.34×10-7 m^2

105. We determine the volumes of O_2 and N_2 that dissolve under the appropriate partial pressures of 0.2095 atm O_2 and 0.7808 atm N_2, and at a temperature of 25 °C, with both gas volumes measured at 1.00 atm and 25 °C. Note that the percent by volume and the percent by partial pressures of the atmosphere are numerically the same.

$$O_2\ \text{volume} = 0.2095\ \text{atm} \times \frac{28.31\ \text{mL}\ O_2}{1\ \text{atm}\cdot\text{L soln}} = 5.931\ \frac{\text{mL}\ O_2}{\text{L solution}}$$

$$N_2\ \text{volume} = 0.7808\ \text{atm} \times \frac{14.34\ \text{mL}\ N_2}{1\ \text{atm}\cdot\text{L soln}} = 11.20\ \frac{\text{mL}\ N_2}{\text{L solution}}$$

$$\text{volume}\ \%\ N_2 = \frac{11.20\ \frac{\text{mL}\ N_2}{\text{L solution}}}{11.20\ \frac{\text{mL}\ N_2}{\text{L solution}} + 5.931\ \frac{\text{mL}\ O_2}{\text{L solution}}} \times 100\% = 65.38\%\ N_2\ \text{by volume}$$

$$\text{volume}\ \%\ O_2 = 100.00\% - 65.38\% = 34.62\%\ O_2\ \text{by volume}$$

107. First we determine the mass of $CuSO_4$ in the original solution at 70 °C.

$$335\ \text{g sample} \times \frac{32.0\ \text{g}\ CuSO_4}{100.0\ \text{g soln}} = 107.\underline{2}\ \text{g}\ CuSO_4$$

We let *x* represent the mass of $CuSO_4$ removed from the solution when the $CuSO_4{\cdot}5H_2O$ recrystallizes. Then the mass of H_2O present in the recrystallized product is determined.

$$\text{mass}\ H_2O = x\ \text{g}\ CuSO_4 \times \frac{1\ \text{mol}\ CuSO_4}{159.6\ \text{g}\ CuSO_4} \times \frac{5\ \text{mol}\ H_2O}{1\ \text{mol}\ CuSO_4} \times \frac{18.02\ \text{g}\ H_2O}{1\ \text{mol}\ H_2O} = 0.565x\ \text{g}\ H_2O$$

Now we determine the value of *x* by using the concentration of the saturated solution at 0 °C.

$$\frac{12.5 \text{ g CuSO}_4}{100.0 \text{ g soln}} = \frac{(107.\underline{2} - x) \text{ g CuSO}_4}{(335 - x - 0.565\,x) \text{ g soln}}$$

$$1.07\underline{2} \times 10^4 - 100.0x = 4.19 \times 10^3 - 19.6x \qquad (100.0 - 19.6)x = 1.07\underline{2} \times 10^4 - 4.19 \times 10^3$$

$$x = \frac{6.5\underline{3} \times 10^3}{80.4} = 81 \text{ g CuSO}_4$$

$$\text{mass CuSO}_4 \cdot 5\text{H}_2\text{O} = 81 \text{ g CuSO}_4 \times \frac{1.000 \text{ g CuSO}_4 + 0.565 \text{ g H}_2\text{O}}{1.000 \text{ g CuSO}_4} = 1.3 \times 10^2 \text{ g CuSO}_4 \cdot 5\text{H}_2\text{O}$$

109.

$$\text{mass of N}_2 = \frac{445 \times 10^{-6} \text{mol N}_2}{\text{L of seawater}} \times \frac{28.0 \text{ g N}_2}{1 \text{ mol}} = 0.0125 \frac{\text{g}}{\text{L}}$$

Partial pressure can be determined from Henry's Law:

$C = k_H P$

$445 \times 10^{-6} \text{ M} = \left(0.61 \times 10^{-3} \text{M} \cdot \text{atm}^{-1}\right) P$

$$P = \frac{445 \times 10^{-6} \text{ M}}{0.61 \times 10^{-3} \text{M} \cdot \text{atm}^{-1}} = 0.73 \text{ atm}$$

111. First, determine what molality of ethylene glycol is needed to cause a 10.0 °C freezing-point depression:

$\Delta \text{T}_\text{f} = -\text{K}_\text{f} \cdot \text{m}$

$-10 \,^\circ\text{C} = \left(-1.86 \,^\circ\text{C} \cdot \text{m}^{-1}\right) \cdot \text{m}$

$\text{m} = 5.376 \text{ m}$

Then, determine the num\ber of moles of ethylene glycol, which can be used to determine the volume, using the density of ethylene glycol given.

$$\text{mol C}_2\text{H}_6\text{O}_2 = \frac{5.376 \text{ mol C}_2\text{H}_6\text{O}_2}{1 \text{ kg H}_2\text{O}} \times \frac{1 \text{ kg H}_2\text{O}}{1 \text{ L H}_2\text{O}} \times \frac{20.0 \text{ L H}_2\text{O}}{\text{sample}} = 107.53 \text{ mol C}_2\text{H}_6\text{O}_2\text{/sample}$$

$$\text{Vol C}_2\text{H}_6\text{O}_2 = 107.53 \text{ mol C}_2\text{H}_6\text{O}_2 \times \frac{62.09 \text{ g C}_2\text{H}_6\text{O}_2}{1 \text{ mol C}_2\text{H}_6\text{O}_2} \times \frac{1 \text{ mL}}{1.12 \text{ g C}_2\text{H}_6\text{O}_2} = 5961 \text{ mL} = 5.96 \text{ L}$$

FEATURE PROBLEMS

114. **(a)** A solution with $\chi_{\text{HCl}} = 0.50$ begins to boil at about 18° C. At that temperature, the composition of the vapor is about $\chi_{\text{HCl}} = 0.63$, reading directly across the tie line at 18° C. The vapor has $\chi_{\text{HCl}} > 0.50$.

(b) The composition of HCl(aq) changes as the solution boils in an open container because the vapor has a different composition than does the liquid. Thus, the component with the lower boiling point is depleted as the solution boils. The boiling point of the remaining solution must change as the vapor escapes due to changing composition.

(c) The azeotrope occurs at the maximum of the curve: at $\chi_{\text{HCl}} = 0.12$ and a boiling temperature of $110\ ^\circ\text{C}$.

(d) We first determine the amount of HCl in the sample.

$$\text{amount HCl} = 30.32 \text{ mL NaOH} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1.006 \text{ mol NaOH}}{1 \text{ L}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}}$$

$$\text{amount HCl} = 0.03050 \text{ mol HCl}$$

The mass of water is the difference between the mass of solution and that of HCl.

$$\text{mass } H_2O = \left(5.00 \text{ mL soln} \times \frac{1.099 \text{ g}}{1 \text{ mL}}\right) - \left(0.03050 \text{ mol HCl} \times \frac{36.46 \text{ g HCl}}{1 \text{ mol HCl}}\right) = 4.38 \text{ g}$$

Now we determine the amount of H_2O and then the mole fraction of HCl.

$$\text{amount } H_2O = 4.38 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 0.243 \text{ mol } H_2O$$

$$\chi_{\text{HCl}} = \frac{0.03050 \text{ mol HCl}}{0.03050 \text{ mol HCl} + 0.243 \text{ mol } H_2O} = 0.112$$

115. **(a)** At $20\ ^\circ\text{C}$, the solubility of NaCl is 35.9 g NaCl / 100 g H_2O. We determine the mole fraction of H_2O in this solution

$$\text{amount } H_2O = 100 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 5.549 \text{ mol } H_2O$$

$$\text{amount NaCl} = 35.9 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} = 0.614 \text{ mol NaCl}$$

$$\chi_{\text{water}} = \frac{5.549 \text{ mol } H_2O}{0.614 \text{ mol NaCl} + 5.549 \text{ mol } H_2O} = 0.9004$$

The approximate relative humidity then will be 90% (90.04%), because the water vapor pressure above the NaCl saturated solution will be 90.04% of the vapor pressure of pure water at 20° C.

(b) $CaCl_2 \cdot 6\ H_2O$ deliquesces if the relative humidity is over 32%. Thus, $CaCl_2 \cdot 6\ H_2O$ will deliquesce (i.e., it will absorb water from the atmosphere).

(c) If the substance in the bottom of the desiccator has high water solubility, its saturated solution will have a low χ_{water}, which in turn will produce a low relative humidity. Thus, a relative humidity lower than 32% is needed to keep $CaCl_2 \cdot 6\ H_2O$ dry.

116. (a) We first compute the molality of a 0.92% mass/volume solution, assuming the solution's density is about 1.00 g/mL, meaning that 100.0 mL solution has a mass of 100.0 g.

$$\text{molality} = \frac{0.92\ \text{g NaCl} \times \dfrac{1\ \text{mol NaCl}}{58.44\ \text{g NaCl}}}{(100.0\ \text{g soln} - 0.92\ \text{g NaCl}) \times \dfrac{1\ \text{kg solvent}}{1000\ \text{g}}} = 0.16\ m$$

Then we compute the freezing-point depression of this solution.

$$\Delta T_f = -iK_f m = \frac{-2.0\ \text{mol ions}}{\text{mol NaCl}} \times \frac{1.86^\circ\text{C}}{m} \times 0.16\, m = -0.60\ ^\circ\text{C}$$

The van't Hoff factor of NaCl most likely is not equal to 2.0, but a bit less and thus the two definitions are in fair agreement.

(b) We calculate the amount of each solute, assume 1.00 L of solution has a mass of 1000 g, and subtract the mass of all solutes to determine the mass of solvent.

$$\text{amount NaCl ions} = 3.5\ \text{g NaCl} \times \frac{1\ \text{mol NaCl}}{58.44\ \text{g NaCl}} \times \frac{2\ \text{mol ions}}{1\ \text{mol NaCl}} = 0.12\ \text{mol ions}$$

$$\text{amount KCl ions} = 1.5\ \text{g} \times \frac{1\ \text{mol KCl}}{74.55\ \text{g KCl}} \times \frac{2\ \text{mol ions}}{1\ \text{mol KCl}} = 0.040\ \text{mol ions}$$

$$\text{amount } Na_3C_6H_5O_7 \text{ ions} = 2.9\ \text{g} \times \frac{1\ \text{mol } Na_3C_6H_5\ O_7}{258.07\ \text{g } Na_3C_6H_5O_7} \times \frac{4\ \text{mol ions}}{1\ \text{mol } Na_3C_6H_5O_7}$$

$$\text{amount } Na_3C_6H_5O_7 \text{ ions} = 0.045\ \text{mol ions}$$

$$\text{amount } C_6H_{12}O_6 = 20.0\ \text{g } C_6H_{12}O_6 \times \frac{1\ \text{mol } C_6H_{12}O_6}{180.2\ \text{g } C_6H_{12}O_6} = 0.111\ \text{mol } C_6H_{12}O_6$$

$$\text{solvent mass} = 1000.0\ \text{g} - (3.5\ \text{g} + 1.5\ \text{g} + 2.9\ \text{g} + 20.0\ \text{g}) = 972.1\ \text{g } H_2O$$

$$\text{solvent mass} = 0.9721\ \text{kg } H_2O$$

$$\text{solution molality} = \frac{(0.120 + 0.040 + 0.045 + 0.111)\ \text{mol}}{0.9721\ \text{kg } H_2O} = 0.325\ m$$

$$\Delta T_f = -K_f m = -1.86\ ^\circ\text{C}/m \times 0.325\ m = -0.60^\circ\text{C}$$

This again is close to the defined freezing point of $-0.52\ ^\circ\text{C}$, with the error most likely arising from the van't Hoff factors not being integral. We can conclude, therefore, that the solution is isotonic.

SELF-ASSESSMENT EXERCISES

120. The answer is (b), because molality is moles solute/kg solvent. Assuming a volume of 1 L, at a concentration of 0.010 *m*, the mass of the water (~1 kg) is nearly the same as the volume of the solution (1 L).

121. The answer is (d), because the other choices either don't form a solution because they are immiscible or the solute-solvent interactions are stronger than intramolecular interactions for either of the pure solute or solvent, making the solutions non-ideal.

122. The answer is (a). As partial pressure of the gas increases, Henry's law shows that the concentration of the gas in the liquid increases.

123. The answer is (d), because the total ionic molality of the $MgCl_2$ is 3×0.008 = 0.024.

124. The answer is (c), because nothing in the information provided suggests that the concentrations of the two volatile species are the same.

125. The mass of NH_4Cl is: 1.12 mol NH_4Cl × (53.45 g/mol) = 59.86 g.
Solubility is 59.86 g NH_4Cl / 150.0 g H_2O = 0.40, or 40 g/100 g.
Based on Figure 13-8, the concentration limit of NH_4Cl is 42 g per 100 g of H_2O. Since the amount of NH_4Cl is below the solubility limit, no crystals will form.

126. **(a)** $$\left[\mathrm{Na^+}\right]=\frac{0.92\text{ g NaCl}}{100\text{ mL H}_2\text{O}}\times\frac{1\text{ mol NaCl}}{58.45\text{ g NaCl}}\times\frac{1\text{ mol Na}^+}{1\text{ mol NaCl}}\times\frac{1000\text{ mL}}{1\text{ L}}=0.16\text{ M Na}^+$$

(b) $$\text{total molarity of ions} = 0.16\text{ M Na}^+\times\frac{1\text{ mol NaCl}}{1\text{ mol Na}^+}\times\frac{2\text{ mol ions}}{1\text{ mol NaCl}} = 0.32\text{ M}$$

(c) $$\Pi=\text{MRT}=(0.32\text{ M})\left(0.08206\text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\right)(310\text{ K})=8.1\text{ atm}$$

(d) Determine the solution molality first, then determine freezing-point depression.

$$\text{molality H}_2\text{O}=\frac{0.32\text{ mol ions}}{1\text{ L solution}}\times\frac{1\text{ L solution}}{1.005\text{ kg solution}}=0.3184\ m$$

$$\Delta T_f=\left(-1.86\ ^\circ\text{C}/m\right)(0.3184\ m)=-0.60\ ^\circ\text{C}$$

127. **(a)**

$$[\mathrm{C_3H_8O_3}]=\frac{62.0\text{ g C}_3\text{H}_8\text{O}_3}{100\text{ g sol'n}}\times\frac{1.159\text{ g sol'n}}{1\text{ mL sol'n}}\times\frac{1000\text{ mL sol'n}}{1\text{ L sol'n}}\times\frac{1\text{ mol C}_3\text{H}_8\text{O}_3}{92.11\text{ g C}_3\text{H}_8\text{O}_3}$$
$$=7.80\text{ M C}_3\text{H}_8\text{O}_3$$

(b)

$$[\mathrm{H_2O}]=\frac{38.0\text{ g H}_2\text{O}}{100\text{ g sol'n}}\times\frac{1.159\text{ g sol'n}}{1\text{ mL sol'n}}\times\frac{1000\text{ mL sol'n}}{1\text{ L sol'n}}\times\frac{1\text{ mol H}_2\text{O}}{18.02\text{ g H}_2\text{O}}$$
$$=24.4\text{ M H}_2\text{O}$$

(c)

$$\left[\mathrm{H_2O}\right]=\frac{38.0\ \mathrm{g\ H_2O}}{62.0\ \mathrm{g\ C_3H_8O_3}}\times\frac{1000\ \mathrm{g\ solvent}}{1\,\mathrm{kg\ solvent}}\times\frac{1\ \mathrm{mol\ H_2O}}{18.02\ \mathrm{g\ H_2O}}$$

$$=34.0\ m\ \mathrm{H_2O}$$

(d) We can determine the moles of $C_3H_8O_3$ and H_2O from the above calculations.
moles of H_2O = 2.11 mol.
moles of $C_3H_8O_3$ = 0.673 mol.

$$x_{\mathrm{C_3H_8O_3}}=\frac{0.673\ \mathrm{mol\ C_3H_8O_3}}{0.673\ \mathrm{mol\ C_3H_8O_3}+2.11\ \mathrm{mol\ H_2O}}=0.242$$

(e) $\mathrm{mol\%\ H_2O}=\dfrac{2.11\ \mathrm{mol\ H_2O}}{0.673\ \mathrm{mol\ C_3H_8O_3}+2.11\ \mathrm{mol\ H_2O}}\times100=75.8\%$

128. (1) Solution with lowest conductivity: (b) 0.15 *m* $C_{12}H_{22}O_{11}$, because it is a non-electrolyte.
(2) Lowest boiling point: (d) 0.05 *m* NaCl, because the molality of the solute is the smallest, making boiling-point elevation the smallest value.
(3) Highest vapor pressure of water: (d), for the same reason as above.
(4) Lowest freezing point: (a), because the molality of the solute is the highest (2×0.10 *m*).

129. The answer is (c). It shows solvation of individual ions by oriented water molecules.

130. The answer is (b), because the charge in all species is the same (+1 or -1), but F^- is the smallest.

131. The magnitude of $\Delta H_{\mathrm{lattice}}$ is larger than the sum of the $\Delta H_{\mathrm{hydration}}$ of the individual ions. Since the test tube turns cold, dissolution of NH_4Cl is endothermic, which means that the final energy of the system, the hydration of the individual ions, is less than the initial energy of the system, which is the lattice energy of the solid.

132. The answer is (a). Lowering temperature increases solubility.

133. The answer is (b), because the HCl dissociates completely in water to give cations and anions, which are then solvated with water (and are none-volatile).

134. The answer is (a). Use Raoult's law to determine the mole fraction:

$$\mathrm{P}_{\mathrm{C_6H_{14}}}=x_{\mathrm{C_6H_{14}}}\cdot\mathrm{P}^*_{\mathrm{C_6H_{14}}}$$

$$600\ \mathrm{mm\ Hg}=x_{\mathrm{solute}}\cdot760\,\mathrm{mm\ Hg}$$

$$x_{\mathrm{C_6H_{14}}}=0.789$$

$$x_{\mathrm{solute}}=1-0.789=0.211$$

135. The answer is (e).

$$\Pi = \mathrm{MRT}$$

$$\Pi = \left(0.312\ \mathrm{M}\right)\left(0.08206\ \mathrm{L \cdot atm \cdot K^{-1}}\right)\left(348\ \mathrm{K}\right) = 8.91\ \mathrm{atm}$$

$$\mathrm{P(barr)} = 8.91\ \mathrm{atm} \times \frac{1.0135\ \mathrm{barr}}{1\ \mathrm{atm}} = 9.03\ \mathrm{barr}$$

136. The answer is (c).

$$10.5\ \mathrm{mol\ H_2O} \times \frac{18.0\ \mathrm{g\ H_2O}}{1\ \mathrm{mol\ H_2O}} = 189\ \mathrm{g\ H_2O}$$

$$\mathrm{mass\%} = \frac{23.4}{189 + 23.4} \times 100 = 11.0\%$$