Solutions

I. Concentration.

A. Definitions—Review

1. Solution = homogeneous mixture of two or more components.
2. Solvent = component present to largest extent. Phase of solution is same as the phase of the solvent.
3. Solute = minor component of the mixture.
   a. The solute is dispersed evenly throughout the solvent.
   b. When the solvent is water the solute is said to be in an aqueous solution.
4. Concentration = number giving the amount of solute dissolved in a given amount solution or dispersed in a given amount of solvent.

B. Concentration Units.

1. Review of molarity and mole fraction
   a. Molarity (M) = moles of solute per liter of solution
      \[ M = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{\text{mmol solute}}{\text{ml of solution}} \]

      1) A solution was prepared by dissolving 10.0 g of NaOH (FM = 40.0) in enough water to give 350 mL of solution. Calculate the Molarity of the solution.

      \[
      \text{mol of NaOH} = \frac{10.0 \text{ g}}{40 \text{ g/mol}} = 0.250 \text{ mol}
      \]

      \[
      \text{Molarity} = \frac{0.250 \text{ mol}}{0.350 \text{ L}} = 0.714 \text{ M} \text{ (or 0.714 molar)}
      \]

      Also note mmol of NaOH = 250 mmol, and mL of solution = 350 mL
      Molarity = 250 mmol / 350 mL = 0.714 M

   b. Mole fraction (X)

      1) The mole fraction of a component , \(i\) , in a solution , \(X_i = \frac{n_i}{n_{total}}\)

      where \(n_i = \text{moles of } i\)

      \[ n_{total} = \text{total number of moles of all components of the solution.} \]

      2) Note that solvent and solute are not used in this expression of concentration.

      Since the sum of all mole fractions must equal unity, the following holds

      \[ \sum_i X_i = 1.000 \]
2. **Molality (m)** = number of moles of solute per kilogram of **solvent**.

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

Suppose that 5.46 g of CH₃OH (FM = 32) is dissolved in 760 g of water.

Calculate the molality of the solution.

\[
\text{moles CH}_3\text{OH} = \frac{5.46 \text{ g}}{32 \text{ g/mol}} = 0.1706 \text{ mol}
\]

\[
\text{kg of solvent} = 0.760 \text{ kg}
\]

\[
\text{molality} = \frac{0.1706 \text{ mol}}{0.760 \text{ kg}} = 0.225 \text{ molal}
\]

3. **Interconversion of Concentration Units.**

   a. The calculations of **molality** and **mole fraction** require the same type of information, namely the amount of solute (moles) dispersed in a given **amount of solvent**, expressed in either moles or kilograms.

   b. The calculation of **molarity** requires knowledge of the amount (moles) of solute dispersed in a given **volume of solution**

   c. One needs to know the **density of the solution** to interconvert.

   d. Example: A solution prepared by dissolving 10.0 g of K₂Cr₂O₇ (FM = 294) in 90.0 g of water has a density of 1.075 g/mL. Calculate

       1) the mole fraction of K₂Cr₂O₇

       \[
       \text{moles of K}_2\text{Cr}_2\text{O}_7 = \frac{10.0 \text{ g}}{294 \text{ g/mol}} = 0.0340 \text{ mol}
       \]

       \[
       \text{moles of H}_2\text{O} = \frac{90.0 \text{ g}}{18.0 \text{ g/mol}} = 5.00 \text{ mol}
       \]

       \[
       X_{K,\text{Cr}_2\text{O}_7} = \frac{0.0340}{5.00 + 0.034} = .00675 = 6.75 \times 10^{-3}
       \]

       2) the molality of the solution

       \[
       \text{moles K}_2\text{Cr}_2\text{O}_7 = 0.0340 \text{ mol}
       \]

       \[
       \text{kg H}_2\text{O} = \frac{90.0 \text{ g}}{1000 \text{ g/kg}} = 0.0900 \text{ kg}
       \]

       \[
       \text{molality} = \frac{0.0340 \text{ mol}}{0.0900 \text{ kg}} = 0.378 \text{ molal}
       \]

       3) the Molarity of the solution

       total mass of solution = 10.0 g + 90.0 g = 100.0 g

       \[
       \text{volume of solution} = \frac{100.0 \text{ g}}{1.075 \text{ g/mL}} = 93.5 \text{ mL} = 0.0935 \text{ L}
       \]

       \[
       \text{Molarity} = \frac{0.0340 \text{ mol}}{0.935 \text{ L}} = 0.364 \text{ molar}
       \]
II. Colligative Properties. Properties of solutions due to their concentrations

A. Vapor Pressure.

1. The vapor pressure of a solution of two volatile liquids will depend on the composition of the mixture and the volatility of the two components.
   a. The volatility can be assessed by the vapor pressures of the pure components at the particular temperature.
   b. The composition is conveniently given by the mole fractions of the components.

2. Raoult's Law.
   a. Many times, mixtures of chemically similar substances act as ideal solutions. The vapor pressure of an ideal solution can be determined using Raoult's Law.
   b. Consider an ideal solution composed of two volatile components, A and B.
      Let \( P_A^o \) = the vapor pressure of pure A and \( X_A \) = mole fraction of A.
      Let \( P_B^o \) = the vapor pressure of pure B and \( X_B = 1-X_A \).
      Raoult’s Law states that the partial pressures of the two components above the solution are:
      
      \[
      \text{Partial pressure of A} = P_A = X_A P_A^o ; \text{Partial pressure of B} = P_B = X_B P_B^o \\
      \therefore \text{Total pressure} = \text{vapor pressure of the solution} = P = P_A + P_B = X_A P_A^o + X_B P_B^o
      \]

   c. Rearranging and using the relationship \( X_B = 1-X_A \), one obtains

![Figure 1. A plot of vapor pressure versus composition for an ideal solution.](image-url)
Solutions

\[ P = X_A P_A^0 + X_B P_B^0 = X_A P_A^0 + (1-X_A)P_B^0 = X_A(P_A^0 - P_B^0) + P_B^0 \]

Therefore, a plot of P vs. \( X_A \) will be a straight line running from \( P_B^0 \) at \( X_A = 0 \) (pure B) to \( P_A^0 \) at \( X_A = 1 \) (pure A), as shown in Figure 1.

3. Composition of the vapor.

a. When Raoult's law is obeyed, the mole fractions of each component in the liquid phase, \( X_A \) and \( X_B \), are related to the mole fractions of the components in the vapor phase, \( Y_A \) and \( Y_B \), by the relationships.

1) \( P = P_A + P_B = X_A P_A^0 + X_B P_B^0 \)  
Raoult's law

2) \( Y_A = \frac{P_A}{P_A + P_B} \) and \( Y_B = \frac{P_B}{P_A + P_B} \)  
Dalton's law

b. Example: Suppose \( P_A^0 = 300 \) Torr, \( P_B^0 = 100 \) Torr, \( X_A = 0.40 \), and \( X_B = 0.60 \), calculate \( Y_A \) and \( Y_B \).

\[ P_A = (0.40)(300 \text{ Torr}) = 120 \text{ Torr} \]
\[ P_B = (0.60)(100 \text{ Torr}) = 60 \text{ Torr} \]
\[ P = 180 \text{ Torr} \]

\[ Y_A = \frac{P_A}{P_A + P_B} = \frac{120 \text{ Torr}}{180 \text{ Torr}} = 0.67 \]
\[ Y_B = \frac{P_B}{P_A + P_B} = \frac{60 \text{ Torr}}{180 \text{ Torr}} = 0.33 \]

1) Note that the vapor phase is richer in the more volatile component than is the liquid phase.

2) A plot of the vapor pressure vs. liquid/vapor mole fraction is shown Figure 2.

![Figure 2 Plot of Vapor Pressure vs. Mole Fraction of A](image-url)

The line connecting the liquid and vapor is called a “tie line”
Solutions

3) If the vapor in equilibrium with the original liquid were condensed, the resulting liquid would be richer in the more volatile. If the vapor from this new solution were condensed, the more volatile component would be further enriched. If such an equilibration-condensation process were repeated enough times, one could end up with a liquid that was essentially 100% the more volatile component. The process is called **fractional distillation**.

a. If the two components of the mixture are chemically very similar, the intermolecular forces of attraction between an A and a B molecule would be the same as that between two A's or two B's. This is the case for an **ideal solution**.

b. Evaporation is a surface phenomenon, therefore, the partial pressure of component A in the mixture will depend on the escaping tendency of A, which can be measured by $P_A^0$ and the fraction of the molecules on the surface that are A, this is $X_A$. Therefore, the partial pressure of A would be $X_A P_A^0$, which is Raoult's Law. A mixture of benzene ($C_6H_6$) and methylbenzene ($CH_3C_6H_5$, toluene) form ideal solution over their complete mole fraction range.

4. Deviations from Raoult's Law.

Many solutions show deviations from ideal behavior. There are two different types of deviations.

a. Solutions in which the vapor pressure is less than that predicted from Raoult's Law. In these solutions the attractive forces between the two components, A and B, are greater than those between two A's and/or two B's. An example is a mixture of acetone ($CH_3COCH_3$) and chloroform ($CHCl_3$). Figure 4 shows a plot of vapor pressure vs. composition for this system. The Figure also shows the vapor-liquid compositions for these solutions.

b. Solutions in which the vapor pressure is greater than that predicted by Raoult's Law. Here the attraction between A and B is less than that between two A's and/or two B's. An example is acetone and carbon disulfide ($CS_2$). See Figure 3 for the vapor pressure vs. composition plots and the vapor-liquid compositions.
Solutions

Figures 3 and 4. Deviations From Raoult's Law
5. Dilute solution Behavior.

a. Figure 5 shows a plot of partial pressure vs. concentration for a component in a solution that deviates from Raoult's Law.

b. Note that in the region where this component is the solvent, the region close to $X_A = 1$, Raoult's Law is obeyed. Therefore, Raoult's Law is said to be a limiting law in that it is always obeyed in dilute solutions.

c. Note that at the other extreme, a dilute solution in which A is the solute, another limiting law, called Henry's Law, is obeyed. Henry's Law states that in dilute solutions the partial pressure of the gaseous solute will be directly proportional to its mole fraction, or $P_{\text{solute}} = K(X_{\text{solute}})$. The Henry's Law constant, K, has the dimensions of reciprocal pressure.

d. Henry's Law ($P_A = K_A X_A$) is often applied to solutions formed when gases dissolve in liquids. In these cases, $P_A$ is the partial pressure of the gas that is in equilibrium with a saturated solution of the gas of concentration $X_A$.

1) Since the "pure solute" is the gas, Henry's Law governs the solubility of the gas in the solution. $P_A$ is the gas pressure needed to dissolve enough of the gas to give a solution of concentration $X_A$.

2) The more soluble gases have smaller values of K. Some values are given below.
Solutions

Henry's Law Constants at 298 K.

<table>
<thead>
<tr>
<th>Gas</th>
<th>K(Torr)</th>
<th>Gas</th>
<th>K(Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>5.34x10⁷</td>
<td>O₂</td>
<td>3.30x10⁷</td>
</tr>
<tr>
<td>N₂</td>
<td>6.51x10⁷</td>
<td>CO₂</td>
<td>1.25x10⁶</td>
</tr>
</tbody>
</table>

B. Solutions of Nonvolatile Solutes, Vapor Pressure Lowering.

1. If an ideal solution is composed of a liquid solvent whose vapor pressure is $P_1^0$ and a nonvolatile, nonelectrolytic solute whose mole fraction is $X_2$, the vapor pressure, $P$, of this solution is

$$P = X_1P_1^0 = (1-X_2)P_1^0$$

a. Note that because $X_1$ is less than 1.00, the vapor pressure of the solution will always be less than that of the pure solvent. That is, the presence of the solute will lead to a vapor pressure lowering. This is one of the colligative properties.

b. The extent of this vapor pressure lowering will depend only on the nature of the solvent and the mole fraction of the solute.

Let $\Delta P =$ the vapor pressure lowering $= P_1^0 - P = P_1^0 - X_1P_1^0 = (1-X_1)P_1^0 =$ $X_2P_1^0$

Note that, provided that the solute is nonvolatile and a nonelectrolyte, the chemical nature of the solute is not important.

2. Effect of the vapor pressure lowering on the phase diagram of the solvent. Consider the following phase diagram for pure water (solid lines) and an aqueous solution of a nonvolatile solute (dashed lines).
Solutions

\[ t_f = \text{the freezing point of the solution}, \quad t_f^o = \text{the freezing point of the solvent} \]
\[ t_b = \text{the boiling point of the solution}, \quad t_b^o = \text{the boiling point of the solvent} \]

a. The vapor pressure lowering of the solution will give rise to a depression of the freezing point and an elevation of the boiling point of the solution.

Freezing point depression = \( \Delta t_f = t_f^o - t_f \propto X_2 \)

Boiling point elevation = \( \Delta t_b = t_b - t_b^o \propto X_2 \)

b. For dilute solutions, the mole fraction of a solute is proportional to its molality.

Therefore, \( \Delta t_f = K_f m \)
\( \Delta t_b = K_b m \)

1) \( K_f = \) molal freezing point depression constant \((\degree/m)\).
\( K_b = \) molal boiling point elevation constant \((\degree/m)\).

2) \( K_f \) and \( K_b \) are functions of the solvent only. Values for some common solvents are listed below.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( t_f^o (\degree) )</th>
<th>( K_f (\degree/m) )</th>
<th>( t_b^o (\degree) )</th>
<th>( K_b (\degree/m) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}O</td>
<td>0.0</td>
<td>1.86</td>
<td>100.0</td>
<td>0.52</td>
</tr>
<tr>
<td>CH\textsubscript{3}CH\textsubscript{2}OH</td>
<td>-117.3</td>
<td>1.99</td>
<td>78.4</td>
<td>1.22</td>
</tr>
<tr>
<td>Ethanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{6}H\textsubscript{6}</td>
<td>5.5</td>
<td>5.12</td>
<td>80.1</td>
<td>2.52</td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH\textsubscript{3}COOH</td>
<td>16.6</td>
<td>3.90</td>
<td>117.9</td>
<td>2.93</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3. Calculations. We will consider only freezing point depressions. Generally, $\Delta t_f$'s are larger than $\Delta t_b$'s and are easier to measure. The calculations would be exactly the same for boiling point elevations.

a. Calculate the freezing point of a solution prepared by dissolving 2.00 g of naphthol (C$_{10}$H$_8$O), a nonvolatile, nonelectrolyte in 50.0 g of the solvent benzene. (The freezing point of pure benzene and $K_f$ are given in the table shown above.)

Molar Mass C$_{10}$H$_8$O = 144 g/mol.

$$\text{mol. C}_{10}\text{H}_8\text{O} = \frac{2.00 \text{ g}}{144 \text{ g/mol}} = 0.014 \text{ mol}$$

$$m = \frac{0.014 \text{ mol}}{0.050 \text{ kg}} = 0.28 \text{ m}$$

$$\Delta t_f = (5.12 \degree/\text{m})(0.28 \text{ m}) = 1.43 \degree \text{C}. \quad t_f = 5.50 \degree \text{C} - 1.43 \degree \text{C} = 4.07 \degree \text{C}$$

b. A solution prepared by dissolving 1.50 g of a nonvolatile, nonelectrolyte in 100 g of benzene gave a freezing point depression of 0.98 $\degree$C. Calculate the molar mass of the solute.

$$m = \frac{\Delta t_f}{K_f} = \frac{0.98 \degree}{5.12 \degree/\text{m}} = 0.191 \text{ m} \quad \text{or} \quad 0.191 \text{ mol solute/kg solvent}$$

$$\frac{\text{g solute}}{\text{kg solvent}} = \frac{1.50 \text{ g}}{0.100 \text{ kg}} = 15.0 \text{ g solute/kg solvent}$$

$$\text{molar mass} = \frac{15.0 \text{ g/kg solvent}}{0.191 \text{ mol/kg solvent}} = 78.5 \text{ g/mol}$$

or

$$\text{number of moles} = 0.191 \text{mol/kg}(0.100\text{kg}) = 0.0191 \text{ mol}$$

$$\text{molar mass} = \frac{1.50\text{g}}{0.0191 \text{ mol}} = 78.5 \text{g/mol}$$

C. Osmotic Pressure.

1. Consider a solution separated from a solvent by a semipermeable membrane, as shown below.
a. **Semipermeable membrane** = one that will allow the passage of only certain molecules, such as solvent, but not other molecules, such as solute.

b. Dilution of the solution is a spontaneous process. Since the solute cannot escape, solvent will spontaneously flow into the solution. This process is called **osmosis**.

c. Osmosis can be prevented by applying a pressure, \( P \), to the solution. The minimum pressure necessary to prevent osmosis is called the **osmotic pressure**, \( \pi \).

1) For ideal solutions, 
\[
\pi = CRT
\]
where \( C \) = the molar concentration, \( R \) = gas constant, and \( T \) = the temperature in K.

2) Note the similarity between this equation and the ideal gas equation, 
\[
P = \frac{n}{V} RT = CRT.
\]

d. If a pressure greater than \( \pi \) were applied to the solution, solvent would be forced out. This process is called **reverse osmosis**, and has been used for water purification.

2. Example:

A solution prepared by dissolving 2.00 g of a nonelectrolyte in enough water to give 75.0 ml of solution generated an osmotic pressure of 1.87 Torr at 37.0 °C. Calculate the molar mass of the substance.
Solutions

\[ C = \frac{\pi}{RT} = \frac{1.87 \text{ torr}}{62.4 \frac{\text{torr L}}{\text{mol K}(310 \text{ K})}} = 9.67 \times 10^{-5} \text{mol/L} \]

\[ \text{g solute/L} = \frac{2.00 \text{ g}}{0.0750 \text{ L}} = 26.7 \text{ g/L} \]

\[ \text{molar mass} = \frac{26.7 \text{ g/L}}{9.67 \times 10^{-5} \text{mol/L}} = 2.76 \times 10^{5} \text{ g/mol} \]

b. Note that the molarity of the above solution is exceedingly small and the molar mass is large. Osmotic pressure measurements are standard ways of obtaining molar masses of large molecules, such as polymers and proteins.

D. Effects of electrolytic solutes.

1. Vapor lowering, freezing point depression, boiling point elevation, and osmotic pressure depend only on the relative number of solute and solvent particles. Therefore, an ion should be just as effective as a neutral solute molecule in producing these effects.
   a. In solutions of electrolytes, the colligative properties depend on the total solute particle concentrations due to all solute species.
   b. For strong electrolytes, \( m_{\text{total}} = m_{\text{cations}} + m_{\text{anions}} \).
   For weak electrolytes, \( m_{\text{total}} = m_{\text{cations}} + m_{\text{anions}} + m_{\text{undissociated solute}} \).

2. Consider the following solutions and their freezing point depressions.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Ions</th>
<th>( m_{\text{total}} )</th>
<th>( \Delta t_{f} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001 m C₆H₁₂O₆</td>
<td>none</td>
<td>0.001</td>
<td>0.00186</td>
</tr>
<tr>
<td>0.001 m NaCl</td>
<td>Na⁺ + Cl⁻</td>
<td>0.001 + 0.001 = 0.002</td>
<td>0.00372</td>
</tr>
<tr>
<td>0.001 m MgCl₂</td>
<td>Mg²⁺ + 2Cl⁻</td>
<td>0.001 + 0.002 = 0.003</td>
<td>0.00558</td>
</tr>
</tbody>
</table>

a. The increased efficiency of electrolytes can be described by using the van't Hoff factor, \( i \), in the different colligative property equations. These now become

\[ \Delta t_{f} = iK_{f}m \quad \Delta t_{b} = iK_{b}m \quad \pi = iCRT \quad \Delta P = iP_{1}^{o}X \]

\( i \) = the effective number of particles per formula unit of the electrolyte.

b. For nonelectrolytes, such as C₆H₁₂O₆, \( i = 1 \).

c. For dilute solutions of strong electrolytes, \( i \) = number of ions per formula unit.

Some examples are: NaCl, \( i = 2 \); MgCl₂, \( i = 3 \); FeCl₃, \( i = 4 \).

d. In more concentrated solutions, \( i \) will actually be slightly less than the number of ions due to activity corrections. However, we will assume that activity corrections are small and use the ions per formula unit for \( i \).
3. Weak electrolytes will show effects between nonelectrolytes and strong electrolytes, depending on the percent dissociation of the weak electrolyte. The value of $i$ will be between that expected for a nonelectrolyte and a strong electrolyte.

II. Factors Effecting Solubility.

A. Nature of the solute and solvent. "Likes dissolve likes."
   1. Ionic and polar solutes tend to be more soluble in polar solvents, such as H$_2$O, while nonpolar solutes are more likely to dissolve in nonpolar solvents, such as benzene (C$_6$H$_6$) and carbon tetrachloride (CCl$_4$).
   2. This is not a fixed rule but should be viewed as a general guiding principal for choosing a solvent.

B. Temperature.
   1. Depends on whether $\Delta H_{\text{Soln}}$ is positive or negative.
   2. Can use Le Chatelier’s Principle
      If the solution process is exothermic ($\Delta H_{\text{Soln}}$ is negative), have the equilibrium
      \[
      \text{Solute} + \text{Solvent} \rightleftharpoons \text{Solution} + \text{Heat}
      \]
      Solubility will **decrease** as temperature **increases**.
      If the solution process is endothermic ($\Delta H_{\text{Soln}}$ is positive), have the equilibrium
      \[
      \text{Heat} + \text{Solute} + \text{Solvent} \rightleftharpoons \text{Solution}
      \]
      Solubility will **increase** as temperature **increases**.
   2. Note that gases always dissolve exothermically. Therefore the solubility of all gases will decrease as the temperature increases.

C. Pressure.
   1. Since solids and liquids are almost incompressible, pressure changes should exert little effect of the solubility of liquid or solid solutes in condensed phase solvents. However, extremely high pressures will effect the solubility.
   2. The solubility of gaseous solutes in liquid solvents will always increase as the partial pressure of the gas above the liquid increases in accordance with **Henry's Law**
Solutions

Problems

1. At 20 °C the solubility of KCl in water is 34.0 g KCl per 100 g water. The density of the resulting saturated solution is 1.17 g / mL. Calculate (a) the mole fraction of KCl in the solution, (b) the molality of the solution, and (c) the molarity of the solution.
   
   [(a) 0.076   (b) 4.55m   (c) 3.98M]

2. Suppose a 8.75 M aqueous CH$_3$OH solution has a density of 0.789 g / mL. Calculate the molality of the solution. (17.2M)

3. A solution prepared by dissolving enough hexachlorobenzene, C$_6$Cl$_6$ (MM = 285), in 300 g of carbon tetrachloride, CCl$_4$ (MM = 154), to give a mole fraction C$_6$Cl$_6$ of 0.15 has a density of 1.237 g/mL.
   a. Calculate the molality of this solution.
   b. Calculate the molarity of this solution. (a. 1.15 m. b. 1.07 M)

4. A solution prepared by dissolving 6.0 g of NaCl in enough water to give 500 mL of solution has a density of 1.05 g / mL. Calculate (a) the molarity of the solution, (b) the molality of the solution, (c) the mole fraction of NaCl in the solution.
   
   [(a) 0.205M  (b) 0.198m  (c) 3.54x10$^{-3}$ ]

5. Heptane, C$_7$H$_{16}$ and hexane, C$_6$H$_{14}$ form an ideal solution. Given that, at 25 °C, the vapor of pure C$_7$H$_{16}$ is 51.4 Torr while that of pure C$_6$H$_{14}$ is 148.5 Torr, calculate the mole fraction of C$_6$H$_{14}$ that must exist in the liquid phase so that the mole fraction of C$_6$H$_{14}$ in the gas phase above the solution is 0.25. (0.103)

6. Benzene (C$_6$H$_6$) and toluene (C$_7$H$_8$) form an ideal solution over the complete concentration range. At 35 °C the vapor pressure of pure benzene is 191 torr and that of pure toluene is 43 torr.
   a. Calculate the partial pressures of benzene and toluene over a solution at 35 °C that was prepared by mixing 20.0 g of benzene and 50.0 g of toluene. (P$_B$ = 61.3 torr, P$_T$ = 29.2 torr)
   b. Calculate the vapor pressure of the above solution. (90.5 torr)
   c. Calculate the mole fraction of benzene in the vapor phase above this solution. (0.677)
   d. How many grams of benzene must be added to 100 g of toluene to produce a solution that would give a mole fraction of benzene of 0.37 in the vapor phase above the resulting solution at 35 °C? (11.2 g)

7. A solution prepared by dissolving 0.150 g of a polymer in enough water to give 200.0 mL of solution had an osmotic pressure of 0.558 torr at 25 °C.
   a. Calculate the molar mass of the polymer assuming that it is a nonelectrolyte.(2.5x10$^4$ g/mol)
   b. Calculate the molar mass of the polymer assuming that it is a strong 1:1 electrolyte. (5.0 x10$^4$ g/mol)
8. A solution of a nonvolatile nonelectrolyte in the solvent benzene, \( \text{C}_6\text{H}_6 \), had a freezing point depression of \( 7.48 \, ^\circ\text{C} \). Given that \( K_f \) for benzene is \( 5.12 \, ^\circ\text{C}/\text{m} \) and that the vapor pressure of pure benzene at \( 20 \, ^\circ\text{C} \) is 22.0 torr, calculate (a) the molality of the solution and (b) the vapor pressure of the solution at \( 20 \, ^\circ\text{C} \). (a. 1.46 m b. 19.7 torr).

9. A normal saline solution contains 9 g of NaCl per liter of water. Estimate its osmotic pressure at \( 37 \, ^\circ\text{C} \). (7.83 atm)

10. The following analyses were carried out on a compound that contains only carbon, hydrogen, and oxygen. A 0.2500 g sample of the compound was burned to give 0.6376 g of CO\(_2\) and 0.1629 g of H\(_2\)O. In another experiment it was found that a solution prepared by dissolving 0.404 g of the compound in 50.0 g of ethanol had a freezing point depression of 0.117 \( ^\circ\text{C} \). Given that \( K_f \) for ethanol is 1.99 \( ^\circ\text{C}/\text{m} \) and the substance is a nonelectrolyte, what is the molecular formula of the compound? (\( \text{C}_8\text{H}_{10}\text{O}_2 \))

11. A solution was prepared by dissolving 20.0 g of the nonvolatile compound, naphthol (\( \text{C}_{10}\text{H}_8\text{O} \)) in 50.0 g of benzene (\( \text{C}_6\text{H}_6 \)). Given that, at \( 35 \, ^\circ\text{C} \), the vapor pressure of pure benzene is 191 Torr, calculate the vapor pressure of the solution at \( 35 \, ^\circ\text{C} \). (157 Torr)

12. A 0.0025 m solution of an ionic solute in water had a freezing point of \( -0.014 \, ^\circ\text{C} \). Which one of the following, if any, could be the ionic solute? KBr, K\(_2\)SO\(_4\), K\(_3\)PO\(_4\), KNO\(_3\)

13. Experimentally it was found that a solution prepared by dissolving 0.200 g of acetic acid, CH\(_3\)COOH, in 100 g of benzene produced a freezing point depression of 0.0861 \( ^\circ\text{C} \). Account for the value of the experimental molar mass.

14. The osmotic pressure expression given in class is a limiting law and is valid only for very dilute solutions. Therefore molar masses determined from this expression will be quite approximate. Shown below are some osmotic pressures measured for a series of sucrose (\( \text{C}_{12}\text{H}_{22}\text{O}_{11} \)) solutions at \( 20 \, ^\circ\text{C} \).

<table>
<thead>
<tr>
<th>Concentration in g sucrose/Liter</th>
<th>( \pi ) (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>126.7</td>
<td>10.14</td>
</tr>
<tr>
<td>155.1</td>
<td>12.75</td>
</tr>
<tr>
<td>182.5</td>
<td>15.39</td>
</tr>
<tr>
<td>208.0</td>
<td>18.13</td>
</tr>
<tr>
<td>234.3</td>
<td>20.91</td>
</tr>
</tbody>
</table>
Solutions

a. Calculate the apparent molar mass of sucrose at each of the concentrations given and compare these values with the correct one.

e. b. Fairly accurate molar masses can be obtained from data such as shown above by calculating the ratio of the osmotic pressure to concentration in g/L, plotting this ratio vs the concentration and determining the limiting value of the ratio at zero concentration. Construct such a plot for the sucrose data, extrapolate to zero concentration and use this limiting value to calculate the molar mass of sucrose.

15. Fill in the missing information in the following table, assume that the solute is a nonelectrolyte.

<table>
<thead>
<tr>
<th>Molar Mass</th>
<th>grams of Solute</th>
<th>grams of Solvent</th>
<th>Δtf (°C)</th>
<th>Kf (°/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>87.0</td>
<td>______</td>
<td>60.0</td>
<td>6.14</td>
<td>5.12</td>
</tr>
<tr>
<td>98.0</td>
<td>4.77</td>
<td>______</td>
<td>1.67</td>
<td>1.99</td>
</tr>
<tr>
<td>______</td>
<td>3.20</td>
<td>39.0</td>
<td>5.21</td>
<td>6.85</td>
</tr>
<tr>
<td>32.0</td>
<td>2.23</td>
<td>75.0</td>
<td>______</td>
<td>1.86</td>
</tr>
<tr>
<td>212</td>
<td>18.7</td>
<td>210</td>
<td>8.44</td>
<td>______</td>
</tr>
</tbody>
</table>

(answers: 6.26, 58.0, 108, 1.73, 20.1)
Other answers.

12. \( \text{K}_2\text{SO}_4 \)

13. Experimental MM of \( \text{CH}_3\text{COOH} \) from fp depression = 119. Actual MM = 60. This indicates that in benzene acetic acid exists as dimers, \((\text{CH}_3\text{COOH})_2\). This is due to hydrogen bonding between the molecules giving a dimeric structure.

\[ \text{CH}_3-\text{C} \equiv \text{O} \quad \text{---} \quad \text{H-O} \quad \text{---} \quad \text{O-C} \equiv \text{O} \quad \text{CH}_3 \]

\[ \text{---} = \text{hydrogen bonds} \]

14.

Molar Mass of \( \text{C}_{12}\text{H}_{22}\text{O}_{11} = 342 \)

![Graph showing relationship between g/L and g/L with various MM values indicated](image-url)