

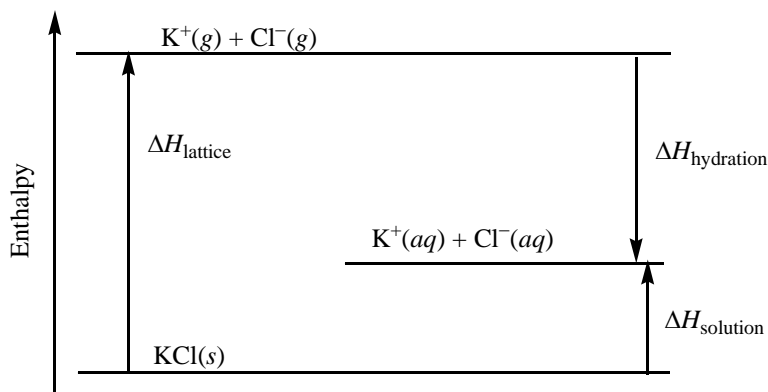
# CHAPTER 13 THE PROPERTIES OF SOLUTIONS

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- 13.1 A heterogeneous mixture has two or more phases, thus seawater has both dissolved and suspended particles. The composition of the seawater is different in various places where a sample may be obtained.
- 13.2 When a salt such as NaCl dissolves, ion-dipole forces cause the ions to separate, and many water molecules cluster around each of them in hydration shells. Ion-dipole forces hold the first shell. Additional shells are held by hydrogen bonding to inner shells.
- 13.3 In  $\text{CH}_3(\text{CH}_2)_n\text{COOH}$ , as  $n$  increases, the hydrophobic (CH) portion of the carboxylic acid increases and the hydrophilic part of the molecule stays the same, with a resulting decrease in water solubility.
- 13.4 a) A more concentrated solution will have more solute dissolved in the solvent. Potassium nitrate,  $\text{KNO}_3$ , is an ionic compound and therefore soluble in a polar solvent like water. Potassium nitrate is not soluble in the nonpolar solvent  $\text{CCl}_4$ . Because potassium nitrate dissolves to a greater extent in water,  **$\text{KNO}_3$  in  $\text{H}_2\text{O}$**  will result in the more concentrated solution.
- 13.5 b) Stearic acid in  $\text{CCl}_4$ . Stearic acid will not dissolve in water. It is nonpolar while water is very polar. Stearic acid will dissolve in carbon tetrachloride, as both are nonpolar.
- 13.6 To identify the strongest type of intermolecular force, check the formula of the solute and identify the forces that could occur. Then look at the formula for the solvent and determine if the forces identified for the solute would occur with the solvent. The strongest force is ion-dipole followed by dipole-dipole (including H bonds). Next in strength is ion-induced dipole force and then dipole-induced dipole force. The weakest intermolecular interactions are dispersion forces.
- a) **Ion-dipole forces** are the strongest intermolecular forces in the solution of the ionic substance cesium chloride in polar water.
- b) **Hydrogen bonding** (type of dipole-dipole force) is the strongest intermolecular force in the solution of polar propanone (or acetone) in polar water.
- c) **Dipole-induced dipole forces** are the strongest forces between the polar methanol and nonpolar carbon tetrachloride.
- 13.7 a) **metallic bonding**  
b) **dipole-dipole**  
c) **dipole-induced dipole**
- 13.8 a) **Hydrogen bonding** occurs between the H atom on water and the lone electron pair on the O atom in dimethyl ether ( $\text{CH}_3\text{OCH}_3$ ). However, none of the hydrogen atoms on dimethyl ether participates in hydrogen bonding because the C–H bond does not have sufficient polarity.
- b) The dipole in water induces a dipole on the  $\text{Ne}(g)$  atom, so **dipole-induced dipole** interactions are the strongest intermolecular forces in this solution.
- c) Nitrogen gas and butane are both nonpolar substances, so **dispersion forces** are the principal attractive forces.
- 13.9 a) **dispersion forces**  
b) **hydrogen bonding**  
c) **dispersion forces**

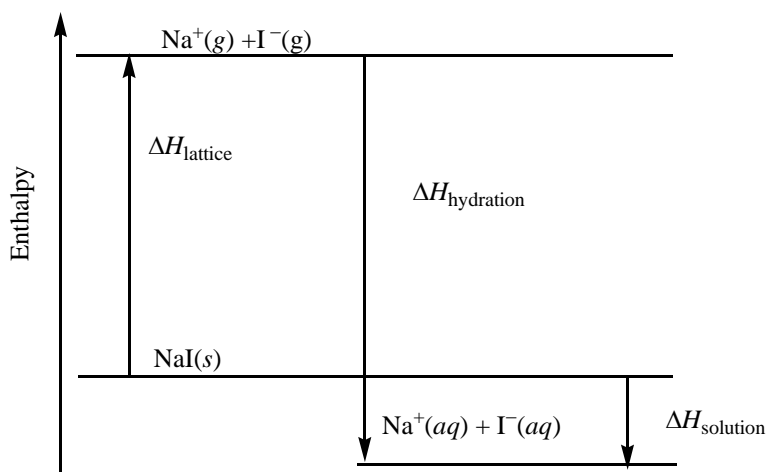
- 13.10  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$  is polar with dipole-dipole interactions as the dominant intermolecular forces. Examine the solutes to determine which has intermolecular forces more similar to those for the diethyl ether. This solute is the one that would be more soluble.
- a) **HCl** would be more soluble since it is a covalent compound with dipole-dipole forces, whereas NaCl is an ionic solid. Dipole-dipole forces between HCl and diethyl ether are more similar to the dipole forces in diethyl ether than the ion-dipole forces between NaCl and diethyl ether.
- b)  **$\text{CH}_3\text{CHO}$**  (acetaldehyde) would be more soluble. The dominant interactions in  $\text{H}_2\text{O}$  are hydrogen bonding, a stronger type of dipole-dipole force. The dominant interactions in  $\text{CH}_3\text{CHO}$  are dipole-dipole. The solute-solvent interactions between  $\text{CH}_3\text{CHO}$  and diethyl ether are more similar to the solvent intermolecular forces than the forces between  $\text{H}_2\text{O}$  and diethyl ether.
- c)  **$\text{CH}_3\text{CH}_2\text{MgBr}$**  would be more soluble.  $\text{CH}_3\text{CH}_2\text{MgBr}$  has a polar end ( $-\text{MgBr}$ ) and a nonpolar end ( $\text{CH}_3\text{CH}_2-$ ), whereas  $\text{MgBr}_2$  is an ionic compound. The nonpolar end of  $\text{CH}_3\text{CH}_2\text{MgBr}$  and diethyl ether would interact with dispersion forces, while the polar end of  $\text{CH}_3\text{CH}_2\text{MgBr}$  and the dipole in diethyl ether would interact with dipole-dipole forces. Recall, that if the polarity continues to increase, the bond will eventually become ionic. There is a continuous sequence from nonpolar covalent to ionic.
- 13.11 a)  **$\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_3(\text{g})$** , due to its smaller size (smaller molar mass).  
 b)  **$\text{CH}_2\text{Cl}_2$** , because it is more polar than  $\text{CCl}_4$ .  
 c) **Tetrahydropyran** is more water soluble due to hydrogen bonding between the oxygen atom and water molecules.
- 13.12 Gluconic acid is a very polar molecule because it has  $-\text{OH}$  groups attached to every carbon. The abundance of  $-\text{OH}$  bonds allows gluconic acid to participate in extensive  $\text{H}-$ bonding with water, hence its great solubility in water. On the other hand, caproic acid has a 5-carbon, nonpolar, hydrophobic (“water hating”) tail that does not easily dissolve in water. The dispersion forces in the nonpolar tail are more similar to the dispersion forces in hexane, hence its greater solubility in hexane.
- 13.13 The  $\Delta H_{\text{solvent}}$  and  $\Delta H_{\text{mix}}$  components of the heat of solution combined together represent the enthalpy change during solvation, the process of surrounding a solute particle with solvent particles. Solution in water is often called hydration.
- 13.14 a) Charge density is the ratio of the ion’s charge to its volume.  
 b)  $- < + < 2- < 3+$   
 c) The higher the charge density, the more negative is  $\Delta H_{\text{hydration}}$ .  $\Delta H_{\text{hydration}}$  increases with charge and decreases with increasing volume.
- 13.15 The solution cycle for ionic compounds in water consists of two enthalpy terms: the lattice energy, and the combined heats of hydration of the cation and anion.
- $$\Delta H_{\text{solution}} = \Delta H_{\text{lattice}} + \Delta H_{\text{hydration of ions}}$$
- For a heat of solution to be zero (or very small)
- $$\Delta H_{\text{lattice}} \approx \Delta H_{\text{hydration of ions}}, \text{ and they would have to have opposite signs.}$$
- 13.16 a) **Endothermic**  
 b) The lattice energy term is much **larger** than the combined ionic heats of hydration.  
 c) The increase in entropy outweighs the increase in enthalpy, so ammonium chloride dissolves.
- 13.17 This compound would be very soluble in water. A large exothermic value in  $\Delta H_{\text{solution}}$  (enthalpy of solution) means that the solution has a much lower energy state than the isolated solute and solvent particles, so the system tends to the formation of the solution. Entropy that accompanies dissolution always favors solution formation. Entropy becomes important when explaining why solids with an endothermic  $\Delta H_{\text{solution}}$  (and higher energy state) are still soluble in water.

13.18



Lattice energy values are always positive as energy is required to separate the ions from each other. Hydration energy values are always negative as energy is released when intermolecular forces between ions and water form. Since the heat of solution for KCl is endothermic, the lattice energy must be greater than the hydration energy for an overall input of energy.

13.19



Lattice energy values are always positive as energy is required to separate the ions from each other. Hydration energy values are always negative as energy is released when intermolecular forces between ions and water form. Since the heat of solution for NaI is exothermic, the negative hydration energy must be greater than the positive lattice energy.

- 13.20 Charge density is the ratio of an ion's charge (regardless of sign) to its volume. An ion's volume is related to its radius. For ions whose charges have the same sign (+ or -), ion size decreases as a group in the periodic table is ascended and as you proceed from left to right in the periodic table.
- Both ions have a +1 charge, but the volume of  $\text{Na}^+$  is smaller, so it has the greater charge density.
  - $\text{Sr}^{2+}$  has a greater ionic charge and a smaller size (because it has a greater  $Z_{\text{eff}}$ ), so it has the greater charge density.
  - $\text{Na}^+$  has a smaller ion volume than  $\text{Cl}^-$ , so it has the greater charge density.
  - $\text{O}^{2-}$  has a greater ionic charge and similar ion volume, so it has the greater charge density.
  - $\text{OH}^-$  has a smaller ion volume than  $\text{SH}^-$ , so it has the greater charge density.

- 13.21 a)  $\text{I}^-$  has a smaller charge density (larger ion volume) than  $\text{Br}^-$ .  
 b)  $\text{Ca}^{2+}$  is less than  $\text{Sc}^{3+}$ , due to its smaller ion charge.  
 c)  $\text{Br}^-$  is less than  $\text{K}^+$ , due to its larger ion volume.  
 d)  $\text{Cl}^-$  is less than  $\text{S}^{2-}$ , due to its smaller ion charge.  
 e)  $\text{Sc}^{3+}$  is less than  $\text{Al}^{3+}$ , due to its larger ion volume.
- 13.22 The ion with the greater charge density will have the larger  $\Delta H_{\text{hydration}}$ .  
 a)  $\text{Na}^+$  would have a larger  $\Delta H_{\text{hydration}}$  than  $\text{Cs}^+$  since its charge density is greater than that of  $\text{Cs}^+$ .  
 b)  $\text{Sr}^{2+}$  would have a larger  $\Delta H_{\text{hydration}}$  than  $\text{Rb}^+$ .  
 c)  $\text{Na}^+$  would have a larger  $\Delta H_{\text{hydration}}$  than  $\text{Cl}^-$ .  
 d)  $\text{O}^{2-}$  would have a larger  $\Delta H_{\text{hydration}}$  than  $\text{F}^-$ .  
 e)  $\text{OH}^-$  would have a larger  $\Delta H_{\text{hydration}}$  than  $\text{SH}^-$ .
- 13.23 a)  $\text{I}^-$     b)  $\text{Ca}^{2+}$     c)  $\text{Br}^-$     d)  $\text{Cl}^-$     e)  $\text{Sc}^{3+}$
- 13.24 a) The two ions in potassium bromate are  $\text{K}^+$  and  $\text{BrO}_3^-$ . The heat of solution for ionic compounds is  $\Delta H_{\text{solution}} = \Delta H_{\text{lattice}} + \Delta H_{\text{hydration of the ions}}$ . Therefore, the combined heats of hydration for the ions is  $(\Delta H_{\text{solution}} - \Delta H_{\text{lattice}})$  or  $41.1 \text{ kJ/mol} - 745 \text{ kJ/mol} = -703.9 = \mathbf{-704 \text{ kJ/mol}}$ .  
 b)  $\text{K}^+$  ion contributes more to the heat of hydration because it has a smaller size and, therefore, a greater charge density.
- 13.25 a)  $\Delta H_{\text{hydration of ions}} = \Delta H_{\text{solution}} - \Delta H_{\text{lattice}}$   
 $\Delta H_{\text{hydration of ions}} = 17.3 \text{ kJ/mol} - 763 \text{ kJ/mol}$   
 $\Delta H_{\text{hydration of ions}} = -745.7 = \mathbf{-746 \text{ kJ/mol}}$   
 b) It is the  $\text{Na}^+$  due to its smaller size (larger charge density).
- 13.26 Entropy increases as the possible states for a system increases.  
 a) Entropy **increases** as the gasoline is burned. Gaseous products at a higher temperature form.  
 b) Entropy **decreases** as the gold is separated from the ore. Pure gold has only the arrangement of gold atoms next to gold atoms, while the ore mixture has a greater number of possible arrangements among the components of the mixture.  
 c) Entropy **increases** as a solute dissolves in the solvent.
- 13.27 a) Entropy **increases**  
 b) Entropy **decreases**  
 c) Entropy **increases**
- 13.28  $\Delta H_{\text{solution}} = \Delta H_{\text{lattice}} + \Delta H_{\text{hydration of ions}}$   
 $\Delta H_{\text{solution}} = 822 \text{ kJ/mol} - 799 \text{ kJ/mol}$   
 $\Delta H_{\text{solution}} = \mathbf{23 \text{ kJ/mol}}$
- 13.29 Add a pinch of the solid solute to each solution. A saturated solution contains the maximum amount of dissolved solute at a particular temperature. When additional solute is added to this solution, it will remain undissolved. An unsaturated solution contains less than the maximum amount of dissolved solute and so will dissolve added solute. A supersaturated solution is unstable and addition of a "seed" crystal of solute causes the excess solute to crystallize immediately, leaving behind a saturated solution.
- 13.30 An increase in temperature produces an increase in kinetic energy; the solute molecules overcome the weak intermolecular forces, which results in a decrease in solubility of any gas in water. In nearly all cases, gases dissolve exothermically ( $\Delta H_{\text{soln}} < 0$ ).
- 13.31 a) Increasing pressure for a gas **increases** the solubility of the gas according to Henry's law.  
 b) Increasing the volume of a gas causes a decrease in its pressure (Boyle's law), which **decreases** the solubility of the gas.

13.32 a) **increase**      b) **stay the same**

13.33 a) Solubility for a gas is calculated from Henry's law:  $S_{\text{gas}} = k_{\text{H}} \times P_{\text{gas}}$ .  $S_{\text{gas}}$  is expressed as mol/L, so convert moles of  $\text{O}_2$  to mass of  $\text{O}_2$  using the molar mass.

$$S_{\text{gas}} = k_{\text{H}} \times P_{\text{gas}}$$
$$S_{\text{gas}} = \left(1.28 \times 10^{-3} \frac{\text{mol}}{\text{L} \cdot \text{atm}}\right)(1.00 \text{ atm}) = 1.28 \times 10^{-3} \text{ mol/L}$$
$$\left(\frac{1.28 \times 10^{-3} \text{ mol O}_2}{\text{L}}\right)\left(\frac{32.0 \text{ g O}_2}{1 \text{ mol O}_2}\right)(2.50 \text{ L}) = 0.1024 = \mathbf{0.102 \text{ g O}_2}$$

b) The amount of gas that will dissolve in a given volume decreases proportionately with the partial pressure of the gas, so

$$S_{\text{gas}} = \left(1.28 \times 10^{-3} \frac{\text{mol}}{\text{L} \cdot \text{atm}}\right)(0.209 \text{ atm}) = 2.6752 \times 10^{-4} \text{ mol/L}$$
$$\left(\frac{2.6752 \times 10^{-4} \text{ mol O}_2}{\text{L}}\right)\left(\frac{32.0 \text{ g O}_2}{1 \text{ mol O}_2}\right)(2.50 \text{ L}) = 0.0214016 = \mathbf{0.0214 \text{ g O}_2}$$

13.34 Solubility =  $\left(1.5 \times 10^{-3} \frac{\text{mol}}{\text{L} \cdot \text{atm}}\right)(1.0 \text{ atm})\left(\frac{0.93\%}{100\%}\right) = 1.395 \times 10^{-5} = \mathbf{1.4 \times 10^{-5} \text{ mol/L}}$

13.35 The solution is **saturated**.

13.36 Solubility for a gas is calculated from Henry's law:  $S_{\text{gas}} = k_{\text{H}} \times P_{\text{gas}}$ .

$$S_{\text{gas}} = k_{\text{H}} \times P_{\text{gas}}$$
$$S_{\text{gas}} = \left(3.7 \times 10^{-2} \frac{\text{mol}}{\text{L} \cdot \text{atm}}\right)(5.5 \text{ atm}) = 0.2035 = \mathbf{0.20 \text{ mol/L}}$$

13.37 Molarity is defined as the number of moles of solute dissolved in one liter of solution. Molality is defined as the number of moles of solute dissolved in 1000 g (1 kg) of solvent. Molal solutions are prepared by measuring masses of solute and solvent, which are additive and not changed by temperature, so the concentration does not change with temperature.

13.38 **No**, 21 g solute/kg of solvent would be 21 g solute/1.021 kg solution.

13.39 Converting between molarity and molality involves conversion between volume of solution and mass of solution. Both of these quantities are given so interconversion is possible. To convert to mole fraction requires that the mass of solvent be converted to moles of solvent. Since the identity of the solvent is not given, conversion to mole fraction is not possible if the molar mass is not known. Why is the identity of the solute not necessary for conversion?

13.40 % w/w, mole fraction, and molality are weight-to-weight relationships that are not affected by changes in temperature. % w/v and molarity are affected by changes in temperature, because the volume is temperature dependant.

13.41 Convert the masses to moles and the volumes to liters and use the definition of molarity:  $M = \frac{\text{mol of solute}}{V(\text{L}) \text{ of solution}}$

$$\text{a) Molarity} = \left(\frac{32.3 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}}{100. \text{ mL}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)\left(\frac{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{342.30 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}}\right) = 0.943617 = \mathbf{0.944 \text{ M C}_{12}\text{H}_{22}\text{O}_{11}}$$

- b) Molarity =  $\left(\frac{5.80 \text{ g LiNO}_3}{505 \text{ mL}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)\left(\frac{1 \text{ mol LiNO}_3}{68.95 \text{ g LiNO}_3}\right) = 0.166572 = \mathbf{0.167 M LiNO}_3$
- 13.42 a) Molarity =  $\left(\frac{0.82 \text{ g C}_2\text{H}_5\text{OH}}{10.5 \text{ mL}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)\left(\frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.07 \text{ g C}_2\text{H}_5\text{OH}}\right) = 1.69514 = \mathbf{1.7 M C}_2\text{H}_5\text{OH}$
- b) Molarity =  $\left(\frac{1.22 \text{ g NH}_3}{33.5 \text{ mL}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)\left(\frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3}\right) = 2.138456 = \mathbf{2.14 M NH}_3$
- 13.43 Dilution calculations can be done using  $M_{\text{conc}}V_{\text{conc}} = M_{\text{dil}}V_{\text{dil}}$
- a)  $M_{\text{conc}} = 0.240 \text{ M NaOH}$   $V_{\text{conc}} = 78.0 \text{ mL}$   $M_{\text{dil}} = ?$   $V_{\text{dil}} = 0.250 \text{ L}$
- $$M_{\text{dil}} = M_{\text{conc}} V_{\text{conc}}/V_{\text{dil}} = \frac{(0.240 \text{ M})(78.0 \text{ mL})}{(0.250 \text{ L})}\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) = 0.07488 = \mathbf{0.0749 M}$$
- b)  $M_{\text{conc}} = 1.2 \text{ M HNO}_3$   $V_{\text{conc}} = 38.5 \text{ mL}$   $M_{\text{dil}} = ?$   $V_{\text{dil}} = 0.130 \text{ L}$
- $$M_{\text{dil}} = M_{\text{conc}} V_{\text{conc}}/V_{\text{dil}} = \frac{(1.2 \text{ M})(38.5 \text{ mL})}{(0.130 \text{ L})}\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) = 0.355385 = \mathbf{0.36 M}$$
- 13.44 Dilution calculations can be done using  $M_{\text{conc}}V_{\text{conc}} = M_{\text{dil}}V_{\text{dil}}$
- a)  $M_{\text{conc}} = 6.25 \text{ M HCl}$   $V_{\text{conc}} = 25.5 \text{ mL}$   $M_{\text{dil}} = ?$   $V_{\text{dil}} = 0.500 \text{ L}$
- $$M_{\text{dil}} = M_{\text{conc}} V_{\text{conc}}/V_{\text{dil}} = \frac{(6.25 \text{ M})(25.5 \text{ mL})}{(0.500 \text{ L})}\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) = 0.31875 = \mathbf{0.319 M}$$
- b)  $M_{\text{conc}} = 2.00 \times 10^{-2} \text{ M KI}$   $V_{\text{conc}} = 8.25 \text{ mL}$   $M_{\text{dil}} = ?$   $V_{\text{dil}} = 12.0 \text{ mL}$
- $$M_{\text{dil}} = M_{\text{conc}} V_{\text{conc}}/V_{\text{dil}} = \frac{(2.00 \times 10^{-2} \text{ M})(8.25 \text{ mL})}{(12.0 \text{ mL})} = 0.01375 = \mathbf{0.0138 M}$$
- 13.45 a) Find the number of moles  $\text{KH}_2\text{PO}_4$  needed to make 365 mL of this solution. Convert moles to mass using the molar mass of  $\text{KH}_2\text{PO}_4$  (Molar mass = 136.09 g/mol)
- $$\text{Mass KH}_2\text{PO}_4 = (365 \text{ mL})\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)\left(\frac{8.55 \times 10^{-2} \text{ mol KH}_2\text{PO}_4}{\text{L}}\right)\left(\frac{136.09 \text{ g KH}_2\text{PO}_4}{1 \text{ mol KH}_2\text{PO}_4}\right)$$
- $$= 4.24703 = 4.25 \text{ g KH}_2\text{PO}_4$$
- Add **4.25 g  $\text{KH}_2\text{PO}_4$**  to enough water to make 365 mL of aqueous solution.
- b) Use the relationship  $M_{\text{conc}}V_{\text{conc}} = M_{\text{dil}}V_{\text{dil}}$  to find the volume of 1.25 M NaOH needed.
- $$M_{\text{conc}} = 1.25 \text{ M NaOH}$$
- $V_{\text{conc}} = ?$
- $M_{\text{dil}} = 0.335 \text{ M NaOH}$
- $V_{\text{dil}} = 465 \text{ mL}$
- $$V_{\text{conc}} = M_{\text{dil}} V_{\text{dil}}/M_{\text{conc}} = \frac{(0.335 \text{ M})(465 \text{ mL})}{(1.25 \text{ M})} = 124.62 = \mathbf{125 \text{ mL}}$$
- Add **125 mL** of 1.25 M NaOH to enough water to make 465 mL of solution.
- 13.46 a) Find the number of moles NaCl needed to make 2.5 L of this solution. Convert moles to mass using the molar mass of NaCl (Molar mass = 58.44 g/mol)
- $$\text{Mass NaCl} = (2.5 \text{ L})\left(\frac{0.65 \text{ mol NaCl}}{\text{L}}\right)\left(\frac{58.44 \text{ g NaCl}}{1 \text{ mol NaCl}}\right) = 94.965 = 95 \text{ g NaCl}$$
- Add **95 g NaCl** to enough water to make 2.5 L of aqueous solution.
- b) Use the relationship  $M_{\text{conc}}V_{\text{conc}} = M_{\text{dil}}V_{\text{dil}}$  to find the volume of 2.1 M urea needed.
- $$M_{\text{conc}} = 2.1 \text{ M urea}$$
- $V_{\text{conc}} = ?$
- $M_{\text{dil}} = 0.3 \text{ M urea}$
- $V_{\text{dil}} = 15.5 \text{ L}$
- $$V_{\text{conc}} = M_{\text{dil}} V_{\text{dil}}/M_{\text{conc}} = (0.3 \text{ M})(15.5 \text{ L}) / (2.1 \text{ M}) = 2.21429 = 2 \text{ L}$$
- Add **2 L** of 2.1 M urea to enough water to make 15.5 L of solution.

13.47 Molality,  $m = \frac{\text{moles of solute}}{\text{kg of solvent}}$

$$\text{a) } m \text{ glycine} = \frac{85.4 \text{ g Glycine} \left( \frac{1 \text{ mol Glycine}}{75.07 \text{ g Glycine}} \right)}{(1.270 \text{ kg})} = 0.895752 = \mathbf{0.896 \text{ } m \text{ glycine}}$$

$$\text{b) } m \text{ glycerol} = \frac{8.59 \text{ g Glycerol} \left( \frac{1 \text{ mol Glycerol}}{92.09 \text{ g Glycerol}} \right)}{(77.0 \text{ g})} \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) = 1.2114 = \mathbf{1.21 \text{ } m \text{ glycerol}}$$

13.48 Molality = moles solute/kg solvent.

$$\text{a) } m \text{ HCl} = \frac{164 \text{ g HCl} \left( \frac{1 \text{ mol HCl}}{36.46 \text{ g HCl}} \right)}{(753 \text{ g})} \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) = 5.9735 = \mathbf{5.97 \text{ } m \text{ HCl}}$$

$$\text{b) } m \text{ naphthalene} = \frac{16.5 \text{ g Naphthalene} \left( \frac{1 \text{ mol Naphthalene}}{128.16 \text{ g Naphthalene}} \right)}{(53.3 \text{ g})} \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) \\ = 2.41548 = \mathbf{2.42 \text{ } m \text{ naphthalene}}$$

13.49 Molality,  $m = \frac{\text{moles of solute}}{\text{kg of solvent}}$  Use density to convert volume to mass.

$$m \text{ benzene} = \frac{(44.0 \text{ mL C}_6\text{H}_6) \left( \frac{0.877 \text{ g}}{\text{mL}} \right) \left( \frac{1 \text{ mol C}_6\text{H}_6}{78.11 \text{ g C}_6\text{H}_6} \right)}{(167 \text{ mL C}_6\text{H}_{14}) \left( \frac{0.660 \text{ g}}{\text{mL}} \right)} \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) = 4.48214 = \mathbf{4.48 \text{ } m \text{ C}_6\text{H}_6}$$

13.50 Molality = moles solute/kg of solvent.

$$m \text{ CCl}_4 = \frac{(2.66 \text{ mL CCl}_4) \left( \frac{1.59 \text{ g}}{\text{mL}} \right) \left( \frac{1 \text{ mol CCl}_4}{153.81 \text{ g CCl}_4} \right)}{(76.5 \text{ mL CH}_2\text{Cl}_2) \left( \frac{1.33 \text{ g}}{\text{mL}} \right)} \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) = 0.2702596 = \mathbf{0.270 \text{ } m \text{ CCl}_4}$$

13.51 a) The total mass of the solution is  $3.10 \times 10^2 \text{ g}$ , so  $\text{mass}_{\text{solute}} + \text{mass}_{\text{solvent}} = 3.10 \times 10^2 \text{ g}$ .

$$\text{Mass of C}_2\text{H}_6\text{O}_2 \text{ in } 1000 \text{ g (1 kg) of H}_2\text{O} = \left( \frac{0.125 \text{ mol C}_2\text{H}_6\text{O}_2}{1 \text{ kg H}_2\text{O}} \right) \left( \frac{62.07 \text{ g C}_2\text{H}_6\text{O}_2}{1 \text{ mol C}_2\text{H}_6\text{O}_2} \right) \\ = 7.75875 \text{ g C}_2\text{H}_6\text{O}_2 \text{ in } 1000 \text{ g H}_2\text{O}$$

$$\text{Grams of this solution} = 1000 \text{ g H}_2\text{O} + 7.75875 \text{ g C}_2\text{H}_6\text{O}_2 = 1007.75875 \text{ g}$$

$$\text{Mass C}_2\text{H}_6\text{O}_2 = \left( \frac{7.75875 \text{ g C}_2\text{H}_6\text{O}_2}{1007.75875 \text{ g solution}} \right) (3.10 \times 10^2 \text{ g solution}) = 2.386695 \text{ g C}_2\text{H}_6\text{O}_2$$

$$\text{Mass}_{\text{solvent}} = 3.10 \times 10^2 \text{ g} - \text{mass}_{\text{solute}} = 3.10 \times 10^2 \text{ g} - 2.386695 \text{ g C}_2\text{H}_6\text{O}_2 = 307.613305 = 308 \text{ g H}_2\text{O}$$

Therefore, **add 2.39 g C<sub>2</sub>H<sub>6</sub>O<sub>2</sub> to 308 g of H<sub>2</sub>O** to make a 0.125 *m* solution.

b) This is a disguised dilution problem. First, determine the amount of solute in your target solution:

$$\left( \frac{2.20\%}{100\%} \right) (1.20 \text{ kg}) = 0.0264 \text{ kg HNO}_3 \text{ (solute)}$$

Then determine the amount of the concentrated acid solution needed to get 0.0264 kg solute:

$$\left(\frac{52.0\%}{100\%}\right)(\text{mass needed}) = 0.0264 \text{ kg}$$

Mass solute needed = 0.050769 = 0.0508 kg

Mass solvent = Mass solution – Mass solute = 1.20 kg – 0.050769 kg = 1.149231 = 1.15 kg

**Add 0.0508 kg of the 52.0% (w/w) HNO<sub>3</sub> to 1.15 kg H<sub>2</sub>O to make 1.20 kg of 2.20% (w/w) HNO<sub>3</sub>.**

- 13.52 a) The total weight of the solution is 1.50 kg, so

$$\text{mass}_{\text{solute}} + \text{mass}_{\text{solvent}} = 1.50 \text{ kg}$$

$$\text{g C}_2\text{H}_6\text{O}_2/1000 \text{ g H}_2\text{O in } 0.0355 \text{ m} = \left(\frac{0.0355 \text{ mol C}_2\text{H}_5\text{OH}}{1 \text{ kg H}_2\text{O}}\right)\left(\frac{46.07 \text{ g C}_2\text{H}_5\text{OH}}{1 \text{ mol C}_2\text{H}_5\text{OH}}\right)$$

$$= 1.635485 \text{ g C}_2\text{H}_5\text{OH}/1000 \text{ g H}_2\text{O (unrounded)}$$

Grams of this solution = 1000 g H<sub>2</sub>O + 1.635485 g C<sub>2</sub>H<sub>5</sub>OH = 1001.635485 g (unrounded)

$$\text{Mass C}_2\text{H}_6\text{O}_2 = [1.635485 \text{ g C}_2\text{H}_5\text{OH}/1001.635485 \text{ g solution}] [1.50 \text{ kg solution } (10^3 \text{ g/1 kg})]$$

$$= 2.449222 = 2.45 \text{ g C}_2\text{H}_5\text{OH}$$

$$\text{Mass}_{\text{solvent}} = 1500 \text{ g} - \text{mass}_{\text{solute}} = 1500 \text{ g} - 2.449222 \text{ g C}_2\text{H}_6\text{O}_2 = 1497.551 = 1498 \text{ g H}_2\text{O}$$

Therefore, **add 2.45 g C<sub>2</sub>H<sub>5</sub>OH to 1498 g of H<sub>2</sub>O to make a 0.0355 m solution.**

- b) This is a disguised dilution problem. First, determine the amount of solute in your target solution:

$$(445 \text{ g}) (13.0\%/100\%) = 57.85 \text{ g HCl (solute) (unrounded)}$$

Then determine the amount of the concentrated acid solution needed to get 57.85 g solute:

$$(\text{Mass needed}) (34.1\%/100\%) = 57.85 \text{ g}$$

$$\text{Mass solute needed} = 169.6481 = 170. \text{ g}$$

$$\text{Mass solvent} = \text{Mass solution} - \text{Mass solute} = 445 \text{ g} - 169.6481 \text{ g} = 275.35191 = 275 \text{ g}$$

**Add 170. g of the 34.1% (w/w) HCl to 275 g H<sub>2</sub>O**

- 13.53 a) Mole fraction is moles of isopropanol per total moles.

$$X_{\text{isopropanol}} = \frac{0.35 \text{ mol Isopropanol}}{(0.35 + 0.85) \text{ mol}} = 0.2916667 = \mathbf{0.29}$$
 (Notice that mole fractions have no units.)

- b) Mass percent =  $\frac{\text{mass of solute}}{\text{mass of solution}}(100)$ . From the mole amounts, find the masses of isopropanol and water:

$$\text{Mass isopropanol} = (0.35 \text{ mol C}_3\text{H}_7\text{OH})\left(\frac{60.09 \text{ g C}_3\text{H}_7\text{OH}}{1 \text{ mol C}_3\text{H}_7\text{OH}}\right) = 21.0315 \text{ g isopropanol}$$

$$\text{Mass water} = (0.85 \text{ mol H}_2\text{O})\left(\frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}}\right) = 15.317 \text{ g water (unrounded)}$$

$$\text{Percent isopropanol} = \frac{(21.0315 \text{ g Isopropanol})}{(21.0315 + 15.317) \text{ g}} \times 100\% = 57.860710 = \mathbf{58\%}$$
 isopropanol

- c) Molality of isopropanol is moles of isopropanol per kg of solvent.

$$\text{Molality isopropanol} = \frac{0.35 \text{ mol Isopropanol}}{15.317 \text{ g Water}}\left(\frac{10^3 \text{ g}}{1 \text{ kg}}\right) = 22.85043 = \mathbf{23 m}$$
 isopropanol

- 13.54 a) Mole fraction is moles of NaCl per total moles.

$$X_{\text{NaCl}} = \frac{0.100 \text{ mol NaCl}}{(0.100 + 8.60) \text{ mol}} = 0.01149425 = \mathbf{0.0115}$$
 (Notice that mole fractions have no units.)

- b) Mass percent is the mass of NaCl per 100 g of solution.

$$\text{Mass NaCl} = (0.100 \text{ mol NaCl}) (58.44 \text{ g/mol}) = 5.844 \text{ g NaCl (unrounded)}$$

$$\text{Mass water} = (8.60 \text{ mol water}) (18.02 \text{ g/mol}) = 154.972 \text{ g water (unrounded)}$$

$$\text{Percent NaCl} = \frac{(5.844 \text{ g NaCl})}{(5.844 + 154.972) \text{ g}} \times 100\% = 3.63396677 = \mathbf{3.63\%}$$
 NaCl



c) Molality of NaCl is moles of NaCl per kg of solvent.

$$\text{Molality NaCl} = \frac{0.100 \text{ mol NaCl}}{154.972 \text{ g Water}} \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) = 0.645277856 = \mathbf{0.645 \text{ m NaCl}}$$

13.55 The information given is 8.00 mass %  $\text{NH}_3$  solution with a density of 0.9651 g/mL. For convenience, choose exactly 100.00 grams of solution. Determine some fundamental quantities:

$$\text{Mass of NH}_3 = (100 \text{ g solution}) \left( \frac{8.00\% \text{ NH}_3}{100\% \text{ solution}} \right) = 8.00 \text{ g NH}_3$$

$$\text{Mass H}_2\text{O} = \text{mass of solution} - \text{mass NH}_3 = (100.00 - 8.00) \text{ g} = 92.00 \text{ g H}_2\text{O}$$

$$\text{Moles NH}_3 = (8.00 \text{ g NH}_3) \left( \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} \right) = 0.469759 \text{ mol NH}_3 \text{ (unrounded)}$$

$$\text{Moles H}_2\text{O} = (92.00 \text{ g H}_2\text{O}) \left( \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \right) = 5.1054 \text{ mol H}_2\text{O} \text{ (unrounded)}$$

$$\text{Volume solution} = (100.00 \text{ g solution}) \left( \frac{1 \text{ mL solution}}{0.9651 \text{ g solution}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) = 0.103616 \text{ L (unrounded)}$$

Using the above fundamental quantities and the definitions of the various units:

$$\text{Molality} = \frac{\text{Moles solute}}{\text{kg solvent}} = \left( \frac{0.469759 \text{ mol NH}_3}{92.00 \text{ g H}_2\text{O}} \right) \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) = 5.106076 = \mathbf{5.11 \text{ m NH}_3}$$

$$\text{Molarity} = \frac{\text{Moles solute}}{\text{L solution}} = \left( \frac{0.469759 \text{ mol NH}_3}{0.103616 \text{ L}} \right) = 4.53365 = \mathbf{4.53 \text{ M NH}_3}$$

$$\text{Mole fraction} = X = \frac{\text{Moles substance}}{\text{total moles}} = \frac{0.469759 \text{ mol NH}_3}{(0.469759 + 5.1054) \text{ mol}} = 0.084259 = \mathbf{0.0843}$$

13.56 The information given is 28.8 mass %  $\text{FeCl}_3$  solution with a density of 1.280 g/mL.

For convenience, choose exactly 100.00 grams of solution.

Determine some fundamental quantities:

$$\text{Mass of FeCl}_3 = (100.00 \text{ grams solution}) (28.8\% \text{ FeCl}_3/100\%) = 28.8 \text{ g FeCl}_3$$

$$\text{Mass H}_2\text{O} = \text{mass of solution} - \text{mass FeCl}_3 = (100.00 - 28.8) \text{ g} = 71.20 \text{ g H}_2\text{O}$$

$$\text{Moles FeCl}_3 = (28.80 \text{ g FeCl}_3) (1 \text{ mol FeCl}_3/162.20 \text{ g FeCl}_3) = 0.1775586 \text{ mol FeCl}_3 \text{ (unrounded)}$$

$$\text{Moles H}_2\text{O} = (71.20 \text{ g H}_2\text{O}) (1 \text{ mol H}_2\text{O}/18.02 \text{ g H}_2\text{O}) = 3.951165 \text{ mol H}_2\text{O} \text{ (unrounded)}$$

$$\text{Volume solution} = (100.00 \text{ g solution}) (1 \text{ mL}/1.280 \text{ g}) (10^{-3} \text{ L}/1 \text{ mL}) = 0.078125 \text{ L (unrounded)}$$

Using the above fundamental quantities and the definitions of the various units:

$$\text{Molality} = \text{Moles solute/kg solvent} = \left( \frac{0.1775586 \text{ mol FeCl}_3}{71.20 \text{ g H}_2\text{O}} \right) \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) = 2.49380 = \mathbf{2.49 \text{ m FeCl}_3}$$

$$\text{Molarity} = \text{Moles solute/L solution} = \frac{0.1775586 \text{ mol FeCl}_3}{0.078125 \text{ L}} = 2.272750 = \mathbf{2.27 \text{ M FeCl}_3}$$

$$\text{Mole fraction} = X = \text{moles substance/total moles} = \frac{0.1775586 \text{ mol FeCl}_3}{(0.1775586 + 3.951165) \text{ mol}} = 0.043005688 = \mathbf{0.0430}$$

$$13.57 \quad \text{ppm} = \left( \frac{\text{mass solute}}{\text{mass solution}} \right) \times 10^6$$

The mass of 100.0 L of waste water solution is  $(100.0 \text{ L solution}) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left( \frac{1.001 \text{ g}}{1 \text{ mL}} \right) = 1.001 \times 10^5 \text{ g}$ .

$$\text{ppm Ca}^{2+} = \left( \frac{0.25 \text{ g Ca}^{2+}}{1.001 \times 10^5 \text{ g solution}} \right) \times 10^6 = 2.49750 = \mathbf{2.5 \text{ ppm Ca}^{2+}}$$

$$\text{ppm Mg}^{2+} = \left( \frac{0.056 \text{ g Mg}^{2+}}{1.001 \times 10^5 \text{ g solution}} \right) \times 10^6 = 0.5594406 = \mathbf{0.56 \text{ ppm Mg}^{2+}}$$

13.58 The information given is ethylene glycol has a density of 1.114 g/mL and a molar mass of 62.07 g/mol. Water has a density of 1.00 g/mL. The solution has a density of 1.070 g/mL.

For convenience, choose exactly 1.0000 Liters as the equal volumes mixed. Ethylene glycol will be designated EG.

Determine some fundamental quantities:

$$\text{Mass of EG} = (1.0000 \text{ L EG}) (1 \text{ mL}/10^{-3} \text{ L}) (1.114 \text{ g EG/mL}) = 1114 \text{ g EG}$$

$$\text{Mass of H}_2\text{O} = (1.0000 \text{ L H}_2\text{O}) (1 \text{ mL}/10^{-3} \text{ L}) (1.00 \text{ g H}_2\text{O/mL}) = 1.00 \times 10^3 \text{ g H}_2\text{O}$$

$$\text{Moles EG} = (1114 \text{ g EG}) (1 \text{ mol EG}/62.07 \text{ g EG}) = 17.94747865 \text{ mol EG (unrounded)}$$

$$\text{Moles H}_2\text{O} = (1.00 \times 10^3 \text{ g H}_2\text{O}) (1 \text{ mol H}_2\text{O}/18.02 \text{ g H}_2\text{O}) = 55.49389567 \text{ mol H}_2\text{O (unrounded)}$$

$$\begin{aligned} \text{Volume solution} &= (1114 \text{ g EG} + 1.00 \times 10^3 \text{ g H}_2\text{O}) (\text{mL}/1.070 \text{ g}) (10^{-3} \text{ L}/1 \text{ mL}) \\ &= 1.97570 \text{ L (unrounded)} \end{aligned}$$

Using the above fundamental quantities and the definitions of the various units:

$$\text{a) Volume percent} = (1.0000 \text{ L EG}/1.97570 \text{ L}) 100\% = 50.61497 = \mathbf{50.61\% \text{ v/v}}$$

$$\text{b) Mass percent} = [(1114 \text{ g EG})/(1114 + 1.00 \times 10^3 \text{ g})] 100\% = 52.6963 = \mathbf{52.7\% \text{ w/w}}$$

$$\text{c) Molarity} = \text{Moles solute} / \text{L solution} = \frac{17.94747865 \text{ mol EG}}{1.97570 \text{ L}} = 9.08411 = \mathbf{9.08 \text{ M ethylene glycol}}$$

$$\begin{aligned} \text{d) Molality} &= \text{Moles solute} / \text{kg solvent} = \frac{17.94747865 \text{ mol EG}}{1.00 \times 10^3 \text{ g H}_2\text{O}} \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) \\ &= 17.94747865 = \mathbf{17.9 \text{ m ethylene glycol}} \end{aligned}$$

$$\begin{aligned} \text{e) Mole fraction} &= X = \text{moles substance} / \text{total moles} = \frac{17.94747865 \text{ mol EG}}{(17.94747865 + 55.49389567) \text{ mol}} \\ &= 0.244378 = \mathbf{0.244} \end{aligned}$$

13.59 Raoult's Law states that the vapor pressure of solvent above the solution equals the mole fraction of the solvent times the vapor pressure of the pure solvent. Raoult's Law is not valid for a solution of a volatile solute in solution. Both solute and solvent would evaporate based upon their respective vapor pressures.

13.60 The boiling point temperature is higher and the freezing point temperature is lower for the solution compared to the solvent because the addition of a solute lowers the freezing point and raises the boiling point of a liquid.

13.61 The boiling point of a 0.01 *m* KF solution is higher than that of 0.01 *m* glucose. KF dissociates into ions in water ( $\text{K}^+$  and  $\text{F}^-$ ) while the glucose does not, so the KF produces more particles.

13.62 Univalent ions behave more ideally than divalent ions. Ionic strength (which affects "activity" concentration) is greater for divalent ions. Thus, **0.01 *m* NaBr** has a freezing point that is closer to its predicted value.

13.63 Cyclohexane, with a freezing point depression constant of 20.1°C/m, would make calculation of molar mass of a substance easier, since  $\Delta T_f$  would be greater.

- 13.64 Strong electrolytes are substances that produce a large number of ions when dissolved in water; strong acids and bases and soluble salts are strong electrolytes. Weak electrolytes produce few ions when dissolved in water; weak acids and bases are weak electrolytes. Nonelectrolytes produce no ions when dissolved in water. Molecular compounds other than acids and bases are nonelectrolytes.
- a) **Strong electrolyte** When hydrogen chloride is bubbled through water, it dissolves and dissociates completely into  $\text{H}^+$  (or  $\text{H}_3\text{O}^+$ ) ions and  $\text{Cl}^-$  ions.
- b) **Strong electrolyte** Potassium nitrate is a soluble salt.
- c) **Nonelectrolyte** Glucose solid dissolves in water to form individual  $\text{C}_6\text{H}_{12}\text{O}_6$  molecules, but these units are not ionic and therefore do not conduct electricity.
- d) **Weak electrolyte** Ammonia gas dissolves in water, but is a weak base that forms few  $\text{NH}_4^+$  and  $\text{OH}^-$  ions.

- 13.65 a)  $\text{NaMnO}_4$  **strong electrolyte**  
 b)  $\text{CH}_3\text{COOH}$  **weak electrolyte**  
 c)  $\text{CH}_3\text{OH}$  **nonelectrolyte**  
 d)  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  **strong electrolyte**

- 13.66 To count solute particles in a solution of an ionic compound, count the number of ions per mole and multiply by the number of moles in solution. For a covalent compound, the number of particles equals the number of molecules.

$$\text{a) } \left( \frac{0.3 \text{ mol KBr}}{\text{L}} \right) \left( \frac{2 \text{ mol particles}}{1 \text{ mol KBr}} \right) (1 \text{ L}) = \mathbf{0.6 \text{ mol of particles}}$$

Each KBr forms 1  $\text{K}^+$  ion and 1  $\text{Br}^-$  ion, 2 particles for each KBr.

$$\text{b) } \left( \frac{0.065 \text{ mol HNO}_3}{\text{L}} \right) \left( \frac{2 \text{ mol particles}}{1 \text{ mol HNO}_3} \right) (1 \text{ L}) = \mathbf{0.13 \text{ mol of particles}}$$

$\text{HNO}_3$  is a strong acid that forms  $\text{H}^+$  ( $\text{H}_3\text{O}^+$ ) ions and  $\text{NO}_3^-$  ions in aqueous solution.

$$\text{c) } \left( \frac{10^{-4} \text{ mol KHSO}_4}{\text{L}} \right) \left( \frac{2 \text{ mol particles}}{1 \text{ mol KHSO}_4} \right) (1 \text{ L}) = \mathbf{2 \times 10^{-4} \text{ mol of particles}}$$

Each  $\text{KHSO}_4$  forms 1  $\text{K}^+$  ion and 1  $\text{HSO}_4^-$  ion in aqueous solution, 2 particles for each  $\text{KHSO}_4$ .

$$\text{d) } \left( \frac{0.06 \text{ mol C}_2\text{H}_5\text{OH}}{\text{L}} \right) \left( \frac{1 \text{ mol particles}}{1 \text{ mol C}_2\text{H}_5\text{OH}} \right) (1 \text{ L}) = \mathbf{0.06 \text{ mol of particles}}$$

Ethanol is not an ionic compound so each molecule dissolves as one particle. The number of moles of particles is the same as the number of moles of molecules, **0.06 mol** in 1 L.

- 13.67 a)  $(0.01 \text{ mol CuSO}_4/\text{L}) (2 \text{ mol particles/mol CuSO}_4) (10^{-3} \text{ L/1 mL}) (1 \text{ mL}) = \mathbf{2 \times 10^{-5} \text{ mol of particles}}$   
 b)  $(0.005 \text{ mol Ba}(\text{OH})_2/\text{L}) (3 \text{ mol particles/mol Ba}(\text{OH})_2) (10^{-3} \text{ L/1 mL}) (1 \text{ mL})$   
 $= 1.5 \times 10^{-5} = \mathbf{2 \times 10^{-5} \text{ mol of particles}}$   
 c)  $(0.06 \text{ mol C}_5\text{H}_5\text{N/L}) (1 \text{ mol particles/mol C}_5\text{H}_5\text{N}) (10^{-3} \text{ L/1 mL}) (1 \text{ mL}) = \mathbf{6 \times 10^{-5} \text{ mol of particles}}$   
 d)  $(0.05 \text{ mol } (\text{NH}_4)_2\text{CO}_3/\text{L}) (3 \text{ mol particles/mol } (\text{NH}_4)_2\text{CO}_3) (10^{-3} \text{ L/1 mL}) (1 \text{ mL})$   
 $= 1.5 \times 10^{-4} = \mathbf{2 \times 10^{-4} \text{ mol of particles}}$

- 13.68 The magnitude of freezing point depression is directly proportional to molality.

$$\text{a) Molality of CH}_3\text{OH} = \frac{(11.0 \text{ g CH}_3\text{OH})}{(100. \text{ g H}_2\text{O})} \left( \frac{1 \text{ mol CH}_3\text{OH}}{32.04 \text{ g CH}_3\text{OH}} \right) \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) = 3.4332085 = \mathbf{3.43 \text{ m CH}_3\text{OH}}$$

$$\text{Molality of CH}_3\text{CH}_2\text{OH} = \frac{(22.0 \text{ g CH}_3\text{CH}_2\text{OH})}{(200. \text{ g H}_2\text{O})} \left( \frac{1 \text{ mol CH}_3\text{CH}_2\text{OH}}{46.07 \text{ g CH}_3\text{CH}_2\text{OH}} \right) \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right)$$

$$= 2.387671 = \mathbf{2.39 \text{ m CH}_3\text{CH}_2\text{OH}}$$

The molality of methanol,  $\text{CH}_3\text{OH}$ , in water is 3.43 m whereas the molality of ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ , in water is 2.39 m. Thus,  **$\text{CH}_3\text{OH}/\text{H}_2\text{O}$  solution** has the lower freezing point.

$$\text{b) Molality of H}_2\text{O} = \frac{(20.0 \text{ g H}_2\text{O})}{(1.00 \text{ kg CH}_3\text{OH})} \left( \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \right) = 1.10988 = 1.11 \text{ m H}_2\text{O}$$

$$\text{Molality of CH}_3\text{CH}_2\text{OH} = \frac{(20.0 \text{ g CH}_3\text{CH}_2\text{OH})}{(1.00 \text{ kg CH}_3\text{OH})} \left( \frac{1 \text{ mol CH}_3\text{CH}_2\text{OH}}{46.07 \text{ g CH}_3\text{CH}_2\text{OH}} \right) = 0.434122 = 0.434 \text{ m CH}_3\text{CH}_2\text{OH}$$

The molality of H<sub>2</sub>O in CH<sub>3</sub>OH is 1.11 *m*, whereas CH<sub>3</sub>CH<sub>2</sub>OH in CH<sub>3</sub>OH is 0.434 *m*. Therefore, **H<sub>2</sub>O/CH<sub>3</sub>OH solution** has the lower freezing point.

13.69 The magnitude of boiling point elevation is directly proportional to molality.

$$\text{a) Molality of C}_3\text{H}_8\text{O}_3 = \frac{(38.0 \text{ g C}_3\text{H}_8\text{O}_3)}{(250. \text{ g Ethanol})} \left( \frac{1 \text{ mol C}_3\text{H}_8\text{O}_3}{92.09 \text{ g C}_3\text{H}_8\text{O}_3} \right) \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) = 1.650559 = 1.65 \text{ m C}_3\text{H}_8\text{O}_3$$

$$\text{Molality of C}_2\text{H}_6\text{O}_2 = \frac{(38.0 \text{ g C}_2\text{H}_6\text{O}_2)}{(250. \text{ g Ethanol})} \left( \frac{1 \text{ mol C}_2\text{H}_6\text{O}_2}{62.07 \text{ g C}_2\text{H}_6\text{O}_2} \right) \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) = 2.44885 = 2.45 \text{ m C}_2\text{H}_6\text{O}_2$$

The molality of C<sub>2</sub>H<sub>6</sub>O<sub>2</sub> in ethanol is 2.45 *m* whereas the molality of C<sub>3</sub>H<sub>8</sub>O<sub>3</sub> in ethanol is 1.65 *m*. Thus, **C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>/ethanol solution** has the higher boiling point.

$$\text{b) Molality of C}_2\text{H}_6\text{O}_2 = \frac{(15 \text{ g C}_2\text{H}_6\text{O}_2)}{(0.50 \text{ kg H}_2\text{O})} \left( \frac{1 \text{ mol C}_2\text{H}_6\text{O}_2}{62.07 \text{ g C}_2\text{H}_6\text{O}_2} \right) = 0.4833253 = 0.48 \text{ m C}_2\text{H}_6\text{O}_2$$

$$\text{Molality of NaCl} = \frac{(15 \text{ g NaCl})}{(0.50 \text{ kg H}_2\text{O})} \left( \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} \right) = 0.513347 = 0.51 \text{ m NaCl}$$

Since the NaCl is a strong electrolyte, the molality of particles would be:

$$(2 \text{ particles/NaCl}) (0.513347 \text{ mol NaCl/kg}) = 1.026694 = 1.0 \text{ m particles}$$

The molality of C<sub>2</sub>H<sub>6</sub>O<sub>2</sub> in H<sub>2</sub>O is 0.48 *m*, whereas NaCl in H<sub>2</sub>O is 1.0 *m*. Therefore, **NaCl/H<sub>2</sub>O solution** has the higher boiling point.

13.70 To rank the solutions in order of increasing osmotic pressure, boiling point, freezing point, and vapor pressure, convert the molality of each solute to molality of particles in the solution. The higher the molality of particles the higher the osmotic pressure and boiling point, and the lower the freezing point and vapor pressure at a given temperature.

$$\text{(I) } (0.100 \text{ m NaNO}_3) \left( \frac{2 \text{ mol particles}}{1 \text{ mol NaNO}_3} \right) = 0.200 \text{ m ions}$$

NaNO<sub>3</sub> consists of Na<sup>+</sup> ions and NO<sub>3</sub><sup>-</sup> ions, 2 particles for each NaNO<sub>3</sub>.

$$\text{(II) } (0.100 \text{ m glucose}) \left( \frac{1 \text{ mol particles}}{1 \text{ mol glucose}} \right) = 0.100 \text{ m molecules}$$

Ethanol is not an ionic compound so each molecule dissolves as one particle. The number of moles of particles is the same as the number of moles of molecules.

$$\text{(III) } (0.100 \text{ m CaCl}_2) \left( \frac{3 \text{ mol particles}}{1 \text{ mol CaCl}_2} \right) = 0.300 \text{ m ions}$$

CaCl<sub>2</sub> consists of Ca<sup>+2</sup> ions and Cl<sup>-</sup> ions, 3 particles for each CaCl<sub>2</sub>.

- |                            |   |
|----------------------------|---|
| a) Osmotic pressure:       | $\Pi_{\text{II}} < \Pi_{\text{I}} < \Pi_{\text{III}}$                   |
| b) Boiling point:          | $\text{bp}_{\text{II}} < \text{bp}_{\text{I}} < \text{bp}_{\text{III}}$ |
| c) Freezing point:         | $\text{fp}_{\text{III}} < \text{fp}_{\text{I}} < \text{fp}_{\text{II}}$ |
| d) Vapor pressure at 50°C: | $\text{vp}_{\text{III}} < \text{vp}_{\text{I}} < \text{vp}_{\text{II}}$ |

- 13.71 I 0.04 *m* (H<sub>2</sub>N)<sub>2</sub>CO x 1 mol particles/1 mol (H<sub>2</sub>N)<sub>2</sub>CO = 0.04 *m* molecules  
 II 0.01 *m* AgNO<sub>3</sub> x 2 mol particles/1 mol AgNO<sub>3</sub> = 0.02 *m* ions  
 III 0.03 *m* CuSO<sub>4</sub> x 2 mol particles/1 mol CuSO<sub>4</sub> = 0.06 *m* ions  
 a) Osmotic pressure:  $\Pi_{\text{II}} < \Pi_{\text{I}} < \Pi_{\text{III}}$   
 b) Boiling point:  $\text{bp}_{\text{II}} < \text{bp}_{\text{I}} < \text{bp}_{\text{III}}$   
 c) Freezing point:  $\text{fp}_{\text{III}} < \text{fp}_{\text{I}} < \text{fp}_{\text{II}}$   
 d) Vapor pressure at 298 K:  $\text{vp}_{\text{III}} < \text{vp}_{\text{I}} < \text{vp}_{\text{II}}$

- 13.72 The mol fraction of solvent affects the vapor pressure according to the equation:  $P_{\text{solvent}} = X_{\text{solvent}} P^{\circ}_{\text{solvent}}$

$$\text{Moles C}_3\text{H}_8\text{O}_3 = (34.0 \text{ g C}_3\text{H}_8\text{O}_3) \left( \frac{1 \text{ mol C}_3\text{H}_8\text{O}_3}{92.09 \text{ g C}_3\text{H}_8\text{O}_3} \right) = 0.369204 \text{ mol C}_3\text{H}_8\text{O}_3 \text{ (unrounded)}$$

$$\text{Moles H}_2\text{O} = (500.0 \text{ g H}_2\text{O}) \left( \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \right) = 27.7469 \text{ mol H}_2\text{O} \text{ (unrounded)}$$

$$X_{\text{solvent}} = \frac{\text{mol H}_2\text{O}}{\text{mol H}_2\text{O} + \text{mol glycerol}} = \frac{27.7469 \text{ mol H}_2\text{O}}{27.7469 \text{ mol H}_2\text{O} + 0.369204 \text{ mol glycerol}} = 0.9868686$$

$$P_{\text{solvent}} = X_{\text{solvent}} P^{\circ}_{\text{solvent}} = (0.9868686) (23.76 \text{ torr}) = 23.447998 = \mathbf{23.4 \text{ torr}}$$

- 13.73 The mole fraction of solvent affects the vapor pressure according to the equation:  $P_{\text{solvent}} = X_{\text{solvent}} P^{\circ}_{\text{solvent}}$

$$X_{\text{solvent}} = (5.4 \text{ mol toluene}) / [(0.39) + (5.4)] \text{ mol} = 0.93264 \text{ (unrounded)}$$

$$P_{\text{solvent}} = X_{\text{solvent}} P^{\circ}_{\text{solvent}} = (0.93264) (41 \text{ torr}) = 38.2382 = \mathbf{38 \text{ torr}}$$

- 13.74 The change in freezing point is calculated from  $\Delta T_f = iK_f m$ , where  $K_f$  is 1.86°C/*m* for aqueous solutions, *i* is the van't Hoff factor, and *m* is the molality of particles in solution. Since urea is a covalent compound and does not ionize in water, *i* = 1. Once  $\Delta T_f$  is calculated, the freezing point is determined by subtracting it from the freezing point of pure water (0.00°C).

$$\Delta T_f = iK_f m = (1) (1.86^\circ\text{C}/m) (0.251 \text{ m}) = 0.46686^\circ\text{C} \text{ (unrounded)}$$

$$\text{The freezing point is } 0.00^\circ\text{C} - 0.46686^\circ\text{C} = -0.46686 = \mathbf{-0.467^\circ\text{C}}.$$

- 13.75  $\Delta T_b = iK_b m = (1) (0.512^\circ\text{C}/m) (0.200 \text{ m}) = 0.1024^\circ\text{C}$  (unrounded)

$$\text{The boiling point is } 100.00^\circ\text{C} + 0.1024^\circ\text{C} = 100.1024 = \mathbf{100.10^\circ\text{C}}$$

- 13.76 The boiling point of a solution is increased relative to the pure solvent by the relationship  $\Delta T_b = iK_b m$ . Vanillin is a nonelectrolyte so *i* = 1. The molality must be calculated, and  $K_b$  is given (1.22°C/*m*).

$$\text{Molality of Vanillin} = \frac{\text{moles of Vanillin}}{\text{kg of solvent (ethanol)}} = \frac{(6.4 \text{ g Vanillin}) \left( \frac{1 \text{ mol Vanillin}}{152.14 \text{ g Vanillin}} \right) \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right)}{(50.0 \text{ g Ethanol})}$$

$$= 0.841330354 \text{ m Vanillin (unrounded)}$$

$$\Delta T_b = iK_b m = (1) (1.22^\circ\text{C}/m) (0.841330354 \text{ m}) = 1.02642^\circ\text{C} \text{ (unrounded)}$$

$$\text{The boiling point is } 78.5^\circ\text{C} + 1.02642^\circ\text{C} = 79.52642 = \mathbf{79.5^\circ\text{C}}.$$

- 13.77 Moles C<sub>10</sub>H<sub>8</sub> = (5.00 g C<sub>10</sub>H<sub>8</sub>) (1 mol C<sub>10</sub>H<sub>8</sub>/128.16 g C<sub>10</sub>H<sub>8</sub>) = 0.0390137 mol C<sub>10</sub>H<sub>8</sub> (unrounded)

C<sub>10</sub>H<sub>8</sub> is a nonelectrolyte so *i* = 1

$$\text{Mass} = (444 \text{ g benzene}) (1 \text{ kg}/10^3 \text{ g}) = 0.444 \text{ kg benzene}$$

$$\text{Molality} = (0.0390137 \text{ mol C}_{10}\text{H}_8) / (0.444 \text{ kg}) = 0.08786869 \text{ m (unrounded)}$$

$$\Delta T_f = i K_f m = (1) (4.90^\circ\text{C}/m) (0.08786869 \text{ m}) = 0.43056^\circ\text{C} \text{ (unrounded)}$$

$$\text{Freezing point} = (5.5 - 0.43056)^\circ\text{C} = 5.06944 = \mathbf{5.1^\circ\text{C}}$$

- 13.78 The molality of the solution can be determined from the relationship  $\Delta T_f = iK_f m$  with the value  $1.86^\circ\text{C}/m$  inserted for  $K_f$  and  $i = 1$  for the nonelectrolyte ethylene glycol (ethylene glycol is a covalent compound that will form one particle per molecule when dissolved). Convert the freezing point of the solution to  $^\circ\text{C}$  and find  $\Delta T_f$ :

$$^\circ\text{C} = (5/9) (^\circ\text{F} - 32.0) = (5/9) ((-12.0)^\circ\text{F} - 32.0) = -24.44444^\circ\text{C} \text{ (unrounded)}$$

$$\Delta T_f = (0.00 - (-24.44444))^\circ\text{C} = 24.44444^\circ\text{C}$$

$$m = \frac{\Delta T_f}{K_f} = \frac{24.44444^\circ\text{C}}{1.86^\circ\text{C}/m} = 13.14217 \text{ m (unrounded)}$$

Ethylene glycol will be abbreviated as EG.

Multiply the molality by the given mass of solvent to find the mass of ethylene glycol that must be in solution.

$$\begin{aligned} \text{Mass ethylene glycol} &= \left( \frac{13.14217 \text{ mol EG}}{1 \text{ kg H}_2\text{O}} \right) (14.5 \text{ kg H}_2\text{O}) \left( \frac{62.07 \text{ g EG}}{1 \text{ mol EG}} \right) \\ &= 1.18282 \times 10^4 = \mathbf{1.18 \times 10^4 \text{ g ethylene glycol}} \end{aligned}$$

To prevent the solution from freezing, dissolve a minimum of  $1.13 \times 10^4$  g ethylene glycol in 14.5 kg water.

- 13.79 The molality of the solution can be determined from the relationship  $\Delta T_f = iK_f m$  with the value  $1.86^\circ\text{C}/m$  inserted for  $K_f$ ,  $i = 1$  for the nonelectrolyte glycerol, and the given  $\Delta T_f$  of  $-15^\circ\text{C}$ .

$$m = \Delta T_f / K_f = (15^\circ\text{C}) / (1.86^\circ\text{C}/m) = 8.06452 \text{ m}$$

Glycerol will be abbreviated as GLY.

$$\begin{aligned} \text{Mass glycerol} &= \left( \frac{8.06452 \text{ mol GLY}}{1 \text{ kg H}_2\text{O}} \right) (11.0 \text{ mg H}_2\text{O}) \left( \frac{10^{-3} \text{ g}}{1 \text{ mg}} \right) \left( \frac{1 \text{ kg}}{10^3 \text{ g}} \right) \left( \frac{92.09 \text{ g GLY}}{1 \text{ mol GLY}} \right) \\ &= 0.0081693 = \mathbf{0.0082 \text{ g glycerol}} \end{aligned}$$

To prevent the solution from freezing, dissolve a minimum of 0.0082 g glycerol in 11.0 mg water.

- 13.80 Convert the mass percent to molality and use  $\Delta T = iK_b m$  to find the van't Hoff factor.

a) Assume exactly 100 grams of solution.

$$\text{Mass NaCl} = (100 \text{ g solution}) \left( \frac{1.00\% \text{ NaCl}}{100\% \text{ solution}} \right) = 1.00 \text{ g NaCl}$$

$$\text{Moles NaCl} = (1.00 \text{ g NaCl}) \left( \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} \right) = 0.0171116 \text{ mol NaCl}$$

$$\text{Mass H}_2\text{O} = 100.00 \text{ g solution} - 1.00 \text{ g NaCl} = 99.00 \text{ g H}_2\text{O}$$

$$\text{Molality NaCl} = \frac{\text{mole NaCl}}{\text{kg H}_2\text{O}} = \frac{0.0171116 \text{ mol NaCl}}{99.00 \text{ g H}_2\text{O}} \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) = 0.172844 = \mathbf{0.173 \text{ m NaCl}}$$

$$\text{Calculate } \Delta T = (0.000 - (-0.593))^\circ\text{C} = 0.593^\circ\text{C}$$

$$\Delta T_f = iK_f m$$

$$i = \frac{\Delta T_f}{K_f m} = \frac{0.593^\circ\text{C}}{(1.86^\circ\text{C}/m)(0.172844 \text{ m})} = 1.844537 = \mathbf{1.84}$$

The value of  $i$  should be close to 2 because NaCl dissociates into 2 particles when dissolving in water.

b) For acetic acid,  $\text{CH}_3\text{COOH}$ :

Assume exactly 100 grams of solution.

$$\text{Mass CH}_3\text{COOH} = (100 \text{ g solution}) \left( \frac{0.500\% \text{ CH}_3\text{COOH}}{100\% \text{ solution}} \right) = 0.500 \text{ g CH}_3\text{COOH}$$

$$\text{Moles CH}_3\text{COOH} = (0.500 \text{ g CH}_3\text{COOH}) \left( \frac{1 \text{ mol CH}_3\text{COOH}}{60.05 \text{ g CH}_3\text{COOH}} \right) = 0.0083264 \text{ mol CH}_3\text{COOH}$$

$$\text{Mass H}_2\text{O} = 100.00 \text{ g solution} - 0.500 \text{ g CH}_3\text{COOH} = 99.500 \text{ g H}_2\text{O}$$

$$\text{Molality CH}_3\text{COOH} = \frac{\text{mole CH}_3\text{COOH}}{\text{kg H}_2\text{O}} = \frac{0.0083264 \text{ mol CH}_3\text{COOH} \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right)}{99.500 \text{ g H}_2\text{O}}$$

$$= 0.083682 = \mathbf{0.0837 \text{ m CH}_3\text{COOH}}$$

$$\text{Calculate } \Delta T = (0.000 - (-0.159))^\circ\text{C} = 0.159^\circ\text{C}$$

$$\Delta T_f = iK_f m$$

$$i = \frac{\Delta T_f}{K_f m} = \frac{0.159^\circ\text{C}}{(1.86^\circ\text{C}/m)(0.083682 \text{ m})} = 1.02153 = \mathbf{1.02}$$

Acetic acid is a weak acid and dissociates to a small extent in solution, hence a van't Hoff factor that is close to 1.

- 13.81 Convert the mass % to molality and use  $\Delta T = iK_f m$  to find the van't Hoff factor.

a) Assume exactly 100 grams of solution. Thus, the solution contains 0.500 grams of KCl in 99.500 grams of water.

$$\text{Molality KCl} = \left( \frac{0.500 \text{ g KCl}}{99.500 \text{ g H}_2\text{O}} \right) \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left( \frac{1 \text{ mol KCl}}{74.55 \text{ g KCl}} \right) = 0.067406 \text{ m KCl (unrounded)}$$

$$\text{Calculate } \Delta T = (0.000 - (-0.234))^\circ\text{C} = 0.234^\circ\text{C}$$

$$\Delta T_f = i K_f m$$

$$i = \Delta T_f / K_f m = (0.234^\circ\text{C}) / [(1.86^\circ\text{C}/m) (0.067406 \text{ m})] = 1.866398 = \mathbf{1.87}$$

The value of  $i$  should be close to 2 because KCl dissociates into 2 particles when dissolving in water.

b) For sulfuric acid,  $\text{H}_2\text{SO}_4$ :

Assume exactly 100 grams of solution. Thus, the solution contains 1.00 grams of  $\text{H}_2\text{SO}_4$  in 99.00 grams of water.

$$\text{Molality H}_2\text{SO}_4 = \left( \frac{1.00 \text{ g H}_2\text{SO}_4}{99.00 \text{ g H}_2\text{O}} \right) \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left( \frac{1 \text{ mol H}_2\text{SO}_4}{98.09 \text{ g H}_2\text{SO}_4} \right) = 0.10297696 \text{ m H}_2\text{SO}_4 \text{ (unrounded)}$$

$$\text{Calculate } \Delta T = (0.000 - (-0.423))^\circ\text{C} = 0.423^\circ\text{C}$$

$$\Delta T_f = i K_f m$$

$$i = \Delta T_f / K_f m = (0.423^\circ\text{C}) / [(1.86^\circ\text{C}/m) (0.10297696 \text{ m})] = 2.2084 = \mathbf{2.21}$$

Sulfuric acid is a strong acid and dissociates to give a hydrogen ion and a hydrogen sulfate ion. The hydrogen sulfate ion may further dissociate to another hydrogen ion and a sulfate ion. If ionization in both steps were complete, the value of the van't Hoff factor would be 3.

- 13.82 Use the osmotic pressure equation ( $\Pi = i MRT$ ) to find the molarity of the solution (assuming  $i = 1$ ).

$$M = \Pi / i RT = \frac{0.272 \text{ atm}}{(1) \left( 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) ((273 + 25) \text{ K})} = 0.01111756 \text{ M (unrounded)}$$

$$\text{Moles} = (0.01111756 \text{ mol/L}) (100.0 \text{ mL}) (10^{-3} \text{ L/1 mL}) = 0.001111756 \text{ mol (unrounded)}$$

$$\text{Molar mass} = (6.053 \text{ g}) / (0.001111756 \text{ mol}) = 5.4445 \times 10^3 = \mathbf{5.44 \times 10^3 \text{ g/mol}}$$

- 13.83 The pressure of each compound is proportional to its mole fraction according to Raoult's law:  $P_A = X_A P^\circ_A$

$$X_{\text{CH}_2\text{Cl}_2} = \frac{\text{moles CH}_2\text{Cl}_2}{\text{moles CH}_2\text{Cl}_2 + \text{mol CCl}_4} = \frac{1.60 \text{ mol}}{1.60 + 1.10 \text{ mol}} = 0.592593$$

$$X_{\text{CCl}_4} = \frac{\text{moles CCl}_4}{\text{moles CH}_2\text{Cl}_2 + \text{mol CCl}_4} = \frac{1.10 \text{ mol}}{1.60 + 1.10 \text{ mol}} = 0.407407$$

$$P_A = X_A P^\circ_A$$

$$= (0.592593) (352 \text{ torr}) = 208.593 = \mathbf{209 \text{ torr CH}_2\text{Cl}_2}$$

$$= (0.407407) (118 \text{ torr}) = 48.0740 = \mathbf{48.1 \text{ torr CCl}_4}$$

- 13.84 C. The principal factor in the solubility of ionic compounds in water is ion-dipole forces. Virtually all of the ionic compound's ions would become separated and surrounded by water molecules (the number depending on the sizes of the ions) interacting with the ions via H-bonding or other forces.

- 13.85 To find the volume of seawater needed, substitute the given information into the equation that describes the ppb concentration, account for extraction efficiency, and convert mass to volume using the density of seawater.

$$1.1 \times 10^{-2} \text{ ppb} = \frac{\text{mass Gold}}{\text{mass seawater}} \times 10^9$$

$$1.1 \times 10^{-2} \text{ ppb} = \frac{31.1 \text{ g Au}}{\text{mass seawater}} \times 10^9$$

$$\text{Mass seawater} = \left[ \frac{31.1 \text{ g}}{1.1 \times 10^{-2}} \times 10^9 \right] = 2.827273 \times 10^{12} \text{ g (with 100\% efficiency)}$$

$$\text{Mass of seawater} = \left( 2.827273 \times 10^{12} \text{ g} \right) \left( \frac{100\%}{81.5\%} \right) = 3.46905 \times 10^{12} \text{ g seawater (unrounded) (81.5\% efficiency)}$$

$$\text{Volume seawater} = \left( 3.46905 \times 10^{12} \text{ g} \right) \left( \frac{1 \text{ mL}}{1.025 \text{ g}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) = 3.384439 \times 10^9 = \mathbf{3.4 \times 10^9 \text{ L}}$$

- 13.86 Xe is a much larger atom than He, so it is much more polarizable. This would increase the dipole-induced dipole forces when Xe is placed in water, increasing the solubility relative to He.

- 13.87 a) Total molarity of ions:

$$\text{Solution A: } M = \frac{(8 \text{ spheres}) \left( \frac{0.010 \text{ mol ions}}{1 \text{ sphere}} \right)}{25 \text{ mL}} \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = \mathbf{3.2 \text{ M}}$$

$$\text{Solution B: } M = \frac{(10 \text{ spheres}) \left( \frac{0.010 \text{ mol ions}}{1 \text{ sphere}} \right)}{50 \text{ mL}} \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = \mathbf{2.0 \text{ M}}$$

$$\text{Solution C: } M = \frac{(12 \text{ spheres}) \left( \frac{0.010 \text{ mol ions}}{1 \text{ sphere}} \right)}{100 \text{ mL}} \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = \mathbf{1.2 \text{ M}}$$

- b) Molarity of compound:

$$\text{Solution A: } M = \frac{(8 \text{ spheres}) \left( \frac{0.010 \text{ mol ions}}{1 \text{ sphere}} \right) \left( \frac{1 \text{ mole compound}}{2 \text{ moles of ions}} \right)}{25 \text{ mL}} \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = \mathbf{1.6 \text{ M}}$$

$$\text{Solution B: } M = \frac{(10 \text{ spheres}) \left( \frac{0.010 \text{ mol ions}}{1 \text{ sphere}} \right) \left( \frac{1 \text{ mole compound}}{2 \text{ moles of ions}} \right)}{50 \text{ mL}} \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = \mathbf{1.0 \text{ M}}$$

$$\text{Solution C: } M = \frac{(12 \text{ spheres}) \left( \frac{0.010 \text{ mol ions}}{1 \text{ sphere}} \right) \left( \frac{1 \text{ mole compound}}{3 \text{ moles of ions}} \right)}{100 \text{ mL}} \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = \mathbf{0.40 \text{ M}}$$

**Solution A has the highest molarity.**

- c) Molality of compound:

$$\text{Solution A: } m = \frac{(8 \text{ spheres}) \left( \frac{0.010 \text{ mol ions}}{1 \text{ sphere}} \right) \left( \frac{1 \text{ mole compound}}{2 \text{ moles of ions}} \right)}{25 \text{ mL}} \left( \frac{1 \text{ mL}}{1.0 \text{ g}} \right) \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) = \mathbf{1.6 \text{ m}}$$

$$\text{Solution B: } m = \frac{(10 \text{ spheres}) \left( \frac{0.010 \text{ mol ions}}{1 \text{ sphere}} \right) \left( \frac{1 \text{ mole compound}}{2 \text{ moles of ions}} \right)}{50 \text{ mL}} \left( \frac{1 \text{ mL}}{1.0 \text{ g}} \right) \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) = \mathbf{1.0 \text{ m}}$$



$$\text{Solution C: } m = \frac{(12 \text{ spheres}) \left( \frac{0.010 \text{ mol ions}}{1 \text{ sphere}} \right) \left( \frac{1 \text{ mole compound}}{3 \text{ moles of ions}} \right)}{100 \text{ mL}} \left( \frac{1 \text{ mL}}{1.0 \text{ g}} \right) \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) = \mathbf{0.40 \text{ } m}$$

**Solution C** has the lowest molality.

d) Osmotic pressure: assume a temperature of 298 K

$$\text{Solution A: } \Pi = i MRT = (2) (1.6 \text{ mol/L}) (0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K}) (298 \text{ K}) = 78.29056 = \mathbf{78 \text{ atm}}$$

$$\text{Solution B: } \Pi = i MRT = (2) (1.0 \text{ mol/L}) (0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K}) (298 \text{ K}) = 48.9316 = \mathbf{49 \text{ atm}}$$

$$\text{Solution C: } \Pi = i MRT = (3) (0.40 \text{ mol/L}) (0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K}) (298 \text{ K}) = 29.35896 = \mathbf{29 \text{ atm}}$$

**Solution A** has the highest osmotic pressure.

- 13.88 Convert mass of O<sub>2</sub> dissolved to moles of O<sub>2</sub>. Use the density to convert the 1 kg mass of solution to volume in L.

0.0°C

$$\left( \frac{14.5 \text{ mg O}_2}{1 \text{ kg H}_2\text{O}} \right) \left( \frac{10^{-3} \text{ g}}{1 \text{ mg}} \right) \left( \frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2} \right) \left( \frac{1 \text{ kg}}{10^3 \text{ g}} \right) \left( \frac{0.99987 \text{ g}}{\text{mL}} \right) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \\ = 4.53066 \times 10^{-4} = \mathbf{4.53 \times 10^{-4} \text{ } M \text{ O}_2}$$

20.0°C

$$\left( \frac{9.07 \text{ mg O}_2}{1 \text{ kg H}_2\text{O}} \right) \left( \frac{10^{-3} \text{ g}}{1 \text{ mg}} \right) \left( \frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2} \right) \left( \frac{1 \text{ kg}}{10^3 \text{ g}} \right) \left( \frac{0.99823 \text{ g}}{\text{mL}} \right) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \\ = 2.829358 \times 10^{-4} = \mathbf{2.83 \times 10^{-4} \text{ } M \text{ O}_2}$$

40.0°C

$$\left( \frac{6.44 \text{ mg O}_2}{1 \text{ kg H}_2\text{O}} \right) \left( \frac{10^{-3} \text{ g}}{1 \text{ mg}} \right) \left( \frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2} \right) \left( \frac{1 \text{ kg}}{10^3 \text{ g}} \right) \left( \frac{0.99224 \text{ g}}{\text{mL}} \right) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \\ = 1.996883 \times 10^{-4} = \mathbf{2.00 \times 10^{-4} \text{ } M \text{ O}_2}$$

- 13.89 Price NaCl (\$/ion) = (\$0.22/kg NaCl) (1 kg/10<sup>3</sup> g) (58.44 g NaCl/1 mol NaCl) (1 mol NaCl/2 ions)  
= \$ 6.4284 x 10<sup>-3</sup>/ion (unrounded)  
Price CaCl<sub>2</sub> (\$/kg) = (\$ 6.4284 x 10<sup>-3</sup>/ion) (3 mol ions/1 mol CaCl<sub>2</sub>) (1 mol CaCl<sub>2</sub>/110.98 g CaCl<sub>2</sub>) (10<sup>3</sup> g/kg)  
= 0.17377 = **\$ 0.17/kg CaCl<sub>2</sub>**

- 13.90 **No**, both are the same because masses are additive.

- 13.91 a) First, find the molality from the freezing point depression and then use the molality, given mass of solute and volume of water to calculate the molar mass of the solute compound. Assume the solute is a nonelectrolyte (*i* = 1).  
 $\Delta T_f = iK_f m = (0.000 - (-0.201)) = 0.201 \text{ } ^\circ\text{C}$

$$m = \frac{\Delta T_f}{K_f i} = \frac{0.201 \text{ } ^\circ\text{C}}{(1.86 \text{ } ^\circ\text{C}/m)(1)} = 0.1080645 \text{ } m \text{ (unrounded)}$$

$$m = \frac{\text{moles solute}}{\text{kg solvent}} \quad (25.0 \text{ mL}) \left( \frac{1.00 \text{ g}}{1 \text{ mL}} \right) \left( \frac{1 \text{ kg}}{10^3 \text{ g}} \right) = 0.0250 \text{ kg water}$$

$$\text{moles solute} = (m)(\text{kg solvent}) = (0.1080656 \text{ } m)(0.0250 \text{ kg}) = 0.0027016 \text{ mol}$$

$$\text{molar mass} = \frac{0.243 \text{ g}}{0.0027016 \text{ mol}} = 89.946698 = \mathbf{89.9 \text{ g/mol}}$$

b) Assume that 100.00 g of the compound gives 53.31 g carbon, 11.18 g hydrogen, and  $100.00 - 53.31 - 11.18 = 35.51$  g oxygen.

$$\text{Moles C} = (53.31 \text{ g C}) \left( \frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 4.43880 \text{ mol C (unrounded)}$$

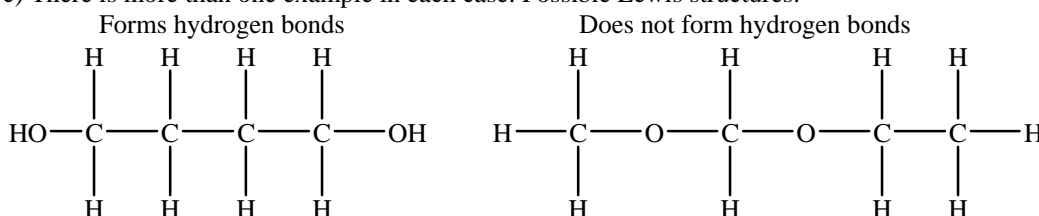
$$\text{Moles H} = (11.18 \text{ g H}) \left( \frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) = 11.09127 \text{ mol H (unrounded)}$$

$$\text{Moles O} = (35.51 \text{ g O}) \left( \frac{1 \text{ mol O}}{16.00 \text{ g O}} \right) = 2.219375 \text{ mol O (unrounded)}$$

Dividing the values by the lowest amount of moles (2.219375) will give 2 mol C, 5 mol H, and 1 mol O for an **empirical formula  $\text{C}_2\text{H}_5\text{O}$**  with molar mass 45.06 g/mol.

Since the molar mass of the compound, 89.9 g/mol from part (a), is twice the molar mass of the empirical formula, the **molecular formula is  $2(\text{C}_2\text{H}_5\text{O})$  or  $\text{C}_4\text{H}_{10}\text{O}_2$** .

c) There is more than one example in each case. Possible Lewis structures:



13.92 Calculate the individual partial pressures from  $P = X P^\circ$ . Assign the “equal masses” as exactly 1 g. Liquid:

$$X(\text{pinene}) = \frac{\left( \frac{1 \text{ g pinene}}{136.23 \text{ g pinene/mol}} \right)}{\left( \frac{1 \text{ g pinene}}{136.23 \text{ g pinene/mol}} \right) + \left( \frac{1 \text{ g terpineol}}{154.24 \text{ g terpineol/mol}} \right)} = 0.53100 \text{ (unrounded)}$$

$$P(\text{pinene}) = (0.53100)(100.3 \text{ torr}) = 53.2593 \text{ torr (unrounded)}$$

$$X(\text{terpineol}) = \frac{\left( \frac{1 \text{ g terpineol}}{154.24 \text{ g terpineol/mol}} \right)}{\left( \frac{1 \text{ g pinene}}{136.23 \text{ g pinene/mol}} \right) + \left( \frac{1 \text{ g terpineol}}{154.24 \text{ g terpineol/mol}} \right)} = 0.4689985 \text{ (unrounded)}$$

$$P(\text{terpineol}) = (0.4689985)(9.8 \text{ torr}) = 4.5961855 \text{ torr (unrounded)}$$

Vapor:

$$X(\text{pinene}) = \frac{53.2593 \text{ torr}}{(53.2593 + 4.5961855) \text{ torr}} = 0.9205575 = \mathbf{0.921}$$

$$X(\text{terpineol}) = \frac{4.5961855 \text{ torr}}{(53.2593 + 4.5961855) \text{ torr}} = 0.0794425 = \mathbf{0.079}$$

13.93 a) Use the boiling point elevation of  $0.45^\circ\text{C}$  to calculate the molality of the solution. Then, with molality, the mass of solute, and volume of water calculate the molar mass.

$$\Delta T = iK_b m \quad i = 1 \text{ (nonelectrolyte)}$$

$$\Delta T = (100.45 - 100.00)^\circ\text{C} = 0.45^\circ\text{C}$$

$$m = \frac{\Delta T_b}{K_b i} = \frac{0.45^\circ\text{C}}{(0.512^\circ\text{C}/m)(1)} = 0.878906 \text{ m} = 0.878906 \text{ mol/kg (unrounded)}$$

$$m = \frac{\text{moles solute}}{\text{kg solvent}} \quad (25.0 \text{ mL}) \left( \frac{0.997 \text{ g}}{1 \text{ mL}} \right) \left( \frac{1 \text{ kg}}{10^3 \text{ g}} \right) = 0.0249250 \text{ kg water}$$

$$\text{moles solute} = (m)(\text{kg solvent}) = (0.878906 m)(0.0249250 \text{ kg}) = 0.0219067 \text{ mol}$$

$$\text{molar mass} = \frac{1.50 \text{ g}}{0.0219067 \text{ mol}} = 68.4722 = \mathbf{68 \text{ g/mol}}$$

b) The molality calculated would be the moles of ions per kg of solvent. If the compound consists of three ions the molality of the compound would be 1/3 of 0.878906 *m* and the calculated molar mass would be three times greater: 3 x 68.4722 = 205.417 =  $\mathbf{2.1 \times 10^2 \text{ g/mol}}$ .

c) The molar mass of CaN<sub>2</sub>O<sub>6</sub> is 164.10 g/mol. This molar mass is less than the 2.1 x 10<sup>2</sup> g/mol calculated when the compound is assumed to be a strong electrolyte and is greater than the 68 g/mol calculated when the compound is assumed to be a nonelectrolyte. Thus, the compound is an electrolyte, since it dissociates into ions in solution. However, the ions do not dissociate completely in solution.

d) Use the molar mass of CaN<sub>2</sub>O<sub>6</sub> to calculate the molality of the compound. Then calculate *i* in the boiling point elevation formula.

$$m = \left( \frac{1.50 \text{ g CaN}_2\text{O}_6}{25.0 \text{ mL}} \right) \left( \frac{\text{mL}}{0.997 \text{ g}} \right) \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left( \frac{1 \text{ mol}}{164.10 \text{ g CaN}_2\text{O}_6} \right) = 0.3667309 m \text{ (unrounded)}$$

$$\Delta T = iK_b m$$

$$i = \frac{\Delta T_b}{K_b m} = \frac{(0.45^\circ\text{C})}{(0.512^\circ/\text{m})(0.3667309 m)} = 2.396597 = \mathbf{2.4}$$

13.94 a) Solution A has a van't Hoff factor of 3, Solutions B and C have a van't Hoff factor of 2, and Solution D's van't Hoff factor is 1. Since Solution A has the largest van't Hoff factor, **Solution A** would have the highest boiling point.

b) **Solution A** also has the lowest freezing point since it has the largest van't Hoff factor.

c) **No**, the solution with the highest osmotic pressure cannot be determined. Osmotic pressure is determined by the molarity, not the molality, of the solution. Since we do not know the identity of the solutes and the density of the solutions, the 0.50 *m* value cannot be converted to molarity.

$$13.95 \quad \frac{\text{mol C}_2\text{H}_5\text{OH(g)}}{\text{mol CH}_3\text{OH(g)}} = \frac{\text{mol C}_2\text{H}_5\text{OH(l)}}{\text{mol CH}_3\text{OH(l)}} \left( \frac{60.5 \text{ torr}}{126.0 \text{ torr}} \right) = \frac{\text{mol C}_2\text{H}_5\text{OH(l)}}{\text{mol CH}_3\text{OH(l)}} (0.4801587) \text{ (unrounded)}$$

A 97:1 mass ratio gives 97 grams of C<sub>2</sub>H<sub>5</sub>OH for every 1 gram of CH<sub>3</sub>OH. (This limits the significant figures.)

$$\frac{97 \text{ g C}_2\text{H}_5\text{OH(g)} \left( \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.07 \text{ g C}_2\text{H}_5\text{OH}} \right)}{1 \text{ g CH}_3\text{OH(g)} \left( \frac{1 \text{ mol CH}_3\text{OH}}{32.04 \text{ g CH}_3\text{OH}} \right)} = \frac{2.10549 \text{ mol C}_2\text{H}_5\text{OH(g)}}{0.03121 \text{ mol CH}_3\text{OH(g)}}$$

$$\frac{\text{mol C}_2\text{H}_5\text{OH(l)}}{\text{mol CH}_3\text{OH(l)}} = \frac{(2.10549/0.03121)}{0.4801587} = 140.4994$$

$$\frac{(140.4994 \text{ mol C}_2\text{H}_5\text{OH}) \left( \frac{46.07 \text{ g C}_2\text{H}_5\text{OH}}{1 \text{ mol C}_2\text{H}_5\text{OH}} \right)}{(1 \text{ mol CH}_3\text{OH}) \left( \frac{32.04 \text{ g CH}_3\text{OH}}{1 \text{ mol CH}_3\text{OH}} \right)} = 202.0227 = \mathbf{2 \times 10^2}$$

13.96 Convert from ppb to pph (part per hundred = mass percent)

$$\left( \frac{100. \text{ ppb}}{10^9} \right) \left( \frac{100 \text{ pph}}{1} \right) = \mathbf{1.00 \times 10^{-5}\%}$$

Determine the molarity of CH<sub>3</sub>Cl in 1.00 L corresponding to 100. ppb. (Assume the density of the solution is the same as for pure water, 1.00 g/mL.)

$$\left(\frac{100. \text{ g CH}_3\text{Cl}}{10^9 \text{ g Solution}}\right)\left(\frac{1 \text{ mol CH}_3\text{Cl}}{50.48 \text{ g CH}_3\text{Cl}}\right)\left(\frac{1.00 \text{ g Solution}}{\text{mL}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)$$

$$= 1.98098 \times 10^{-6} = \mathbf{1.98 \times 10^{-6} M \text{ CH}_3\text{Cl}}$$

If the density is 1.00 g/mL then 1.00 L of solution would weigh 1.00 kg. The mass of CH<sub>3</sub>Cl is insignificant compared to 1.00 kg, thus the mass of the solution may be taken as the mass of the solvent. This makes the molarity equal to the molality, in other words: **1.98 x 10<sup>-6</sup> m CH<sub>3</sub>Cl**

Still using 1.00 L of solution:

$$\text{Moles CH}_3\text{Cl} = (1.98098 \times 10^{-6} \text{ mol/L})(1.00 \text{ L}) = 1.98098 \times 10^{-6} \text{ mol CH}_3\text{Cl} \text{ (unrounded)}$$

$$\text{Moles H}_2\text{O} = (1.00 \text{ kg})(10^3 \text{ g/1 kg})(1 \text{ mol H}_2\text{O} / 18.02 \text{ g H}_2\text{O}) = 55.49389567 \text{ mol H}_2\text{O} \text{ (unrounded)}$$

$$X_{\text{chloroform}} = (1.98098 \times 10^{-6} \text{ mol CH}_3\text{Cl}) / [(1.98098 \times 10^{-6} + 55.49389567) \text{ mol}]$$

$$= 3.569726 \times 10^{-8} = \mathbf{3.57 \times 10^{-8}}$$

- 13.97 a) The solution in U-tube **B** is the most concentrated since it has the highest osmotic pressure.  
b) Solution **C** has the smallest number of dissolved ions and thus the smallest osmotic pressure.
- 13.98 a) From the osmotic pressure, the molarity of the solution can be found. The ratio of mass per volume to moles per volume gives the molar mass of the compound.

$$\Pi V = nRT$$

$$\Pi = MRT$$

$$M = \frac{\Pi}{RT} = \frac{(0.340 \text{ torr})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)\left((273 + 25) \text{ K}\right)} \left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) = 1.828546 \times 10^{-5} M \text{ (unrounded)}$$

$$(M)(V) = \text{moles}$$

$$\text{Moles} = (1.828546 \times 10^{-5} M)(30.0 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) = 5.48564 \times 10^{-7} \text{ mol}$$

$$\text{Molar mass} = \frac{(10.0 \text{ mg}) \left(\frac{10^{-3} \text{ g}}{1 \text{ mg}}\right)}{5.48564 \times 10^{-7} \text{ mol}} = 1.82294 \times 10^4 = \mathbf{1.82 \times 10^4 \text{ g/mol}}$$

b) To find the freezing point depression, the molarity of the solution must be converted to molality.

Then use  $\Delta T_f = iK_f m$ . ( $i = 1$ )

Mass solvent = mass of solution – mass of solute

$$\text{Mass solvent} = \left[ (30.0 \text{ mL}) \left(\frac{0.997 \text{ g}}{1 \text{ mL}}\right) - (10.0 \text{ mg}) \left(\frac{10^{-3} \text{ g}}{1 \text{ mg}}\right) \right] \left(\frac{1 \text{ kg}}{10^3 \text{ g}}\right) = 0.0299 \text{ kg}$$

$$\text{Moles solute} = \left(\frac{1.828546 \times 10^{-5} \text{ mol}}{\text{L}}\right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) (30.0 \text{ mL}) = 5.485638 \times 10^{-7} \text{ mol (unrounded)}$$

$$\text{Molality} = \frac{5.485638 \times 10^{-7} \text{ mol}}{0.0299 \text{ kg}} = 1.83466 \times 10^{-5} m \text{ (unrounded)}$$

$$\Delta T_f = iK_f m = (1)(1.86^\circ\text{C}/m)(1.83466 \times 10^{-5} m) = 3.412 \times 10^{-5} = \mathbf{3.41 \times 10^{-5}^\circ\text{C}}$$

(So the solution would freeze at  $0 - 3.41 \times 10^{-5}^\circ\text{C} = -3.41 \times 10^{-5}^\circ\text{C}$ .)

- 13.99 The vapor pressure of H<sub>2</sub>O above the pure water is greater than that above the sugar solution. This means that water molecules will leave the pure water and enter the sugar solution in order to make their vapor pressures closer to equal.

13.100 Glyphosate will be abbreviated Gly.

a) Mass Gly = (16.0 fl oz) (1 gal/128 fl oz) (8.94 lb/1 gal) (1 kg/2.205 lb) ( $10^3$  g/1 kg) (18.0%/100%)  
= 91.224 = **91.2 g glyphosate**

b) Mass Gly = (3.00 fl oz) (1 gal/128 fl oz) (8.94 lb/1 gal) (1 kg/2.205 lb) ( $10^3$  g/1 kg) (18.0%/100%)  
= 17.10459 g glyphosate (unrounded)

Assume that the volume of solution is equal to the volume of solvent, because the volume of glyphosate is insignificant. Assume the density of H<sub>2</sub>O is 1.00 g/mL.

Mass of water = (1.00 gal) (3.785 L/1 gal) (1 mL/ $10^{-3}$  L) (1.00 g/mL) = 3785 g H<sub>2</sub>O (unrounded)

Mass percent =  $\frac{(17.10459 \text{ g Gly})}{(17.10459 + 3785) \text{ g}} \times 100\% = 0.44987 = \mathbf{0.450\%}$

13.101 The fraction remaining in the water ( $f_w$ ) is related to the volume of water ( $V_w$ ), the volume of dichloromethane ( $V_d$ ), and the distribution ratio for the solubility ( $D = 8.35/1$ ).

$$f_w = V_w / (V_w + DV_d)$$

Mass remaining in water =  $f_w$  (original mass)

a) Mass in water =  $\frac{(100.0 \text{ mL})}{(100.0 + 8.35(60.0)) \text{ mL}} (10.0 \text{ mg}) = 1.66389 = \mathbf{1.66 \text{ mg}}$  remaining

b) Perform a similar calculation to part (a), then take the result and repeat the procedure. Combine the results to get the total removed.

$$\text{Mass in water} = \frac{(100.0 \text{ mL})}{(100.0 + 8.35(30.0)) \text{ mL}} (10.0 \text{ mg}) = 2.853067 \text{ mg remaining after first extraction}$$

$$\text{Mass in water} = \frac{(100.0 \text{ mL})}{(100.0 + 8.35(30.0)) \text{ mL}} (2.853067 \text{ mg})$$

$$= 0.813999 = \mathbf{0.814 \text{ mg}}$$
 remaining after second extraction

c) The two-step extraction extracts more of the caffeine.

13.102 a)  $X_{\text{N}_2} = \frac{\text{moles of N}_2}{\text{total moles}}$

Mixture A:  $X_{\text{N}_2} = \frac{3 \text{ moles N}_2}{3 + 2 + 3 \text{ moles}} = 0.38$

Mixture B:  $X_{\text{N}_2} = \frac{4 \text{ moles N}_2}{4 + 4 + 2 \text{ moles}} = 0.40$

Mixture C:  $X_{\text{N}_2} = \frac{4 \text{ moles N}_2}{4 + 3 + 5 \text{ moles}} = 0.33$

**Mixture C** has the smallest mole fraction of N<sub>2</sub>.

b) Mixture A:  $X_{\text{Ne}} = \frac{2 \text{ moles Ne}}{3 + 2 + 3 \text{ moles}} = 0.25$

Mixture B:  $X_{\text{Ne}} = \frac{4 \text{ moles Ne}}{4 + 4 + 2 \text{ moles}} = 0.40$

Mixture C:  $X_{\text{Ne}} = \frac{3 \text{ moles Ne}}{4 + 3 + 5 \text{ moles}} = 0.25$

**Mixtures A and C** have the same mole fraction of Ne.

c) Mixture A:  $X_{\text{Cl}_2} = \frac{3 \text{ moles Cl}_2}{3 + 2 + 3 \text{ moles}} = 0.38$

Mixture B:  $X_{\text{Cl}_2} = \frac{2 \text{ moles Cl}_2}{4 + 4 + 2 \text{ moles}} = 0.20$

Mixture C:  $X_{\text{Cl}_2} = \frac{5 \text{ moles Cl}_2}{4 + 3 + 5 \text{ moles}} = 0.42$

**Mixture B < Mixture A < Mixture C**

- 13.103 To determine the molecular formula, both the empirical formula and the molar mass are needed. First, determine the empirical formula assuming exactly 100 grams of sample, which makes the percentages equal to the mass of each element present:

$$\text{Moles C} = 32.3 \text{ g C} \left( \frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 2.6894 \text{ mol C (unrounded)}$$

$$\text{Moles H} = 3.97 \text{ g H} \left( \frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) = 3.93849 \text{ mol H (unrounded)}$$

$$\text{Moles O} = (100 - 32.3 - 3.97) \text{ g O} \left( \frac{1 \text{ mol O}}{16.00 \text{ g O}} \right) = 3.9831 \text{ mol O (unrounded)}$$

Dividing each mole value by the smallest value (moles C) gives: C = 1, H = 1.5, and O = 1.5 leading to an empirical formula of: **C<sub>2</sub>H<sub>3</sub>O<sub>3</sub>**.

The molar mass comes from the freezing point depression:

$$\Delta T_f = iK_f m \quad (\text{Assume the compound is a nonelectrolyte, } i = 1.)$$

$$m = \Delta T_f / iK_f = (1.26^\circ\text{C}) / [(1)(1.86^\circ\text{C}/m)] = 0.677419 \text{ } m \text{ (unrounded)}$$

$$\text{Molar mass} = \left( \frac{\text{kg Solvent}}{0.677419 \text{ mol}} \right) \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left( \frac{0.981 \text{ g}}{11.23 \text{ g Solvent}} \right) = 128.953 \text{ g/mol (unrounded)}$$

The empirical formula mass is approximately 75 g/mol.

The ratio of the molar to the empirical formula mass normally gives the conversion factor to change the empirical formula to the molecular formula. In this case,  $129/75 = 1.72$ , this is not near a whole number. (This result is low due to dissociation of the weak acid; the assumption of  $i = 1$  is too low. If  $i = 1.2$ , then the molar mass would increase to about 154 g/mol.) The 1.72 value implies the molecular formula is twice the empirical formula, or **C<sub>4</sub>H<sub>6</sub>O<sub>6</sub>**.

$$13.104 \text{ Moles} = (5.66 \text{ g NH}_4\text{NO}_3) \left( \frac{1 \text{ mol NH}_4\text{NO}_3}{80.05 \text{ g NH}_4\text{NO}_3} \right) \left( \frac{1 \text{ mol NH}_4^+}{1 \text{ mol NH}_4\text{NO}_3} \right) = 7.07058 \times 10^{-2} \text{ mol NH}_4^+ \text{ (unrounded)}$$

$$\begin{aligned} \text{Moles} &= (4.42 \text{ g (NH}_4)_3\text{PO}_4) \left( \frac{1 \text{ mol (NH}_4)_3\text{PO}_4}{149.10 \text{ g (NH}_4)_3\text{PO}_4} \right) \left( \frac{3 \text{ mol NH}_4^+}{1 \text{ mol (NH}_4)_3\text{PO}_4} \right) \\ &= 8.89336 \times 10^{-2} \text{ mol NH}_4^+ \text{ (unrounded)} \end{aligned}$$

$$\begin{aligned} \text{Moles} &= (4.42 \text{ g (NH}_4)_3\text{PO}_4) \left( \frac{1 \text{ mol (NH}_4)_3\text{PO}_4}{149.10 \text{ g (NH}_4)_3\text{PO}_4} \right) \left( \frac{1 \text{ mol PO}_4^{3-}}{1 \text{ mol (NH}_4)_3\text{PO}_4} \right) \\ &= 2.96445 \times 10^{-2} \text{ mol PO}_4^{3-} \text{ (unrounded)} \end{aligned}$$

$$M \text{ NH}_4^+ = [(7.07058 \times 10^{-2}) + (8.89336 \times 10^{-2})] \text{ mol NH}_4^+ / 20.0 \text{ L} = 7.98197 \times 10^{-3} = \mathbf{7.98 \times 10^{-3} M \text{ NH}_4^+}$$

$$M \text{ PO}_4^{3-} = (2.96445 \times 10^{-2} \text{ mol PO}_4^{3-}) / 20.0 \text{ L} = 1.482225 \times 10^{-3} = \mathbf{1.48 \times 10^{-3} M \text{ PO}_4^{3-}}$$

- 13.105 a) There is a **positive deviation** since benzene molecules are held together only by weak dispersion forces while methanol molecules are held together by relatively strong hydrogen bonding. The two components will not interact with each other since the intermolecular forces are so different.  
 b) There is a **positive deviation** since ethyl acetate will have weaker hydrogen bonding to water than water has with itself.  
 c) Since hexane and heptane are very similar compounds with weak dispersion forces, they will obey Raoult's Law. The behavior will be **nearly ideal**.  
 d) The behavior will be **nearly ideal** since the hydrogen bonding in methanol and water is very similar.  
 e) There is a **negative deviation** because HCl exists as ions in solution and water is in the hydration shells around the H<sub>3</sub>O<sup>+</sup> and Cl<sup>-</sup> ions.

- 13.106 a) Assume a 100 g sample of urea. This leads to the mass of each element being equal to the percent of that element.

$$\text{Moles C} = (20.1 \text{ g C}) \left( \frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 1.6736 \text{ mol C (unrounded)}$$

$$\text{Moles H} = (6.7 \text{ g H}) \left( \frac{1 \text{ mol H}}{1.008 \text{ g H}} \right) = 6.6468 \text{ mol H (unrounded)}$$

$$\text{Moles N} = (46.5 \text{ g N}) \left( \frac{1 \text{ mol N}}{14.01 \text{ g N}} \right) = 3.31906 \text{ mol N (unrounded)}$$

$$\text{Moles O} = ((100 - 20.1 - 6.7 - 46.5) \text{ g O}) \left( \frac{1 \text{ mol O}}{16.00 \text{ g O}} \right) = 1.66875 \text{ mol O (unrounded)}$$

Dividing all by the smallest value (1.66875 mol O) gives: C = 1, H = 4, N = 2, O = 1. Thus, the empirical formula is **CH<sub>4</sub>N<sub>2</sub>O**. The empirical formula weight is 60.06 g/mol.

b) Use  $\Pi = MRT$  to solve for the molarity of the urea solution. The solution molarity is related to the concentration expressed in % w/v by using the molar mass.

$$M = \Pi/RT = \frac{(2.04 \text{ atm})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) \left((273 + 25) \text{ K}\right)} = 0.0833817 \text{ M (unrounded)}$$

$$\text{Molar mass} = \frac{\left(\frac{5.0 \text{ g}}{\text{L}}\right)}{\left(\frac{0.0833817 \text{ mol}}{\text{L}}\right)} = 59.965 = \mathbf{60. \text{ g/mol}}$$

Because the molecular weight equals the empirical weight, the molecular formula is also **CH<sub>4</sub>N<sub>2</sub>O**.

$$13.107 \text{ a) Mass glucose} = (2.5 \text{ h}) \left( \frac{100. \text{ mL}}{\text{h}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left( \frac{0.30 \text{ mol Glucose}}{1 \text{ L}} \right) \left( \frac{180.16 \text{ g Glucose}}{1 \text{ mol Glucose}} \right) \\ = 13.512 = \mathbf{14 \text{ g glucose}}$$

b) At low concentrations sodium chloride dissociates completely, forming twice as many dissolved particles per mole as glucose, so a sodium chloride solution would have to have a molarity that is one-half of glucose to be isotonic: 0.15 M

$$\text{c) Mass NaCl} = (1.5 \text{ h}) \left( \frac{150. \text{ mL}}{\text{h}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left( \frac{0.15 \text{ mol NaCl}}{1 \text{ L}} \right) \left( \frac{58.44 \text{ g NaCl}}{1 \text{ mol NaCl}} \right) \\ = 1.97235 = \mathbf{2.0 \text{ g NaCl}}$$

13.108 a) Use Henry's law:

$$S_{\text{gas}} = k_{\text{H}} \times P_{\text{gas}}$$

$$k_{\text{H}} = S_{\text{gas}}/P_{\text{gas}}$$

$$k_{\text{H}} = 1.64 \times 10^{-3} \text{ M}/0.2095 \text{ atm}$$

$$k_{\text{H}} = 7.8282 \times 10^{-3} = \mathbf{7.83 \times 10^{-3} \text{ mol/L} \cdot \text{atm}}$$

$$\text{b) } S_{\text{gas}} = k_{\text{H}} \times P_{\text{gas}}$$

$$S_{\text{gas}} = (7.8282 \times 10^{-3} \text{ mol/L} \cdot \text{atm})(0.005 \text{ atm})$$

$$S_{\text{gas}} = 3.9141 \times 10^{-5} = \mathbf{4 \times 10^{-5} \text{ M}}$$

c) Assume a 1.0 L sample. Acrylic acid is 14.6 mol/L or 14.6 mol in 1.0 L.

Oxygen is  $4 \times 10^{-5}$  mol/L or  $4 \times 10^{-5}$  mol in 1.0 L.

$$X_{\text{O}_2} = \frac{\text{moles of O}_2}{\text{moles of O}_2 + \text{moles of acrylic acid}} = \frac{4 \times 10^{-5} \text{ mol}}{\left(4 \times 10^{-5}\right) + 14.6} \text{ mol} = 2.73972 \times 10^{-6} = \mathbf{3 \times 10^{-6}}$$

$$\text{d) Mass of acrylic acid} = \left( \frac{14.6 \text{ mol acrylic acid}}{\text{L}} \right) \left( \frac{72.06 \text{ g acrylic acid}}{1 \text{ mol acrylic acid}} \right) = 1052.076 \text{ g/L}$$

$$\text{Mass of oxygen} = \left( \frac{4 \times 10^{-5} \text{ mol O}_2}{\text{L}} \right) \left( \frac{32.0 \text{ g O}_2}{1 \text{ mol O}_2} \right) = 0.00128 \text{ g/L}$$

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \left(1 \times 10^6\right) = \frac{0.00128 \text{ g}}{0.00128 \text{ g} + 1052.176 \text{ g}} \left(1 \times 10^6\right) = 1.2165 = \mathbf{1 \text{ ppm}}$$

13.109 a)  $\Delta T_f = iK_f m$  Assume NaCl is a strong electrolyte with  $i = 2$ .

$$m = \Delta T_f / iK_f = (5.0^\circ\text{C}) / [(2)(1.86^\circ\text{C}/m)] = 1.344086 \text{ } m \text{ NaCl (unrounded)}$$

$$\text{Mass} = \left( \frac{1.344086 \text{ mol NaCl}}{\text{kg}} \right) (5.5 \text{ kg}) \left( \frac{58.44 \text{ g NaCl}}{\text{mol NaCl}} \right) = 432.016 = \mathbf{4.3 \times 10^2 \text{ g NaCl}}$$

b)  $\Delta T_f = iK_f m$  Assume  $\text{CaCl}_2$  is a strong electrolyte with  $i = 3$ .

$$m = \Delta T_f / iK_f = (5.0^\circ\text{C}) / [(3)(1.86^\circ\text{C}/m)] = 0.896057 \text{ } m \text{ CaCl}_2 \text{ (unrounded)}$$

$$\text{Mass} = \left( \frac{0.896057 \text{ mol CaCl}_2}{\text{kg}} \right) (5.5 \text{ kg}) \left( \frac{110.98 \text{ g CaCl}_2}{\text{mol CaCl}_2} \right) = 546.944 = \mathbf{5.5 \times 10^2 \text{ g CaCl}_2}$$

13.110 a) Moles  $\text{CO}_2 = (355 \text{ mL}) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left( \frac{3.3 \times 10^{-2} \text{ mol}}{\text{L} \cdot \text{atm}} \right) (4 \text{ atm}) = 0.04686 = \mathbf{0.05 \text{ mol CO}_2}$

b) If it is completely flat there is no  $\text{CO}_2$  remaining or 0.00 moles  $\text{CO}_2$ , however a small amount will remain in solution:

$$\text{Moles CO}_2 = (355 \text{ mL}) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left( \frac{3.3 \times 10^{-2} \text{ mol}}{\text{L} \cdot \text{atm}} \right) (3 \times 10^{-4} \text{ atm}) = 3.5145 \times 10^{-6} = \mathbf{4 \times 10^{-6} \text{ mol CO}_2}$$

c) The difference in the moles will determine the number of moles entering the gas phase.

$$PV = nRT \text{ so } V = nRT/P = \frac{\left[ (0.04686 - 3.5145 \times 10^{-6}) \text{ mol} \right] \left( 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) ((273 + 25) \text{ K})}{(1.00 \text{ atm})}$$
$$= 1.14638 = \mathbf{1 \text{ L CO}_2}$$

13.111 a) **Scene C** represents the system at the higher temperature of 298 K. At the higher temperature, the solubility of oxygen decreases so more oxygen leaves the solution to go into the vapor phase.

b) **Scene B** represents the system when the pressure of oxygen is increased by half. The increase in pressure would result in  $4 + \frac{1}{2}(4) = 6$  moles of oxygen in the vapor phase. The increased pressure results in increased solubility of oxygen in the water. Of the 6 moles of oxygen in the vapor phase, 1 mole dissolves in the water to bring the dissolved moles to 3.