CHAPTER 13 THE PROPERTIES OF SOLUTIONS

END–OF–CHAPTER PROBLEMS

13.1 The composition of seawater, like all mixtures, is variable. The components of seawater (water and various ions) have not been changed and thus retain some of their properties. For example, seawater has a salty taste due to the presence of salts such as NaCl.

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 $CH_3(CH_2)_nCOOH$, 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 Plan: A more concentrated solution will have more solute dissolved in the solvent. Determine the types of intermolecular forces in the solute and solvents. A solute tends to be more soluble in a solvent whose intermolecular forces are similar to its own.
Solution:
Potassium nitrate, KNO_3, is an ionic compound and can form ion-dipole forces with a polar solvent like water, thus dissolving in the water. Potassium nitrate is not soluble in the nonpolar solvent CCl_4. Because potassium nitrate dissolves to a greater extent in water, **a) KNO_3 in H_2O** will result in the more concentrated solution.

13.5 **b) Stearic acid in 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 Plan: 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. Ionic forces are present in ionic compounds; dipole-dipole forces are present in polar substances, while nonpolar substances exhibit only dispersion forces. 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.
Solution:
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 Plan: 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. Ionic forces are present in ionic compounds; dipole-dipole forces are present in polar substances, while nonpolar substances exhibit only dispersion forces. 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.

Solution:
a) **Hydrogen bonding** occurs between the H atom on water and the lone electron pair on the O atom in dimethyl ether (CH_3OCH_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 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 Plan: $CH_3CH_2OCH_2CH_3$ is polar with dipole-dipole interactions as the dominant intermolecular forces. Examine the solutes to determine which has intermolecular forces more similar to those in diethyl ether. This solute is the one that would be more soluble.
       Solution:
       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) **CH_3CHO** (acetaldehyde) would be more soluble. The dominant interactions in H_2O are hydrogen bonding, a stronger type of dipole-dipole force. The dominant interactions in CH_3CHO are dipole-dipole. The solute-solvent interactions between CH_3CHO and diethyl ether are more similar to the solvent intermolecular forces than the forces between H_2O and diethyl ether.
       c) **CH_3CH_2MgBr** would be more soluble. CH_3CH_2MgBr has a polar end (–MgBr) and a nonpolar end (CH_3CH_2–), whereas $MgBr_2$ is an ionic compound. The nonpolar end of CH_3CH_2MgBr and diethyl ether would interact with dispersion forces, while the polar end of CH_3CH_2MgBr and the dipole in diethyl ether would interact with dipole-dipole forces.

13.11 a) **CH_3CH_2-O-CH_3(g)**, due to its smaller size (smaller molar mass).
       b) **CH_2Cl_2**, because it is more polar than CCl_4.
       c) **Tetrahydropyran** is more water soluble due to hydrogen bonding between the oxygen atom and water molecules.

13.12 Plan: Determine the types of intermolecular forces present in the two compounds and in water and hexane. Substances with similar types of forces tend to be soluble while substances with different type of forces tend to be insoluble.
       Solution:
       Gluconic acid is a very polar molecule because it has –OH groups attached to every carbon. The abundance of –OH bonds allows gluconic acid to participate in extensive H bonding with water, hence its great solubility in water. On the other hand, caproic acid has a five 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 $\Delta H_{solvent}$ and ΔH_{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. When the solvent is water, solvation is called hydration.

13.14 a) Charge density is the ratio of the ion's charge to its volume. An ion's charge and size affect its charge density.
       b) $- < + < 2- < 3+$
       c) The higher the charge density, the more negative the $\Delta H_{hydration}$. $\Delta H_{hydration}$ increases with increasing charge and decreases with increasing size.

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.

$$\Delta H_{solution} = \Delta H_{lattice} +\ \Delta H_{hydration\ of\ ions}$$

For a heat of solution to be very small, $\Delta H_{lattice} \approx \Delta H_{hydration\ of\ ions}$, and they would have to have opposite signs.
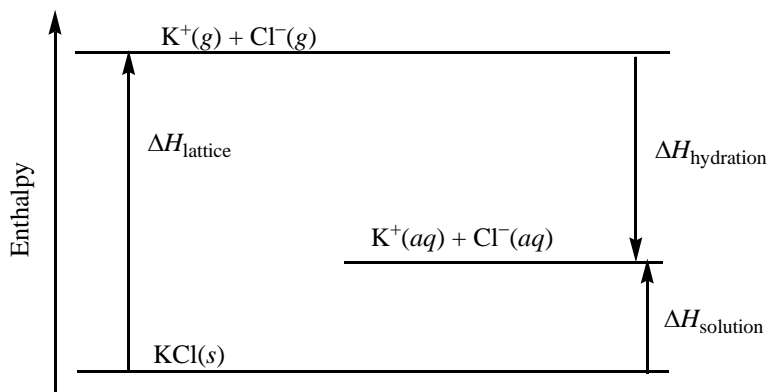
13.16   a) **Endothermic**

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 $\Delta H_{solution}$ (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 endothermic $\Delta H_{solution}$ values (and higher energy states) are still soluble in water.

13.18   Plan: $\Delta H_{solution} = \Delta H_{lattice} +\ \Delta H_{hydration}$. 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.

Solution:

$\Delta H_{solution} > 0$ (endothermic)

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.

13-3
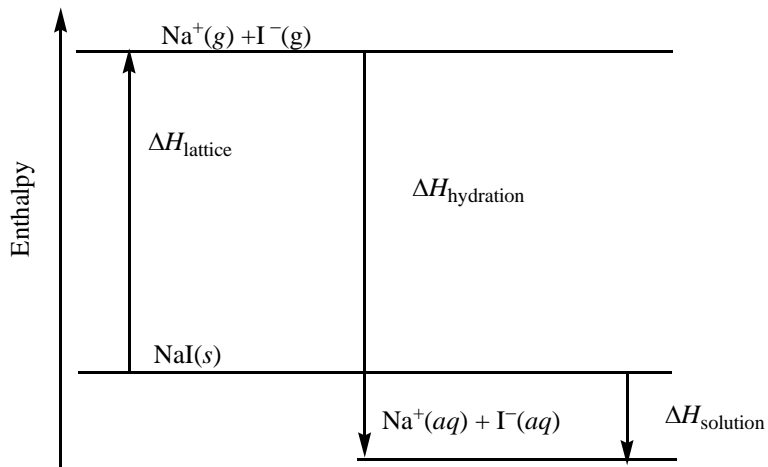
13.20   Plan: Charge density is the ratio of an ion's charge (regardless of sign) to its volume. An ion's volume is
         related to its radius. For ions whose charges have the same sign (+ or −), ion size decreases as a group in
         the periodic table is ascended and as you proceed from left to right in the periodic table. Charge density increases
         with increasing charge and increases with decreasing size.
         Solution:
         a) Both ions have a +1 charge, but the volume of Na^+ is smaller, so it has the greater charge density.
         b) Sr^{2+} has a greater ionic charge and a smaller size (because it has a greater Z_{eff}), so it has the greater charge
         density.
         c) Na^+ has a smaller ion volume than Cl^-, so it has the greater charge density.
         d) O^{2-} has a greater ionic charge and similar ion volume, so it has the greater charge density.
         e) OH^- has a smaller ion volume than SH^- (O is smaller than S), so it has the greater charge density.
         f) Mg^{2+} has the higher charge density because it has a smaller ion volume.
         g) Mg^{2+} has the higher charge density because it has both a smaller ion volume and greater charge.
         h) CO_3^{2-} has the higher charge density because it has both a smaller ion volume and greater charge.

13.21   a) I^- has a smaller charge density (larger ion volume) than Br^-.
         b) Ca^{2+} has a lower ratio than Sc^{3+}, due to its smaller ion charge.
         c) Br^- has a lower ratio than K^+, due to its larger ion volume.
         d) Cl^- has a lower ratio than S^{2-}, due to its smaller ion charge.
         e) Sc^{3+} has a lower ratio than Al^{3+}, due to its larger ion volume.
         f) ClO_4^- has a lower ratio due to its smaller ion charge.
         g) Fe^{2+} has a lower ratio due to its smaller ion charge.
         h) K^+ has a lower ratio due to its smaller ion charge.

13.22   Plan: The ion with the greater charge density will have the larger $\Delta H_{hydration}$.
         Solution:
         a) Na^+ would have a larger $\Delta H_{hydration}$ than Cs^+ since its charge density is greater than that of Cs^+.
         b) Sr^{2+} would have a larger $\Delta H_{hydration}$ than Rb^+.
         c) Na^+ would have a larger $\Delta H_{hydration}$ than Cl^-.
         d) O^{2-} would have a larger $\Delta H_{hydration}$ than F^-.
         e) OH^- would have a larger $\Delta H_{hydration}$ than SH^-.
         f) Mg^{2+} would have a larger $\Delta H_{hydration}$ than Ba^{2+}.
         g) Mg^{2+} would have a larger $\Delta H_{hydration}$ than Na^+.
         h) CO_3^{2-} would have a larger $\Delta H_{hydration}$ than NO_3^-.

13.23   a) I^- b) Ca^{2+} c) Br^- d) Cl^- e) Sc^{3+} f) ClO_4^- g) Fe^{2+} h) K^+

13.24   Plan: Use the relationship $\Delta H_{solution} = \Delta H_{lattice} + \Delta H_{hydration}$. Given $\Delta H_{solution}$ and $\Delta H_{lattice}$, $\Delta H_{hydration}$ can be
         calculated. $\Delta H_{hydration}$ increases with increasing charge density, and charge density increases with increasing
         charge and decreasing size.
         Solution:
         a) The two ions in potassium bromate are K^+ and BrO_3^-.
         $\Delta H_{solution} = \Delta H_{lattice} + \Delta H_{hydration}$
         $\Delta H_{hydration} = \Delta H_{solution} - \Delta H_{lattice}$ = 41.1 kJ/mol – 745 kJ/mol = –703.9 = **–704 kJ/mol**
         b) K^+ ion contributes more to the heat of hydration because it has a smaller size and, therefore, a greater charge
         density.

13.25   a) $\Delta H_{hydration} = \Delta H_{solution} - \Delta H_{lattice}$
         $\Delta H_{hydration}$ = 17.3 kJ/mol –763 kJ/mol
         $\Delta H_{hydration}$ = –745.7 = **– 746 kJ/mol**
         b) Na^+ ion contributes more to the heat of hydration due to its smaller size (larger charge density).

13.26 Plan: Entropy increases as the possible states for a system increase, which is related to the freedom of motion of its particles and the number of ways they can be arranged.
Solution:
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 $\Delta H_{solution} = \Delta H_{lattice} + \Delta H_{hydration}$
$\Delta H_{solution} = 822 \text{ kJ/mol} + (-799 \text{ kJ/mol})$
$\Delta H_{solution} = \textbf{23 kJ/mol}$

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 gaseous 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 ($\Delta H_{soln} < 0$).

13.31 Plan: The solubility of a gas in water decreases with increasing temperature and increases with increasing pressure.
Solution:
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 Plan: Solubility for a gas is calculated from Henry's law: $S_{gas} = k_H \times P_{gas}$. We know k_H and P_{gas}, so S_{gas} can be calculated with units of mol/L. To calculate the mass of oxygen gas, convert moles of O_2 to mass of O_2 using the molar mass.
Solution:
a) $S_{gas} = k_H \times P_{gas}$

$S_{gas} = \left(1.28\text{x}10^{-3}\dfrac{\text{mol}}{\text{L•atm}}\right)(1.00 \text{ atm}) = 1.28\text{x}10^{-3} \text{ mol/L}$

$\text{Mass (g) of } O_2 = \left(\dfrac{1.28\text{x}10^{-3} \text{ mol } O_2}{\text{L}}\right)\left(\dfrac{32.0 \text{ g } O_2}{1 \text{ mol } O_2}\right)(2.50 \text{ L}) = 0.1024 = \textbf{0.102 g } \textbf{O}_2$

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

$S_{gas} = \left(1.28\text{x}10^{-3}\dfrac{\text{mol}}{\text{L•atm}}\right)(0.209 \text{ atm}) = 2.6752\text{x}10^{-4} \text{ mol/L}$

$\text{Mass (g) of } O_2 = \left(\dfrac{2.6752\text{x}10^{-4} \text{ mol } O_2}{\text{L}}\right)\left(\dfrac{32.0 \text{ g } O_2}{1 \text{ mol } O_2}\right)(2.50 \text{ L}) = 0.0214016 = \textbf{0.0214 g } \textbf{O}_2$

13.34 $\text{Solubility} = \left(1.5\text{x}10^{-3} \dfrac{\text{mol}}{\text{L•atm}}\right)(1.0 \text{ atm})\left(\dfrac{0.93\%}{100\%}\right) = 1.395\text{x}10^{-5} = \textbf{1.4x10}^{-5} \textbf{ mol/L}$

13.35 The solution is **saturated**.

13.36 Plan: Solubility for a gas is calculated from Henry's law: $S_{\text{gas}} = k_{\text{H}} \times P_{\text{gas}}$. We know k_{H} and P_{gas}, so S_{gas} can be calculated with units of mol/L.
Solution:
$S_{\text{gas}} = k_{\text{H}} \times P_{\text{gas}} = (3.7\text{x}10^{-2} \text{ mol/L•atm})(5.5 \text{ atm}) = 0.2035 = \textbf{0.20 mol/L}$

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 in molality does not change with temperature and is the preferred unit when the temperature of the solution may change.

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.

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 Plan: The molarity is the number of moles of solute in each liter of solution: $\text{M} = \dfrac{\text{mol of solute}}{\text{V(L) of solution}}$. Convert the masses to moles and the volumes to liters and divide moles by volume.
Solution:
a) $\text{Molarity} = \left(\dfrac{32.3 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}}{100. \text{ mL}}\right)\left(\dfrac{1 \text{ mL}}{10^{-3} \text{ L}}\right)\left(\dfrac{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{342.30 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}}\right) = 0.943617 = \textbf{0.944 } \textbf{\textit{M}} \textbf{ C}_{12}\textbf{H}_{22}\textbf{O}_{11}$

b) $\text{Molarity} = \left(\dfrac{5.80 \text{ g LiNO}_3}{505 \text{ mL}}\right)\left(\dfrac{1 \text{ mL}}{10^{-3} \text{ L}}\right)\left(\dfrac{1 \text{ mol LiNO}_3}{68.95 \text{ g LiNO}_3}\right) = 0.166572 = \textbf{0.167 } \textbf{\textit{M}} \textbf{ LiNO}_3$

13.42 a) $\text{Molarity} = \left(\dfrac{0.82 \text{ g C}_2\text{H}_5\text{OH}}{10.5 \text{ mL}}\right)\left(\dfrac{1 \text{ mL}}{10^{-3} \text{ L}}\right)\left(\dfrac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.07 \text{ g C}_2\text{H}_5\text{OH}}\right) = 1.69514 = \textbf{1.7 } \textbf{\textit{M}} \textbf{ C}_2\textbf{H}_5\textbf{OH}$

b) $\text{Molarity} = \left(\dfrac{1.27 \text{ g NH}_3}{33.5 \text{ mL}}\right)\left(\dfrac{1 \text{ mL}}{10^{-3} \text{ L}}\right)\left(\dfrac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3}\right) = 2.2261 = \textbf{2.23 } \textbf{\textit{M}} \textbf{ NH}_3$

13.43 Plan: Dilution calculations can be done using $M_{\text{conc}}V_{\text{conc}} = M_{\text{dil}}V_{\text{dil}}$.
Solution:
a) $M_{\text{conc}} = 0.240 \text{ } M \text{ NaOH} \qquad V_{\text{conc}} = 78.0 \text{ mL} \qquad M_{\text{dil}} = ? \qquad V_{\text{dil}} = 0.250 \text{ L}$
$$M_{\text{dil}} = \dfrac{(M_{\text{conc}})(V_{\text{conc}})}{(V_{\text{dil}})} = \dfrac{(0.240 \text{ } M)(78.0 \text{ mL})}{(0.250 \text{ L})}\left(\dfrac{10^{-3} \text{ L}}{1 \text{ mL}}\right) = 0.07488 = \textbf{0.0749 } \textbf{\textit{M}}$$
b) $M_{\text{conc}} = 1.2 \text{ } M \text{ HNO}_3 \qquad V_{\text{conc}} = 38.5 \text{ mL} \qquad M_{\text{dil}} = ? \qquad V_{\text{dil}} = 0.130 \text{ L}$
$$M_{\text{dil}} = \dfrac{(M_{\text{conc}})(V_{\text{conc}})}{(V_{\text{dil}})} = \dfrac{(1.2 \text{ } M)(38.5 \text{ mL})}{(0.130 \text{ L})}\left(\dfrac{10^{-3} \text{ L}}{1 \text{ mL}}\right) = 0.355385 = \textbf{0.36 } \textbf{\textit{M}}$$

13.44 Dilution calculations can be done using $M_{conc}V_{conc} = M_{dil}V_{dil}$

a) $M_{conc} = 6.25\ M$ HCl $V_{conc} = 25.5$ mL $M_{dil} = ?$ $V_{dil} = 0.500$ L

$$M_{dil} = \frac{(M_{conc})(V_{conc})}{(V_{dil})} = \frac{(6.25\ M)(25.5\ \text{mL})}{(0.500\ \text{L})}\left(\frac{10^{-3}\ \text{L}}{1\ \text{mL}}\right) = 0.31875 = \mathbf{0.319\ M}$$

b) $M_{conc} = 2.00\text{x}10^{-2}\ M$ KI $V_{conc} = 8.25$ mL $M_{dil} = ?$ $V_{dil} = 12.0$ mL

$$M_{dil} = \frac{(M_{conc})(V_{conc})}{(V_{dil})} = \frac{(2.00\text{x}10^{-2}\ M)(8.25\ \text{mL})}{(12.0\ \text{mL})} = 0.01375 = \mathbf{0.0138\ M}$$

13.45 Plan: For part a), find the number of moles of KH_2PO_4 needed to make 365 mL of a solution of this molarity. Convert moles to mass using the molar mass of KH_2PO_4. For part b), use the relationship $M_{conc}V_{conc} = M_{dil}V_{dil}$ to find the volume of 1.25 M NaOH needed.

Solution:

a) Moles of $KH_2PO_4 = (365\ \text{mL})\left(\frac{10^{-3}\ \text{L}}{1\ \text{mL}}\right)\left(\frac{8.55\text{x}10^{-2}\ \text{mol}\ KH_2PO_4}{\text{L}}\right) = 0.0312075$ mol

Mass (g) of $KH_2PO_4 = (0.0312075\ \text{mol}\ KH_2PO_4)\left(\frac{136.09\ \text{g}\ KH_2PO_4}{1\ \text{mol}\ KH_2PO_4}\right) = 4.24703 = 4.25$ g KH_2PO_4

Add **4.25 g KH_2PO_4** to enough water to make 365 mL of aqueous solution.

b) $M_{conc} = 1.25\ M$ NaOH $V_{conc} = ?$ $M_{dil} = 0.335\ M$ NaOH $V_{dil} = 465$ mL

$$V_{conc} = \frac{(M_{dil})(V_{dil})}{(V_{conc})} = \frac{(0.335\ M)(465\ \text{mL})}{(1.25\ M)} = 124.62 = \mathbf{125\ mL}$$

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.

Mass (g) of NaCl $= (2.5\ \text{L})\left(\frac{0.65\ \text{mol}\ \text{NaCl}}{\text{L}}\right)\left(\frac{58.44\ \text{g}\ \text{NaCl}}{1\ \text{mol}\ \text{NaCl}}\right) = 94.965 = 95$ g NaCl

Add **95 g NaCl** to enough water to make 2.5 L of aqueous solution.

b) Use the relationship $M_{conc}V_{conc} = M_{dil}V_{dil}$ to find the volume of 2.1 M urea needed.

$M_{conc} = 2.1\ M$ urea $V_{conc} = ?$ $M_{dil} = 0.3\ M$ urea $V_{dil} = 15.5$ L

$$V_{conc} = \frac{(M_{dil})(V_{dil})}{(V_{conc})} = \frac{(0.3\ M)(15.5\ \text{L})}{(2.1\ M)} = 2.21429 = 2\ \text{L}$$

Add **2 L** of 2.1 M urea to enough water to make 15.5 L of solution.

Note because of the uncertainty in the concentration of the dilute urea (0.3 M), only one significant figure is justified in the answer.

13.47 Plan: Molality, m, $= \dfrac{\text{moles of solute}}{\text{kg of solvent}}$. Convert the mass of solute to moles and divide by the mass of solvent in units of kg.

Solution:

a) Moles of glycine $= 85.4\ \text{g glycine}\left(\dfrac{1\ \text{mol glycine}}{75.07\ \text{g glycine}}\right) = 1.137605$ mol

m glycine $= \dfrac{1.137605\ \text{mol glycine}}{1.270\ \text{kg}} = 0.895752 = \mathbf{0.896\ \textit{m}\ glycine}$

b) Moles of glycerol $= 8.59\ \text{g glycerol}\left(\dfrac{1\ \text{mol glycerol}}{92.09\ \text{g glycerol}}\right) = 0.093278$ mol

$$\text{Volume (kg) of solvent} = 77.0 \text{ g}\left(\frac{1 \text{ kg}}{10^3 \text{ g}}\right) = 0.0770 \text{ kg}$$

$$m \text{ glycerol} = \frac{0.093278 \text{ mol glycerol}}{0.0770 \text{ kg}} = 1.2114 = \textbf{1.21 } \boldsymbol{m} \textbf{ glycerol}$$

13.48 Molality = moles solute/kg solvent.

a) $$m \text{ HCl} = \frac{174 \text{ g HCl}\left(\dfrac{1 \text{ mol HCl}}{36.46 \text{ g HCl}}\right)}{(757 \text{ g})}\left(\frac{10^3 \text{ g}}{1 \text{ kg}}\right) = 6.3043 = \textbf{6.30 } \boldsymbol{m} \textbf{ HCl}$$

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

13.49 <u>Plan:</u> Molality, $m, = \dfrac{\text{moles of solute}}{\text{kg of solvent}}$. Use the density of benzene to find the mass and then the moles of benzene; use the density of hexane to find the mass of hexane and convert to units of kg. Divide the moles of benzene by the mass of hexane.
<u>Solution:</u>

$$\text{Mass (g) of benzene} = (44.0 \text{ mL C}_6\text{H}_6)\left(\frac{0.877 \text{ g}}{1 \text{ mL}}\right) = 38.588 \text{ g benzene}$$

$$\text{Moles of benzene} = (38.588 \text{ g C}_6\text{H}_6)\left(\frac{1 \text{ mol C}_6\text{H}_6}{78.11 \text{ g C}_6\text{H}_6}\right) = 0.49402 \text{ mol benzene}$$

$$\text{Mass (kg) of hexane} = (167 \text{ mL C}_6\text{H}_{14})\left(\frac{0.660 \text{ g}}{\text{mL}}\right)\left(\frac{1 \text{kg}}{10^3 \text{ g}}\right) = 0.11022 \text{ kg hexane}$$

$$m = \frac{\text{moles of solute}}{\text{kg of solvent}} = \frac{(0.49402 \text{ mol C}_6\text{H}_6)}{(0.11022 \text{ kg C}_6\text{H}_{14})} = 4.48213 = \textbf{4.48 } \boldsymbol{m} \textbf{ C}_\textbf{6}\textbf{H}_\textbf{6}$$

13.50 Molality = moles solute/kg solvent.

$$\text{Molality of CCl}_4 = \frac{(2.66 \text{ mL CCl}_4)\left(\dfrac{1.59 \text{ g}}{\text{mL}}\right)\left(\dfrac{1 \text{ mol CCl}_4}{153.81 \text{ g CCl}_4}\right)}{(76.5 \text{ mL CH}_2\text{Cl}_2)\left(\dfrac{1.33 \text{ g}}{\text{mL}}\right)}\left(\frac{10^3 \text{ g}}{1 \text{ kg}}\right) = 0.2702596 = \textbf{0.270 } \boldsymbol{m} \textbf{ CCl}_\textbf{4}$$

13.51 <u>Plan:</u> In part a), the total mass of the <u>solution</u> is 3.10×10^2 g, so mass$_{\text{solute}}$ + mass$_{\text{solvent}}$ = 3.10×10^2 g. Assume that you have 1000 g of the solvent water and find the mass of $C_2H_6O_2$ needed to make a 0.125 m solution. Then a ratio can be used to find the mass of $C_2H_6O_2$ needed to make 3.10×10^2 g of a 0.125 m solution. Part b) is a dilution problem. First, determine the amount of solute in your target solution and then determine the amount of the concentrated acid solution needed to get that amount of solute.
<u>Solution:</u>

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

$$= 7.75875 \text{ g C}_2\text{H}_6\text{O}_2 \text{ in 1000 g H}_2\text{O}$$

Mass (g) of this solution = 1000 g H$_2$O + 7.75875 g C$_2$H$_6$O$_2$ = 1007.75875 g

$$\text{Mass (g) of C}_2\text{H}_6\text{O}_2 \text{ for } 3.10\times10^2 \text{ g of solution} = \left(\frac{7.75875 \text{ g C}_2\text{H}_6\text{O}_2}{1007.75875 \text{ g solution}}\right)(3.10\times10^2 \text{ g solution})$$

$$= 2.386695 \text{ g } C_2H_6O_2$$

$Mass_{solvent} = 3.10\text{x}10^2 \text{ g} - mass_{solute} = 3.10\text{x}10^2 \text{ g} - 2.386695 \text{ g } C_2H_6O_2 = 307.613305 = 308 \text{ g } H_2O$

Therefore, **add 2.39 g $C_2H_6O_2$ to 308 g of H_2O** to make a 0.125 m solution.

b) Mass (kg) of HNO_3 in the 2.20% solution $= \left(1.20 \text{ kg}\right)\left(\dfrac{2.20\%}{100\%}\right) = 0.0264 \text{ kg } HNO_3$ (solute)

$$\text{Mass \%} = \dfrac{\text{mass of solute}}{\text{mass of solution}}(100)$$

Mass of 52.0% solution containing 0.0264 kg $HNO_3 = \dfrac{\text{mass of solute}(100)}{\text{mass \%}} = \dfrac{0.0264 \text{ kg}(100)}{52.0\%}$

$$= 0.050769 = 0.0508 \text{ kg}$$

Mass of water added = mass of 2.2% solution – mass of 52.0% solution

$$= 1.20 \text{ kg} - 0.050769 \text{ kg} = 1.149231 = 1.15 \text{ kg}$$

Add 0.0508 kg of the 52.0% (w/w) HNO_3 to 1.15 kg H_2O to make 1.20 kg of 2.20% (w/w) HNO_3.

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

$$mass_{solute} + mass_{solvent} = 1.50 \text{ kg}$$

Mass (g) of C_2H_5OH in 1000 g (1 kg) of $H_2O = \left(1 \text{ kg } H_2O\right)\left(\dfrac{0.0355 \text{ mol } C_2H_5OH}{1 \text{ kg } H_2O}\right)\left(\dfrac{46.07 \text{ g } C_2H_5OH}{1 \text{ mol } C_2H_5OH}\right)$

$$= 1.635485 \text{ g } C_2H_5OH$$

Mass (g) of this solution = 1000 g H_2O + 1.635485 g C_2H_5OH = 1001.635485 g

Mass (g) of C_2H_5OH for 1.50 kg of solution $= \left(\dfrac{1.635485 \text{ g } C_2H_5OH}{1001.635485 \text{ g solution}}\right)\left(1500 \text{ g solution}\right)$

$$= 2.449222 = 2.45 \text{ g } C_2H_5OH$$

$Mass_{solvent} = 1500 \text{ g} - mass_{solute} = 1500 \text{ g} - 2.449222 \text{ g } C_2H_5OH = 1497.551 = 1498 \text{ g } H_2O$

Therefore, **add 2.45 g C_2H_5OH to 1498 g of H_2O** to make a 0.0355 m solution.

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

Mass (kg) of HCl in the 13.0% solution $= \left(445 \text{ g}\right)\left(\dfrac{13.0\%}{100\%}\right) = 57.85 \text{ g HCl}$ (solute)

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

$$\text{Mass \%} = \dfrac{\text{mass of solute}}{\text{mass of solution}}(100)$$

Mass of 34.1% solution containing 57.85 g HCl $= \dfrac{\text{mass of solute}(100)}{\text{mass \%}} = \dfrac{57.85 \text{ g}(100)}{34.1\%} = 169.6481 = 170. \text{ g}$

Mass of water added = mass of 13.0% solution – mass of 34.1% solution

$$= 445 \text{ g} - 169.6481 \text{ g} = 275.35191 = 275 \text{ g}$$

Add 170. g of the 34.1% (w/w) HCl to 275 g H_2O

13.53 Plan: You know the moles of solute (C_3H_7OH) and the moles of solvent (H_2O). Divide moles of C_3H_7OH by the total moles of C_3H_7OH and H_2O to obtain mole fraction. To calculate mass percent, convert moles of solute and solvent to mass and divide the mass of solute by the total mass of solution (solute + solvent). For molality, divide the moles of C_3H_7OH by the mass of water expressed in units of kg.
Solution:
a) Mole fraction is moles of isopropanol per total moles.

$$X_{isopropanol} = \dfrac{\text{moles of isopropanol}}{\text{moles of isopropanol + moles of water}} = \dfrac{0.35 \text{ mol isopropanol}}{\left(0.35 + 0.85\right) \text{ mol}} = 0.2916667 = \mathbf{0.29}$$

(Notice that mole fractions have no units.)

b) Mass percent $= \dfrac{\text{mass of solute}}{\text{mass of solution}}(100)$. From the mole amounts, find the masses

of isopropanol and water:

$$\text{Mass (g) of isopropanol} = \left(0.35 \text{ mol } C_3H_7OH\right)\left(\frac{60.09 \text{ g } C_3H_7OH}{1 \text{ mol } C_3H_7OH}\right) = 21.0315 \text{ g isopropanol}$$

$$\text{Mass (g) of water} = \left(0.85 \text{ mol } H_2O\right)\left(\frac{18.02 \text{ g } H_2O}{1 \text{ mol } H_2O}\right) = 15.317 \text{ g water}$$

$$\text{Mass percent } = \frac{\text{mass of solute}}{\text{mass of solution}}(100) = \frac{21.0315 \text{ g isopropanol}}{(21.0315 + 15.317) \text{ g}}(100) = 57.860710 = \textbf{58\%}$$

c) Molality of isopropanol is moles of isopropanol per kg of water.

$$m = \frac{\text{moles of solute}}{\text{kg of solvent}} = \frac{0.35 \text{ mol isopropanol}}{15.317 \text{ g water}}\left(\frac{10^3 \text{ g}}{1 \text{ kg}}\right) = 22.85043 = \textbf{23 } \textbf{\textit{m}} \text{ isopropanol}$$

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

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

b) Mass percent is the mass of NaCl per 100 g of solution.
Mass (g) of NaCl = (0.100 mol NaCl)(58.44 g/mol) = 5.844 g NaCl
Mass (g) of water = (8.60 mol water)(18.02 g/mol) = 154.972 g water

$$\text{Mass percent NaCl} = \frac{(5.844 \text{ g NaCl})}{(5.844 + 154.972)\text{g}} \times 100\% = 3.63396677 = \textbf{3.63\%} \text{ NaCl}$$

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

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

13.55   Plan: You are given the mass percent of the solution. Assuming 100. g of solution allows us to express the mass % as the mass of solute, NH_3. To find the mass of solvent, subtract the mass of NH_3 from the mass of solution and convert to units of kg. To find molality, convert mass of NH_3 to moles and divide by the mass of solvent in kg. To find molarity, you will need the volume of solution. Use the density of the solution to convert the 100. g of solution to volume in liters; divide moles of NH_3 by volume of solution. To find the mole fraction, convert mass of solvent to moles and divide moles of NH_3 by the total moles.
Solution:
Determine some fundamental quantities:

$$\text{Mass (g) of } NH_3 = \left(100 \text{ g solution}\right)\left(\frac{8.00\% \text{ } NH_3}{100\% \text{ solution}}\right) = 8.00 \text{ g } NH_3$$

Mass (g) H_2O = mass of solution – mass NH_3 = (100.00 – 8.00) g = 92.00 g H_2O

$$\text{Mass (kg) of } H_2O = \left(92.00 \text{ g } H_2O\right)\left(\frac{1 \text{ kg}}{10^3 \text{ g}}\right) = 0.09200 \text{ kg } H_2O$$

$$\text{Moles of } NH_3 = \left(8.00 \text{ g } NH_3\right)\left(\frac{1 \text{ mol } NH_3}{17.03 \text{ g } NH_3}\right) = 0.469759 \text{ mol } NH_3$$

$$\text{Moles of } H_2O = \left(92.00 \text{ g } H_2O\right)\left(\frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O}\right) = 5.1054 \text{ mol } H_2O$$

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

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

$$\text{Molality} = m = \frac{\text{moles of solute}}{\text{kg of solvent}} = \left(\frac{0.469759 \text{ mol } NH_3}{0.09200 \text{ kg } H_2O}\right) = 5.106076 = \textbf{5.11 } \textbf{\textit{m}} \textbf{ NH}_3$$

$$\text{Molarity} = M = \frac{\text{moles of solute}}{\text{L of solution}} = \left(\frac{0.469759 \text{ mol NH}_3}{0.103616 \text{ L}}\right) = 4.53365 = \textbf{4.53 } \boldsymbol{M} \textbf{ NH}_3$$

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

13.56   The information given is 28.8 mass % $FeCl_3$ solution with a density of 1.280 g/mL.
For convenience, choose exactly 100.00 g of solution.
Determine some fundamental quantities:
Mass (g) of $FeCl_3$ = (100.00 g solution)(28.8% $FeCl_3$/100%) = 28.8 g $FeCl_3$
Mass (g) of H_2O = mass of solution – mass $FeCl_3$ = (100.00 – 28.8) g = 71.20 g H_2O
Moles of $FeCl_3$ = (28.80 g $FeCl_3$)(1 mol $FeCl_3$/162.20 g $FeCl_3$) = 0.1775586 mol $FeCl_3$
Moles of H_2O = (71.20 g H_2O)(1 mol H_2O/18.02 g H_2O) = 3.951165 mol H_2O
Volume of solution = (100.00 g solution)(1 mL/1.280 g)(10^{-3} L/1 mL) = 0.078125 L
Using the above fundamental quantities and the definitions of the various units:

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

$$\text{Molarity} = m = \text{moles solute/L solution} = \frac{0.1775586 \text{ mol FeCl}_3}{0.078125 \text{ L}} = 2.272750 = \textbf{2.27 } \boldsymbol{M} \textbf{ FeCl}_3$$

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

13.57   <u>Plan:</u> Use the equation for parts per million, ppm. Use the given density of solution to find the mass of solution; divide the mass of each ion by the mass of solution and multiply by 1×10^6.
<u>Solution:</u>

$$\text{Mass (g) of solution is } (100.0 \text{ L solution})\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)\left(\frac{1.001 \text{ g}}{1 \text{ mL}}\right) = 1.001\times10^5 \text{ g}$$

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

$$\text{ppm Ca}^{2+} = \left(\frac{0.25 \text{ g Ca}^{2+}}{1.001\times10^5 \text{ g solution}}\right) \times 10^6 = 2.49750 = \textbf{2.5 ppm Ca}^{2+}$$

$$\text{ppm Mg}^{2+} = \left(\frac{0.056 \text{ g Mg}^{2+}}{1.001\times10^5 \text{ g solution}}\right) \times 10^6 = 0.5594406 = \textbf{0.56 ppm Mg}^{2+}$$

13.58   The information given is that 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 L as the equal volumes mixed. Ethylene glycol will be designated EG.
Determine some fundamental quantities:
Mass (g) of EG = (1.0000 L EG)(1mL/10^{-3} L)(1.114 g EG/mL) = 1114 g EG
Mass (g) of H_2O = (1.0000 L H_2O)(1mL/10^{-3} L)(1.00 g H_2O/mL) = 1.00×10^3 g H_2O
Moles of EG = (1114 g EG)(1 mol EG/62.07 g EG) = 17.94747865 mol EG
Moles of H_2O = (1.00×10^3 g H_2O)(1 mol H_2O/18.02 g H_2O) = 55.49389567 mol H_2O
Volume (L) of solution = (1114 g EG + 1.00×10^3 g H_2O)(1 mL/1.070 g)(10^{-3} L/1 mL)
                = 1.97570 L
Using the above fundamental quantities and the definitions of the various units:
a) Volume percent = (1.0000 L EG/1.97570 L)100% = 50.61497 = **50.61% v/v**
b) Mass percent = [(1114 g EG)/(1114 + 1.00×10^3) g]100% = 52.6963 = **52.7% w/w**

c) Molarity = moles solute/L solution = $\dfrac{17.94747865 \text{ mol EC}}{1.97570 \text{ L}}$ = 9.08411 = **9.08 *M* ethylene glycol**

d) Molality = moles solute/kg solvent = $\dfrac{17.94747865 \text{ mol EG}}{1.00 \times 10^3 \text{ g H}_2\text{O}}\left(\dfrac{10^3 \text{ g}}{1 \text{ kg}}\right)$

$= 17.94747865 =$ **17.9 *m* ethylene glycol**

e) Mole fraction = X_{EG} = moles substance/total moles = $\dfrac{17.94747865 \text{ mol EG}}{(17.94747865 + 55.49389567)\text{ mol}}$

$= 0.244378 =$ **0.244**

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 (K^+ and 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 ΔT_f would be greater.

13.64 <u>Plan:</u> 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.
<u>Solution:</u>
a) **Strong electrolyte** When hydrogen chloride is bubbled through water, it dissolves and dissociates completely into H^+ (or H_3O^+) ions and Cl^- ions. HCl is a strong acid.
b) **Strong electrolyte** Potassium nitrate is a soluble salt and dissociates into K^+ and NO_3^- ions in water.
c) **Nonelectrolyte** Glucose solid dissolves in water to form individual $C_6H_{12}O_6$ molecules, but these units are not ionic and therefore do not conduct electricity. Glucose is a molecular compound.
d) **Weak electrolyte** Ammonia gas dissolves in water, but is a weak base that forms few NH_4^+ and OH^- ions.

13.65 a) $NaMnO_4$ **strong electrolyte**
b) CH_3COOH **weak electrolyte**
c) CH_3OH **nonelectrolyte**
d) $Ca(C_2H_3O_2)_2$ **strong electrolyte**

13.66 <u>Plan:</u> 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.
<u>Solution:</u>
a) $\left(\dfrac{0.3 \text{ mol KBr}}{\text{L}}\right)\left(\dfrac{2 \text{ mol particles}}{1 \text{ mol KBr}}\right)(1 \text{ L}) =$ **0.6 mol of particles**

Each KBr forms one K^+ ion and one Br^- ion, two particles for each KBr.

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

HNO_3 is a strong acid that forms $H^+(H_3O^+)$ ions and NO_3^- ions in aqueous solution.

c) $\left(\dfrac{10^{-4} \text{ mol } KHSO_4}{L}\right)\left(\dfrac{2 \text{ mol particles}}{1 \text{ mol } KHSO_4}\right)(1 \text{ L}) = \textbf{2x10}^{-4} \textbf{ mol of particles}$

Each $KHSO_4$ forms one K^+ ion and one HSO_4^- ion in aqueous solution, two particles for each $KHSO_4$.

d) $\left(\dfrac{0.06 \text{ mol } C_2H_5OH}{L}\right)\left(\dfrac{1 \text{ mol particles}}{1 \text{ mol } C_2H_5OH}\right)(1 \text{ L}) = \textbf{0.06 mol of particles}$

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) (0.02 mol $CuSO_4$/L)(2 mol particles/mol $CuSO_4$)(10^{-3} L/1 mL)(1 mL) = **4x10^{-5} mol of particles**
   b) (0.004 mol $Ba(OH)_2$/L)(3 mol particles/mol $Ba(OH)_2$)(10^{-3} L/1 mL)(1 mL)
       = 1.2x10^{-5} = **1x10^{-5} mol of particles**
   c) (0.08 mol C_5H_5N/L)(1 mol particles/mol C_5H_5N)(10^{-3} L/1 mL)(1 mL) = **8x10^{-5} mol of particles**
   d) (0.05 mol $(NH_4)_2CO_3$/L)(3 mol particles/mol $(NH_4)_2CO_3$)(10^{-3} L/1 mL)(1 mL)
       = 1.5x10^{-4} = **2x10^{-4} mol of particles**

13.68   <u>Plan:</u> The magnitude of freezing point depression is directly proportional to molality. Calculate the molality of solution by dividing the moles of solute by the mass of solvent in kg. The solution with the larger molality will have the lower freezing point.
   <u>Solution:</u>

a) Molality of $CH_3OH = \dfrac{(11.0 \text{ g } CH_3OH)}{(100. \text{ g } H_2O)}\left(\dfrac{1 \text{ mol } CH_3OH}{32.04 \text{ g } CH_3OH}\right)\left(\dfrac{10^3 \text{ g}}{1 \text{ kg}}\right) = 3.4332085 = 3.43 \ m \ CH_3OH$

Molality of $CH_3CH_2OH = \dfrac{(22.0 \text{ g } CH_3CH_2OH)}{(200. \text{ g } H_2O)}\left(\dfrac{1 \text{ mol } CH_3CH_2OH}{46.07 \text{ g } CH_3CH_2OH}\right)\left(\dfrac{10^3 \text{ g}}{1 \text{ kg}}\right)$
$= 2.387671 = 2.39 \ m \ CH_3CH_2OH$

The molality of methanol, CH_3OH, in water is 3.43 m whereas the molality of ethanol, CH_3CH_2OH, in water is 2.39 m. Thus, **CH_3OH/H_2O solution** has the lower freezing point.

b) Molality of $H_2O = \dfrac{(20.0 \text{ g } H_2O)}{(1.00 \text{ kg } CH_3OH)}\left(\dfrac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O}\right) = 1.10988 = 1.11 \ m \ H_2O$

Molality of $CH_3CH_2OH = \dfrac{(20.0 \text{ g } CH_3CH_2OH)}{(1.00 \text{ kg } CH_3OH)}\left(\dfrac{1 \text{ mol } CH_3CH_2OH}{46.07 \text{ g } CH_3CH_2OH}\right) = 0.434122 = 0.434 \ m \ CH_3CH_2OH$

The molality of H_2O in CH_3OH is 1.11 m, whereas CH_3CH_2OH in CH_3OH is 0.434 m. Therefore, **H_2O/CH_3OH solution** has the lower freezing point.

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

a) Molality of $C_3H_8O_3 = \dfrac{(38.0 \text{ g } C_3H_8O_3)}{(250. \text{ g ethanol})}\left(\dfrac{1 \text{ mol } C_3H_8O_3}{92.09 \text{ g } C_3H_8O_3}\right)\left(\dfrac{10^3 \text{ g}}{1 \text{ kg}}\right) = 1.650559 = 1.65 \ m \ C_3H_8O_3$

Molality of $C_2H_6O_2 = \dfrac{(38.0 \text{ g } C_2H_6O_2)}{(250. \text{ g ethanol})}\left(\dfrac{1 \text{ mol } C_2H_6O_2}{62.07 \text{ g } C_2H_6O_2}\right)\left(\dfrac{10^3 \text{ g}}{1 \text{ kg}}\right) = 2.44885 = 2.45 \ m \ C_2H_6O_2$

The molality of $C_2H_6O_2$, in ethanol is 2.45 m whereas the molality of $C_3H_8O_3$, in ethanol is 1.65 m. Thus, **$C_2H_6O_2$/ethanol solution** has the higher boiling point.

b) Molality of $C_2H_6O_2 = \dfrac{(15 \text{ g } C_2H_6O_2)}{(0.50 \text{ kg } H_2O)}\left(\dfrac{1 \text{ mol } C_2H_6O_2}{62.07 \text{ g } C_2H_6O_2}\right) = 0.4833253 = 0.48 \ m \ C_2H_6O_2$

Molality of $NaCl = \dfrac{(15 \text{ g } NaCl)}{(0.50 \text{ kg } H_2O)}\left(\dfrac{1 \text{ mol } NaCl}{58.44 \text{ g } NaCl}\right) = 0.513347 = 0.51 \ m \ NaCl$

Since the NaCl is a strong electrolyte, the molality of particles would be:
       (2 particles/NaCl)(0.513347 mol NaCl/kg) = 1.026694 = 1.0 m particles

The molality of $C_2H_6O_2$ in H_2O is 0.48 m, whereas NaCl in H_2O is 1.0 m. Therefore, **NaCl/H_2O solution** has the higher boiling point.

13.70   Plan: 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, the higher the boiling point, the lower the freezing point, and the lower the vapor pressure at a given temperature.
Solution:

$$(I)\,(0.100\ m\ NaNO_3)\left(\frac{2\ \text{mol particles}}{1\ \text{mol NaNO}_3}\right) = 0.200\ m\ \text{ions}$$

$NaNO_3$ consists of Na^+ ions and NO_3^- ions, two particles for each $NaNO_3$.

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

Glucose 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.

$$(III)\,(0.100\ m\ CaCl_2)\left(\frac{3\ \text{mol particles}}{1\ \text{mol CaCl}_2}\right) = 0.300\ m\ \text{ions}$$

$CaCl_2$ consists of Ca^{+2} ions and Cl^- ions, three particles for each $CaCl_2$.
a) Osmotic pressure: $\Pi_{II} < \Pi_I < \Pi_{III}$
b) Boiling point: $bp_{II} < bp_I < bp_{III}$
c) Freezing point: $fp_{III} < fp_I < fp_{II}$
d) Vapor pressure at 50°C: $vp_{III} < vp_I < vp_{II}$

13.71   I 0.04 m $(H_2N)_2CO$ x 1 mol particles/1 mol $(H_2N)_2CO$ = 0.04 m molecules
II 0.01 m $AgNO_3$ x 2 mol particles/1 mol $AgNO_3$ = 0.02 m ions
III 0.03 m $CuSO_4$ x 2 mol particles/1 mol $CuSO_4$ = 0.06 m ions
a) Osmotic pressure: $\Pi_{III} > \Pi_I > \Pi_{II}$
b) Boiling point: $bp_{III} > bp_I > bp_{II}$
c) Freezing point: $fp_{II} > fp_I > fp_{III}$
d) Vapor pressure at 298 K: $vp_{II} > vp_I > vp_{III}$

13.72   Plan: The mole fraction of solvent affects the vapor pressure according to the equation $P_{solvent} = X_{solvent}P°_{solvent}$. Convert the masses of glycerol and water to moles and find the mole fraction of water by dividing moles of water by the total number of moles. Multiply the mole fraction of water by the vapor pressure of water to find the vapor pressure of the solution.
Solution:

$$\text{Moles of } C_3H_8O_3 = (34.0\ g\ C_3H_8O_3)\left(\frac{1\ \text{mol C}_3H_8O_3}{92.09\ g\ C_3H_8O_3}\right) = 0.369204\ \text{mol } C_3H_8O_3$$

$$\text{Moles of } H_2O = (500.0\ g\ H_2O)\left(\frac{1\ \text{mol H}_2O}{18.02\ g\ H_2O}\right) = 27.7469\ \text{mol } H_2O$$

$$X_{solvent} = \frac{\text{mol H}_2O}{\text{mol H}_2O + \text{mol glycerol}} = \frac{27.7469\ \text{mol H}_2O}{27.7469\ \text{mol H}_2O + 0.369204\ \text{mol glycerol}} = 0.9868686$$

$P_{solvent} = X_{solvent}P°_{solvent} = (0.9868686)(23.76\ \text{torr}) = 23.447998 = $ **23.4 torr**

13.73   The mole fraction of solvent affects the vapor pressure according to the equation $P_{solvent} = X_{solvent}P°_{solvent}$.
$X_{solvent}$ = (5.4 mol toluene)/[(0.39) + (5.4)] mol = 0.93264
$P_{solvent} = X_{solvent}P°_{solvent} = (0.93264)(41\ \text{torr}) = 38.2382 = $ **38 torr**

13.74   Plan: 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 ΔT_f is calculated, the freezing point is determined by subtracting it from the freezing point of pure water (0.00°C).
Solution:
$\Delta T_f = iK_f m = (1)(1.86°C/m)(0.251\ m) = 0.46686°C$
The freezing point is 0.00°C – 0.46686°C = –0.46686 = **–0.467°C**.

13.75 $\Delta T_b = iK_b m = (1)(0.512°C/m)(0.200\ m) = 0.1024°C$
The boiling point is 100.00°C + 0.1024°C = 100.1024 = **100.10°C**.

13.76   Plan: 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 (it is a molecular compound) so $i = 1$. To find the molality, convert mass of vanillin to moles and divide by the mass of solvent expressed in units of kg. K_b is given (1.22°C/m).
Solution:

$$\text{Moles of vanillin} = \left(6.4\ \text{g vanillin}\right)\left(\frac{1\ \text{mol vanillin}}{152.14\ \text{g vanillin}}\right) = 0.0420665\ \text{mol}$$

$$\text{Molality of vanillin} = \frac{\text{moles of vanillin}}{\text{kg of solvent (ethanol)}} = \frac{0.042065\ \text{mol vanillin}}{50.0\ \text{g ethanol}}\left(\frac{10^3\ \text{g}}{1\ \text{kg}}\right)$$

$$= 0.8413\ m\ \text{vanillin}$$

$\Delta T_b = iK_b m = (1)(1.22°C/m)(0.8413\ m) = 1.026386°C$
The boiling point is 78.5°C + 1.026386°C = 79.5264 = **79.5°C**.

13.77   Moles of $C_{10}H_8$ = (5.00 g $C_{10}H_8$)(1 mol $C_{10}H_8$/128.16 g $C_{10}H_8$) = 0.0390137 mol $C_{10}H_8$
$C_{10}H_8$ is a nonelectrolyte so $i = 1$.
Mass = (444 g benzene)(1 kg/10^3 g) = 0.444 kg benzene
Molality = (0.0390137 mol $C_{10}H_8$)/(0.444 kg) = 0.08786869 m
$\Delta T_f = iK_f m = (1)(4.90°C/m)(0.08786869\ m) = 0.43056°C$
Freezing point = (5.5 – 0.43056)°C = 5.06944 = **5.1°C**

13.78   Plan: The molality of the solution can be determined from the relationship $\Delta T_f = iK_f m$ with the value 1.86°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 °C and find ΔT_f by subtracting the freezing point of the solvent from the freezing point of the solution. Once the molality of the solution is known, the mass of ethylene glycol needed for a solution of that molality can be found.
Solution:
°C = (5/9)(°F – 32.0) = (5/9)(–12.0°F – 32.0) = –24.44444°C
$\Delta T_f = T_{f(\text{solution})} - T_{f(\text{solvent})} = (0.00 - (-24.44444))°C = 24.44444°C$
$\Delta T_f = iK_f m$

$$m = \frac{\Delta T_f}{K_f} = \frac{24.44444°C}{1.86°C/m} = 13.14217\ m$$

Ethylene glycol will be abbreviated as EG.

$$\text{Molality of EG} = \frac{\text{moles of EG}}{\text{kg of solvent (water)}}$$

$$\text{Moles of EG} = \text{molality x kg of solvent} = \left(\frac{13.14217\ \text{mol EG}}{1\ \text{kg H}_2\text{O}}\right)(14.5\ \text{kg H}_2\text{O}) = 190.561465\ \text{mol EG}$$

$$\text{Mass (g) of ethylene glycol} = \left(190.561465\ \text{mol EG}\right)\left(\frac{62.07\ \text{g EG}}{1\ \text{mol EG}}\right)$$

$$= 1.18282 \times 10^4 = \textbf{1.18} \times \textbf{10}^{\textbf{4}}\ \textbf{g ethylene glycol}$$

To prevent the solution from freezing, dissolve a minimum of 1.18×10^4 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°C/m inserted for K_f, $i = 1$ for the nonelectrolyte glycerol, and the given ΔT_f of –15°C.
$m = \Delta T_f / K_f = (15°C/(1.86°C/m)) = 8.06452\ m$
Glycerol will be abbreviated as GLY.

$$\text{Mass (g) of glycerol} = \left(\frac{8.06452\ \text{mol GLY}}{1\ \text{kg H}_2\text{O}}\right)(11.0\ \text{mg H}_2\text{O})\left(\frac{10^{-3}\ \text{g}}{1\ \text{mg}}\right)\left(\frac{1\ \text{kg}}{10^3\ \text{g}}\right)\left(\frac{92.09\ \text{g GLY}}{1\ \text{mol GLY}}\right)$$

$$= 0.0081693 = \textbf{0.0082 g glycerol}$$

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

13.80 Plan: Assume 100. g of solution so that the mass of solute = mass percent. Convert the mass of solute to moles. Subtract the mass of the solute from 100. g to obtain the mass of solution. Divide moles of solute by the mass of solvent in kg to obtain molality. Use $\Delta T = iK_f m$ to find the van't Hoff factor. K_f for water = 1.86°C/m.
Solution:
a) Assume exactly 100 g of solution.

$$\text{Mass (g) of NaCl} = (100.00\ \text{g solution})\left(\frac{1.00\%\ \text{NaCl}}{100\%\ \text{solution}}\right) = 1.00\ \text{g NaCl}$$

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

Mass of H_2O = 100.00 g solution – 1.00 g NaCl = 99.00 g H_2O

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

$\Delta T_f = T_{f(\text{solution})} - T_{f(\text{solvent})} = 0.000°C - (-0.593)°C = 0.593°C$
$\Delta T_f = iK_f m$

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

The value of i should be close to two because NaCl dissociates into two particles when dissolving in water.
b) For acetic acid, CH_3COOH:
Assume exactly 100 g of solution.

$$\text{Mass (g) of CH}_3\text{COOH} = (100.00\ \text{g solution})\left(\frac{0.500\%\ \text{CH}_3\text{COOH}}{100\%\ \text{solution}}\right) = 0.500\ \text{g CH}_3\text{COOH}$$

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

Mass (g) of H_2O = 100.00 g solution – 0.500 g CH_3COOH = 99.500 g H_2O

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

$$= 0.083682 = \textbf{0.0837 \textit{m} CH}_3\textbf{COOH}$$

$\Delta T_f = T_{f(\text{solution})} - T_{f(\text{solvent})} = 0.000°C - (-0.159)°C = 0.159°C$
$\Delta T_f = iK_f m$

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

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 g of solution. Thus, the solution contains 0.500 g of KCl in 99.500 g of water.

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

Calculate $\Delta T_f = 0.000°C - (-0.234)°C = 0.234°C$

$\Delta T_f = iK_f m$

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

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

b) For sulfuric acid, H_2SO_4:

Assume exactly 100 g of solution. Thus, the solution contains 1.00 g of H_2SO_4 in 99.00 g of water.

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

Calculate $\Delta T = 0.000°C - (-0.423)°C = 0.423°C$

$\Delta T_f = iK_f m$

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

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 ($\Pi = iMRT$) to find the molarity of the solution (assuming $i = 1$).

$$M = \Pi/iRT = \frac{0.272 \text{ atm}}{(1)\left(0.0821\dfrac{\text{L•atm}}{\text{mol•K}}\right)((273 + 25)\text{K})} = 0.01111756 \text{ } M$$

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

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 <u>Plan:</u> The mole fraction of solvent affects the vapor pressure according to the equation $P_{\text{solvent}} = X_{\text{solvent}}P°_{\text{solvent}}$. Find the mole fraction of each substance by dividing moles of substance by the total number of moles. Multiply the mole fraction of each compound by its vapor pressure to find the vapor pressure of the compounds above the solution.

<u>Solution:</u>

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

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

$P_A = X_A P°_A$

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

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

13.84 a) Total molarity of ions:

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

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

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

b) Molarity of compound:

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

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

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

Solution A has the highest molarity.

c) Molality of compound:

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

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

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

Solution C has the lowest molality.

d) Osmotic pressure: assume a temperature of 298 K

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

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

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

Solution A has the highest osmotic pressure.

13.85   Plan: 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.
Solution:
1 troy ounce = 31.1 g gold

$1.1 \times 10^{-2} \text{ ppb} = \dfrac{\text{mass of gold}}{\text{mass of seawater}} \times 10^9$

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

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

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

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

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　**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.

13.88　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.

13.89　Price NaCl ($/ion) = ($0.22/kg NaCl)(1 kg/10^3 g)(58.44 g NaCl/1 mol NaCl)(1 mol NaCl/2 ions)
　　　　　　= $ 6.4284 x 10^{-3}/ion
Price CaCl$_2$ ($/kg) = ($ 6.4284 x 10^{-3}/ion)(3 mol ions/1 mol CaCl$_2$)(1 mol CaCl$_2$/110.98 g CaCl$_2$)(10^3 g/kg)
　　　　　　= 0.17377 = **$ 0.17/kg CaCl$_2$**

13.90　Plan: Convert the mass of O_2 dissolved to moles of O_2. Use the density to convert the 1 kg mass of solution to volume in L. Divide moles of O_2 by volume of solution in L to obtain molarity.
Solution:
0.0°C:

Moles of $O_2 = \left(\dfrac{14.5\ \text{mg}\ O_2}{1\ \text{kg}\ H_2O}\right)\left(\dfrac{10^{-3}\ \text{g}}{1\ \text{mg}}\right)\left(\dfrac{1\ \text{mol}\ O_2}{32.00\ \text{g}\ O_2}\right) = 4.53125\text{x}10^{-4}\ \text{mol}\ O_2$

Volume (L) of solution $= \left(1\ \text{kg}\right)\left(\dfrac{10^3\ \text{g}}{1\text{kg}}\right)\left(\dfrac{1\ \text{mL}}{0.99987\ \text{g}}\right)\left(\dfrac{10^{-3}\ \text{L}}{1\text{mL}}\right) = 1.000130017\ \text{L}$

$M = \dfrac{\text{moles of}\ O_2}{\text{L of solution}} = \dfrac{4.53125\text{x}10^{-4}\ \text{mol}}{1.000130017\ \text{L}} = 4.53066\text{x}10^{-4} = \mathbf{4.53\text{x}10^{-4}\ \textit{M}\ O_2}$
20.0°C:

Moles of $O_2 = \left(\dfrac{9.07\ \text{mg}\ O_2}{1\ \text{kg}\ H_2O}\right)\left(\dfrac{10^{-3}\ \text{g}}{1\ \text{mg}}\right)\left(\dfrac{1\ \text{mol}\ O_2}{32.00\ \text{g}\ O_2}\right) = 2.834375\text{x}10^{-4}\ \text{mol}\ O_2$

Volume (L) of solution $= \left(1\ \text{kg}\right)\left(\dfrac{10^3\ \text{g}}{1\text{kg}}\right)\left(\dfrac{1\ \text{mL}}{0.99823\ \text{g}}\right)\left(\dfrac{10^{-3}\ \text{L}}{1\text{mL}}\right) = 1.001773138\ \text{L}$

$M = \dfrac{\text{moles of}\ O_2}{\text{L of solution}} = \dfrac{2.834375\text{x}10^{-4}\ \text{mol}}{1.001773138\ \text{L}} = 2.829358\text{x}10^{-4} = \mathbf{2.83\text{x}10^{-4}\ \textit{M}\ O_2}$
40.0°C:

Moles of $O_2 = \left(\dfrac{6.44\ \text{mg}\ O_2}{1\ \text{kg}\ H_2O}\right)\left(\dfrac{10^{-3}\ \text{g}}{1\ \text{mg}}\right)\left(\dfrac{1\ \text{mol}\ O_2}{32.00\ \text{g}\ O_2}\right) = 2.0125\text{x}10^{-4}\ \text{mol}\ O_2$

Volume (L) of solution $= \left(1\ \text{kg}\right)\left(\dfrac{10^3\ \text{g}}{1\text{kg}}\right)\left(\dfrac{1\ \text{mL}}{0.99224\ \text{g}}\right)\left(\dfrac{10^{-3}\ \text{L}}{1\text{mL}}\right) = 1.007820689\ \text{L}$

$M = \dfrac{\text{moles of}\ O_2}{\text{L of solution}} = \dfrac{2.0125\text{x}10^{-4}\ \text{mol}}{1.007820689\ \text{L}} = 1.996883\text{x}10^{-4} = \mathbf{2.00\text{x}10^{-4}\ \textit{M}\ O_2}$

13.91 Plan: First, find the molality from the freezing point depression using the relationship $\Delta T = iK_f m$ 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 ($i = 1$). Use the mass percent data to find the empirical formula of the compound; the molar mass is used to convert the empirical formula to the molecular formula. A Lewis structure that forms hydrogen bonds must have H atoms bonded to O atoms.

Solution:

a) $\Delta T_f = iK_f m = 0.000\,°C - (-0.201\,°C) = 0.201\,°C$

$$m = \frac{\Delta T_f}{K_f i} = \frac{0.201°\mathrm{C}}{\left(1.86°\mathrm{C}/m\right)(1)} = 0.1080645\ m$$

$$\text{Mass (kg) of solvent} = \left(25.0\ \mathrm{mL}\right)\left(\frac{1.00\ \mathrm{g}}{1\ \mathrm{mL}}\right)\left(\frac{1\ \mathrm{kg}}{10^3\ \mathrm{g}}\right) = 0.0250\ \mathrm{kg\ water}$$

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

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

$$\text{Molar mass} = \frac{0.243\ \mathrm{g}}{0.0027016\ \mathrm{mol}} = 89.946698 = \textbf{89.9 g/mol}$$

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.

$$\text{Moles C} = \left(53.31\ \mathrm{g\ C}\right)\left(\frac{1\ \mathrm{mol\ C}}{12.01\ \mathrm{g\ C}}\right) = 4.43880\ \mathrm{mol\ C};\qquad \frac{4.43880}{2.219375} = 2$$

$$\text{Moles H} = \left(11.18\ \mathrm{g\ H}\right)\left(\frac{1\ \mathrm{mol\ H}}{1.008\ \mathrm{g\ H}}\right) = 11.09127\ \mathrm{mol\ H};\qquad \frac{11.09127}{2.219375} = 5$$

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

Dividing the values by the lowest amount of moles (2.219375) gives an **empirical formula of C_2H_5O** 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 $2(C_2H_5O)$ or $C_4H_{10}O_2$**.

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

Forms hydrogen bonds   Does not form hydrogen bonds
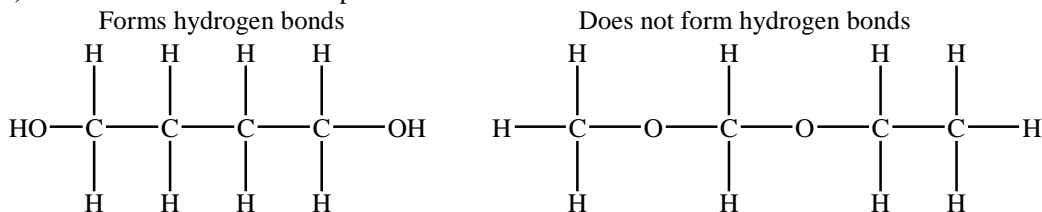
13.92 **No**, both are the same because masses are additive.

13.93 a) $X_{N_2} = \dfrac{\text{moles of N}_2}{\text{total moles}}$

Mixture A: $X_{N_2} = \dfrac{3\ \text{moles N}_2}{3 + 2 + 3\ \text{moles}} = 0.38$ Mixture B: $X_{N_2} = \dfrac{4\ \text{moles N}_2}{4 + 4 + 2\ \text{moles}} = 0.40$

Mixture C: $X_{N_2} = \dfrac{4\ \text{moles N}_2}{4 + 3 + 5\ \text{moles}} = 0.33$

Mixture C has the smallest mole fraction of N_2.

b) Mixture A: $X_{Ne} = \dfrac{2 \text{ moles Ne}}{3 + 2 + 3 \text{ moles}} = 0.25$ Mixture B: $X_{Ne} = \dfrac{4 \text{ moles Ne}}{4 + 4 + 2 \text{ moles}} = 0.40$

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

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

c) Mixture A: $X_{Cl_2} = \dfrac{3 \text{ moles Cl}_2}{3 + 2 + 3 \text{ moles}} = 0.38$ Mixture B: $X_{Cl_2} = \dfrac{2 \text{ moles Cl}_2}{4 + 4 + 2 \text{ moles}} = 0.20$

Mixture C: $X_{Cl_2} = \dfrac{5 \text{ moles Cl}_2}{4 + 3 + 5 \text{ moles}} = 0.42$

Mixture B < Mixture A < Mixture C

13.94   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.

13.95   Calculate the individual partial pressures from $P_{solvent} = X_{solvent}P°_{solvent}$. Assign the "equal masses" as exactly 1 g.
        Liquid:

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

$P_{solvent} = X_{solvent}P°_{solvent}$
$P(\text{pinene}) = (0.53100)(100.3 \text{ torr}) = 53.2593 \text{ torr}$

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

$P_{solvent} = X_{solvent}P°_{solvent}$
$P(\text{terpineol}) = (0.4689985)(9.8 \text{ torr}) = 4.5961853 \text{ torr}$

Vapor:

$$X \text{ (pinene)} = \dfrac{53.2593 \text{ torr}}{(53.2593 + 4.5961853) \text{ torr}} = 0.9205575 = \mathbf{0.921}$$

$$X \text{ (terpineol)} = \dfrac{4.5961855 \text{ torr}}{(53.2593 + 4.5961853) \text{ torr}} = 0.0794425 = \mathbf{0.079}$$

13.96   <u>Plan:</u> Use the boiling point elevation of 0.45°C to calculate the molality of the solution using the relationship
        $\Delta T_b = iK_b m$ and then use the molality, given mass of solute and volume of water, to calculate the molar mass of
        the solute compound. If the solute is a nonelectrolyte, $i = 1$. If the formula is AB_2 or A_2B, then $i = 3$. For part d),
        use the molar mass of CaN_2O_6 to calculate the molality of the compound. Then calculate i in the boiling point
        elevation formula.
        <u>Solution:</u>
        a) $\Delta T_b = iK_b m$ $i = 1$ (nonelectrolyte)
        ΔT = boiling point of solution – boiling point of solvent = $(100.45 - 100.00)°C = 0.45°C$

$$m = \dfrac{\Delta T_b}{K_b i} = \dfrac{0.45°C}{(0.512°C/m)(1)} = 0.878906 \ m = 0.878906 \text{ mol/kg}$$

$$\text{Mass (kg) of water} = (25.0 \text{ mL})\left(\dfrac{0.997 \text{ g}}{1 \text{ mL}}\right)\left(\dfrac{1 \text{ kg}}{10^3 \text{ g}}\right) = 0.0249250 \text{ kg water}$$

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

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

$$\text{Molar mass} = \frac{1.50\ \text{g}}{0.0219067\ \text{mol}} = 68.4722 = \textbf{68 g/mol}$$

b) $\Delta T_b = iK_b m$ $i = 3$ (AB$_2$ or A$_2$B)

$$m = \frac{\Delta T_b}{K_b i} = \frac{0.45^\circ\text{C}}{\left(0.512^\circ\text{C}/m\right)(3)} = 0.29296875\ m = 0.29296875\ \text{mol/kg}$$

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

Moles solute = (m)(kg solvent) = $(0.29296875\ m)(0.0249250\ \text{kg})$ = 0.00730225 mol

$$\text{Molar mass} = \frac{1.50\ \text{g}}{0.00730225\ \text{mol}} = 205.416 = \textbf{2.1x10}^2\ \textbf{g/mol}$$

c) The molar mass of CaN$_2$O$_6$ is 164.10 g/mol. This molar mass is less than the 2.1x10^2 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) Moles of CaN$_2$O$_6$ = $\left(1.50\ \text{g CaN}_2\text{O}_6\right)\left(\dfrac{1\ \text{mol}}{164.10\ \text{g CaN}_2\text{O}_6}\right)$ = 0.0091408 mol

$$m = \frac{\text{moles of solute}}{\text{kg of solvent}} = \frac{0.00914078\ \text{mol}}{0.0249250\ \text{kg}} = 0.3667314\ m$$

$$\Delta T_b = iK_b m$$

$$i = \frac{\Delta T_b}{K_b m} = \frac{\left(0.45^\circ\text{C}\right)}{\left(0.512^\circ/m\right)\left(0.3667314\ m\right)} = 2.39659 = \textbf{2.4}$$

13.97 $\dfrac{\text{mol C}_2\text{H}_5\text{OH}(g)}{\text{mol CH}_3\text{OH}(g)} = \dfrac{\text{mol C}_2\text{H}_5\text{OH}(l)}{\text{mol CH}_3\text{OH}(l)}\left(\dfrac{60.5\ \text{torr}}{126.0\ \text{torr}}\right) = \dfrac{\text{mol C}_2\text{H}_5\text{OH}(l)}{\text{mol CH}_3\text{OH}(l)}(0.4801587)$

A 97:1 mass ratio gives 97 g of C$_2$H$_5$OH for every 1 g of CH$_3$OH. (This limits the significant figures.)

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

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

$$\frac{\left(140.4994\ \text{mol C}_2\text{H}_5\text{OH}\right)\left(\dfrac{46.07\ \text{g C}_2\text{H}_5\text{OH}}{1\ \text{mol C}_2\text{H}_5\text{OH}}\right)}{\left(1\ \text{mol CH}_3\text{OH}\right)\left(\dfrac{32.04\ \text{g CH}_3\text{OH}}{1\ \text{mol CH}_3\text{OH}}\right)} = 202.0227 = \textbf{2x10}^2$$

13.98 Determine the molarity of CH$_3$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.)

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

$$= 1.98098\text{x}10^{-6} = \textbf{1.98x10}^{-6}\ \textbf{\textit{M}\ CH}_3\textbf{Cl}$$

If the density is 1.00 g/mL, then 1.00 L of solution would weigh 1.00 kg. The mass of CH_3Cl 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: **1.98×10^{-6} m CH_3Cl**.

Still using 1.00 L of solution:

Moles of CH_3Cl = $(1.98098 \times 10^{-6}$ mol/L$)(1.00$ L$) = 1.98098 \times 10^{-6}$ mol CH_3Cl

Moles of H_2O = $(1.00$ kg$)(10^3$ g/1 kg$)(1$ mol H_2O/18.02 g H_2O) = 55.49389567 mol H_2O

$X_{\text{chloroform}}$ = $(1.98098 \times 10^{-6}$ mol CH_3Cl)/$[(1.98098 \times 10^{-6} + 55.49389567)$ mol$]$

$\quad\quad\quad = 3.569726 \times 10^{-8}$ = **3.57×10^{-8}**

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

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

13.99   Plan: From the osmotic pressure, the molarity of the solution can be found using the relationship $\Pi = MRT$. Convert the osmotic pressure from units of torr to atm, and the temperature from °C to K. Use the molarity of the solution to find moles of solute; divide the given mass of solute in grams by the moles of solute to obtain molar mass. To find the freezing point depression, the molarity of the solution must be converted to molality by using the density of the solution to convert volume of solution to mass of solution. Then use $\Delta T_f = iK_f m$. ($i = 1$).

Solution:

a) $\Pi = MRT$

Osmotic pressure (atm), $\Pi = (0.340\ \text{torr})\left(\dfrac{1\ \text{atm}}{760\ \text{torr}}\right) = 4.47368 \times 10^{-4}$ atm

$T = 25°C + 273 = 298$ K

$$M = \frac{\Pi}{RT} = \frac{\left(4.47368 \times 10^{-4}\ \text{atm}\right)}{\left(0.0821\dfrac{\text{L·atm}}{\text{mol·K}}\right)(298\ \text{K})} = 1.828544 \times 10^{-5}\ M$$

$(M)(V)$ = moles

$$\text{Moles} = \left(1.828544 \times 10^{-5}\ M\right)(30.0\ \text{mL})\left(\frac{10^{-3}\ \text{L}}{1\ \text{mL}}\right) = 5.48563 \times 10^{-7}\ \text{mol}$$

$$\text{Molar mass} = \frac{(10.0\ \text{mg})\left(\dfrac{10^{-3}\ \text{g}}{1\ \text{mg}}\right)}{5.48563 \times 10^{-7}\ \text{mol}} = 1.82294 \times 10^4 = \textbf{1.82} \times \textbf{10}^{\textbf{4}}\ \textbf{g/mol}$$

b) Mass (g) of solution = $(30.0\ \text{mL})\left(\dfrac{0.997\ \text{g}}{1\ \text{mL}}\right) = 29.91$ g

Mass (g) of solute = $(10.0\ \text{mg})\left(\dfrac{10^{-3}\ \text{g}}{1\ \text{mg}}\right) = 0.0100$ g

Mass (kg) of solvent = mass of solution – mass of solute = 29.91 g – 0.0100 g $\left(\dfrac{1\ \text{kg}}{10^3\ \text{g}}\right) = 0.0299$ kg

Moles of solute = 5.48563×10^{-7} mol (from part a))

Molality = $\dfrac{\text{moles of solute}}{\text{kg of solvent}} = \dfrac{5.48563 \times 10^{-7}\ \text{mol}}{0.0299\ \text{kg}} = 1.83466 \times 10^{-5}\ m$

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

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

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$)(18.0\%/100\%)$

$\quad\quad\quad = 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%)

$\qquad\qquad$ = 17.10459 g glyphosate

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_2O 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_2O

Mass percent = $\dfrac{(17.10459 \text{ g Gly})}{(17.10459 + 3785)\text{g}}$ x 100% = 0.44987 = **0.450%**

13.101 The vapor pressure of H_2O 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.

13.102 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 ($D = 8.35/1$).

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

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

a) Mass (mg) in water = $\dfrac{(100.0 \text{ mL})}{(100.0 + 8.35(60.0))\text{mL}}(10.0 \text{ mg})$ = 1.66389 = **1.66 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.

Mass (mg) in water = $\dfrac{(100.0 \text{ mL})}{(100.0 + 8.35(30.0))\text{mL}}(10.0 \text{ mg})$ = 2.853067 = **2.85 mg** remains after first extraction

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

$\qquad\qquad$ = 0.813999 = **0.814 mg** remains after second extraction

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

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 g of sample, which makes the percentages equal to the mass of each element present:

Moles C = 32.3 g C(1 mol C/12.01 g C) = 2.6894 mol C

Moles H = 3.97 g H(1 mol H/1.008 g H) = 3.93849 mol H

Moles O = (100 – 32.3 – 3.97) g O(1 mol O/16.00 g O) = 3.9831 mol O

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: **$C_2H_3O_3$**.

The molar mass comes from the freezing point depression:

$\Delta T_f = iK_f m$ $\qquad\qquad$ (Assume the compound is a nonelectrolyte, $i = 1$.)

$m = \Delta T_f/iK_f = (1.26°C)/(1)(1.86°C/m)] = 0.677419$ m

m = moles of solute/kg of solvent

Moles of solute = (m)(kg of solvent) = (0.677419 m)[(11.23 g)(1 kg/10^3 g)] = 0.007607415 mol

Molar mass = $\left(\dfrac{0.981 \text{ g}}{0.007607415 \text{ mol}}\right)$ = 128.953 g/mol

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 **$C_4H_6O_6$**.

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

$\text{Moles} = \left(4.42 \text{ g (NH}_4)_3\text{PO}_4\right)\left(\dfrac{1 \text{ mol (NH}_4)_3\text{PO}_4}{149.10 \text{ g (NH}_4)_3\text{PO}_4}\right)\left(\dfrac{3 \text{ mol NH}_4{}^+}{1 \text{ mol (NH}_4)_3\text{PO}_4}\right) = 8.89336\text{x}10^{-2} \text{ mol NH}_4{}^+$

$\text{Moles} = \left(4.42 \text{ g (NH}_4)_3\text{PO}_4\right)\left(\dfrac{1 \text{ mol (NH}_4)_3\text{PO}_4}{149.10 \text{ g (NH}_4)_3\text{PO}_4}\right)\left(\dfrac{1 \text{ mol PO}_4{}^{3-}}{1 \text{ mol (NH}_4)_3\text{PO}_4}\right) = 2.96445\text{x}10^{-2} \text{ mol PO}_4{}^{3-}$

$M \text{ NH}_4{}^+ = [(7.07058\text{x}10^{-2}) + (8.89336\text{x}10^{-2})] \text{ mol NH}_4{}^+/20.0 \text{ L} = 7.98197\text{x}10^{-3} = \mathbf{7.98x10^{-3} \textit{ M} NH_4{}^+}$
$M \text{ PO}_4{}^{3-} = (2.96445\text{x}10^{-2} \text{ mol PO}_4{}^{3-})/20.0 \text{ L} = 1.482225\text{x}10^{-3} = \mathbf{1.48x10^{-3} \textit{ M} PO_4{}^{3-}}$

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

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

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

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

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

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_4N_2O**. 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.

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

Moles of urea = $(M)(V) = (0.0833817 \text{ }M)(1 \text{ L}) = 0.0833817 \text{ mol}$
Molar mass = 5.0 g/0.0833817 mol = 59.965 = **60. g/mol**
Because the molecular weight equals the empirical weight, the molecular formula is also **CH_4N_2O**.

13.106 a) $\text{Mass (g) of glucose} = \left(2.5 \text{h}\right)\left(\dfrac{100. \text{ mL}}{\text{h}}\right)\left(\dfrac{10^{-3} \text{ L}}{1 \text{ mL}}\right)\left(\dfrac{0.30 \text{ mol glucose}}{1 \text{ L}}\right)\left(\dfrac{180.16 \text{ g glucose}}{1 \text{ mol glucose}}\right)$

$= 13.512 = \textbf{14 g glucose}$
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** .

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

$= 1.97235 = \textbf{2.0 g NaCl}$

13.107 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_3O^+ and Cl^- ions.

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

$$m = \frac{\Delta T_f}{iK_f} = \frac{5.0°C}{(2)1.86°C/m} = 1.344086\ m\ NaCl$$

$$Mass\ (g) = \left(\frac{1.344086\ mol\ NaCl}{kg}\right)(5.5\ kg)\left(\frac{58.44\ g\ NaCl}{mol\ NaCl}\right) = 432.016 = \mathbf{4.3x10^2\ g\ NaCl}$$

b) $\Delta T_f = iK_f m$ Assume $CaCl_2$ is a strong electrolyte with $i = 3$.

$$m = \frac{\Delta T_f}{iK_f} = \frac{5.0°C}{(3)1.86°C/m} = 0.896057\ m\ CaCl_2$$

$$Mass\ (g) = \left(\frac{0.896057\ mol\ CaCl_2}{kg}\right)(5.5\ kg)\left(\frac{110.98\ g\ CaCl_2}{mol\ CaCl_2}\right) = 546.944 = \mathbf{5.5x10^2\ g\ CaCl_2}$$

13.109 a) Moles of $CO_2 = (355\ mL)\left(\frac{10^{-3}\ L}{1\ mL}\right)\left(\frac{3.3x10^{-2}\ mol}{L•atm}\right)(4\ atm) = 0.04686 = \mathbf{0.05\ mol\ CO_2}$

b) If it is completely flat there is no CO_2 remaining or 0.00 moles CO_2, however, a small amount will remain in solution:

$$Moles\ CO_2 = (355\ mL)\left(\frac{10^{-3}\ L}{1\ mL}\right)\left(\frac{3.3x10^{-2}\ mol}{L•atm}\right)(3\ x\ 10^{-4}\ atm) = 3.5145x10^{-6} = \mathbf{4x10^{-6}\ mol\ CO_2}$$

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

$$PV = nRT\ so\ V = nRT/P = \frac{\left[(0.04686 - 3.5145x10^{-6})\ mol\right]\left(0.0821\frac{L•atm}{mol•K}\right)((273 + 25)\ K)}{(1.00\ atm)}$$

$$= 1.14638 = \mathbf{1\ L\ CO_2}$$

13.110 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 $4 + ½(4) = 6$ moles of oxygen in the vapor phase. The increased pressure results in increased solubility of oxygen in the water. Of the six moles of oxygen in the vapor phase, one mole dissolves in the water to bring the dissolved moles to three.