SOLUTION CONCENTRATIONS

- The amount of solute in a solution (concentration) is an important property of the solution. A dilute solution contains small quantities of solute relative to the solvent, while a concentrated solution contains large quantities of solute relative to the solvent.

- The concentration of a solution can be expressed in various ways, such as: molarity, molality, mass percent and mole fraction. Molarity was discussed earlier in Chapter 4. The other methods of expressing concentration will be discussed in this section.

Mass Percent:

- Concentration can be expressed as mass percent defined as:

\[
\text{Mass percent} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100
\]

- Mass of solution is defined as mass of solute + mass of solvent.

Mole Fraction:

- For some applications, it is more convenient to express concentration as mole fraction. Mole fraction of solute (\(X_{\text{solute}}\)) is defined as:

\[
X_{\text{solute}} = \frac{\text{amount of solute (in mol)}}{\text{total amount of solute and solvent (in mol)}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}
\]

Molality:

- A concentration unit that is independent of temperature is molality (m). Molality is defined as:

\[
\text{Molality (m)} = \frac{\text{amount of solute (in mol)}}{\text{mass of solvent (in kg)}}
\]
SOLUTION CONCENTRATIONS

- Examples that follow show how various concentration units can be calculated and their interconversions.

**Examples:**

1. A solution is prepared by dissolving 17.2 g of ethylene glycol (C₂H₆O₂) in 0.500 kg of water. The final volume of solution is 515 mL. Calculate the concentration of this solution in units of:

   a) molarity

   b) molality

   c) mass percent of solute

   d) mole fraction of solute
SOLUTION CONCENTRATIONS

Examples (cont’d):

2. What is the molarity of a 6.56% by mass glucose (C₆H₁₂O₆) solution? The density of the solution is 1.03 g/mL.

3. What is the molality of a 10.5% by mass glucose (C₆H₁₂O₆) solution? The density of the solution is 1.03 g/mL.
COLLIGATIVE PROPERTIES

- Properties of solution that depends on the number of particles dissolved in solution are called **colligative properties**. Some important colligative properties are vapor pressure lowering, freezing point depression and boiling point elevation.

- Since these properties depend on the number of particles in solution, nonelectrolytes are treated slightly differently that electrolytes when determining colligative properties. Recall that when one mol of nonelectrolyte dissolves in water, it produces one mol of particles.

- By contrast, when one mol of electrolyte dissolves in water, it produces more than one mol of particles. For example, when one mol of NaCl dissolves in water, it produces two mol of ions (particles).

**Freezing Point Depression**

- Addition of a nonvolatile solute to a solvent lowers its freezing point.

- This freezing point depression is proportional to the amount of solute in a solution.

\[
\Delta T_f = m K_f
\]

\(\Delta T_f\) = freezing point depression  
\(K_f\) = freezing point depression constant  
\(m\) = molality of solution

**Boiling Point Elevation**

- Addition of a nonvolatile solute to a solvent increases its boiling point.

- This boiling point elevation is proportional to the amount of solute in a solution.

\[
\Delta T_b = m K_b
\]

\(\Delta T_b\) = boiling point elevation  
\(K_b\) = boiling point elevation constant  
\(m\) = molality of solution
Examples:
1. A solution of antifreeze contains 135 g of ethylene glycol (C$_2$H$_6$O$_2$) per 500. g of water. What is the freezing point of this solution? ($K_f = 1.86 \, ^\circ C/m$)

2. What is the boiling point of the antifreeze solution in the previous problem? ($K_b = 0.512 \, ^\circ C/m$)

3. A solution is prepared by dissolving 215 g of methanol (CH$_3$OH) in 800. g of water. What is the freezing point of this solution? ($K_f = 1.86 \, ^\circ C/m$)

4. What mass of ethylene glycol must be added to 1.0 kg of water to produce a solution that boils at 105.0$^\circ$C?
COLLIGATIVE PROPERTIES OF IONIC SOLUTIONS

- When evaluating colligative properties of ionic solutions, the total concentration of the ions must be considered.

- The number of ions produced from each formula unit is designated \(i\).

\[
\begin{align*}
\text{NaCl} & \rightarrow \text{Na}^+ + \text{Cl}^- \quad i = 2 \\
\text{MgCl}_2 & \rightarrow \text{Mg}^{2+} + 2 \text{Cl}^- \quad i = 3
\end{align*}
\]

- The colligative properties of ionic solutions can be calculated with the following modifications:

\[
\begin{align*}
\Delta T_b &= i \ m \ K_b \\
\Delta T_f &= i \ m \ K_f
\end{align*}
\]

Examples:

1. Calculate the freezing point of 0.010 m solution of aluminum sulfate, \(\text{Al}_2(\text{SO}_4)_3\). (\(K_f\) for water = 1.86 m/°C)

\[
\begin{align*}
\text{Al}_2(\text{SO}_4)_3 & \rightarrow \\
\Delta T_f &= \\
T_f &=
\end{align*}
\]

2. Which of the following solutions will have the lowest freezing point?

- 0.15 m \(\text{NaCl}\)
- 0.25 m \(\text{C}_6\text{H}_{12}\text{O}_6\)
- 0.10 m \(\text{Fe(NO}_3)_3\)
VAPOR PRESSURE LOWERING

- The pressure of a gas above a liquid at a particular temperature is defined as its vapor pressure. At a particular temperature, gas and liquid molecules for a substance are in dynamic equilibrium (meaning rate of vaporization equals the rate of condensation).

\[ \text{H}_2\text{O (l)} \xrightarrow{\text{vaporization}} \text{H}_2\text{O (g)} \]

- What is the effect of a nonvolatile solute on the vapor pressure of a the liquid into which it dissolves?

- When a nonvolatile solute is added to a liquid, the solute particles (red) interfere with the ability of the solvent particles (blue) to vaporize. As a result, the vapor pressure of the liquid is lowered by addition of the solute.

- The vapor pressure of a solution can be quantified with Raoult’s Law:

\[ P_{\text{solution}} = X_{\text{solvent}} P^\circ_{\text{solvent}} \]

\[ P_{\text{solution}} = \text{vapor pressure of solution} \]

\[ X_{\text{solvent}} = \text{mole fraction of solvent} \]

\[ P^\circ_{\text{solvent}} = \text{vapor pressure of pure solvent at the same } T \]

- For example, for an aqueous solution at 25°C that contains 0.90 mol water and 0.10 mol of a non-volatile solute (such as sucrose), the vapor pressure can be calculated as shown below:

\[ P_{\text{solution}} = X_{\text{solvent}} P^\circ_{\text{solvent}} = (0.90)(23.8 \text{ mmHg}) = 21.4 \text{ mmHg} \]

- Vapor pressure lowering (\(\Delta P\)) is defined as the difference in vapor pressure between the pure solvent and the solution, and can be shown to be equal to:

\[ \Delta P = X_{\text{solute}} P^\circ_{\text{solvent}} \]

- For example, for the aqueous solution described above, \(\Delta P\) can be calculated by two different methods:

\[ \Delta P = P^\circ - P_{\text{solution}} = 23.8 \text{ mmHg} - 21.4 \text{ mmHg} = 2.4 \text{ mmHg} \]

\[ \Delta P = X_{\text{solute}} P^\circ_{\text{solvent}} = (0.10)(23.8 \text{ mmHg}) = 2.4 \text{ mmHg} \]
Examples:
1. Calculate the vapor pressure at 25°C of a solution containing 99.5 g of sucrose (C\textsubscript{12}H\textsubscript{22}O\textsubscript{11}) and 300.0 mL of water. The vapor pressure of pure water at 25°C is 23.8 mmHg. Assume density of water to be 1.00 g/mL.

2. Calculate the vapor pressure at 25°C of a solution containing 55.3 g of ethylene glycol and 285.2 g of water.

3. A solution containing ethylene glycol and water has a vapor pressure of 7.88 mmHg at 10°C. Pure water has a vapor pressure of 9.21 mmHg at 10°C. What is the mole fraction of ethylene glycol in this solution?
VAPOR PRESSURE OF SOLUTIONS CONTAINING VOLATILE (NONELECTROLYTE) SOLUTE

- The previous examples consisted of solutions containing nonvolatile solutes. Some solutions contain a volatile solvent and a volatile solute. In these solutions, both the solute and the solvent contribute to the overall vapor pressure of the solution.

- A solution as described above may be an ideal solution (one that follows Raoult’s law) or it maybe non-ideal solution (one that does not follow Raoult’s law).

- Similar to an ideal gas (which follows the ideal gas law exactly, an ideal solution follows Raoult’s law exactly because the solute–solvent interactions are similar in magnitude to solute–solute and solvent–solvent interactions.

- In an ideal solution, the vapor pressure of each of the solution components is described by Raoult’s law throughout the entire composition range of the solution. For example, for a two component solution containing liquids A and B, the vapor pressure of each component can be calculated as shown below:

\[
\begin{align*}
P_A &= X_A P^\circ_A \\
P_B &= X_B P^\circ_B
\end{align*}
\]

- The total pressure above the solution is the sum of the partial pressure of the components. Therefore,

\[
P_{\text{tot}} = P_A + P_B
\]

- The graph below is a plot of vapor pressure versus solution composition for an ideal 2-component system.
**Examples:**
1. A solution contains 3.95 g of CS$_2$ and 2.43 g of acetone (CH$_3$COCH$_3$). The vapore pressure at 35°C of pure CS$_2$ and pure acetone are 515 mmHg and 332 mmHg, respectively. Assuming ideal behavior, calculate the vapor pressure of each of the components and the total pressure above the solution.

   Step 1: Calculate mole fraction of each solution component:

   Step 2: Calculate the partial pressure of each component:

   Step 3: Calculate the total vapor pressure of solution:
Examples (cont’d):

2. A solution of benzene (C₆H₆) and toluene (C₇H₈) is 25% benzene by mass. The vapor pressure of pure benzene and pure toluene at 25°C are 94.2 mmHg and 28.4 mmHg, respectively. Assuming ideal behavior, calculate the following:

a) The vapor pressure of each of the solution components in the mixture.

b) The total pressure above the solution.

c) The composition of the vapor in mass percent.

3. A solution contains a mixture of pentane and hexane at room temperature. The solution has a vapor pressure of 258 mmHg. Pure pentane and hexane have vapor pressures of 425 mmHg and 151 mmHg, respectively, at room temperature. Assuming ideal behavior, what is the mole fraction composition of the mixture?
IDEAL SOLUTIONS WITH 2 OR MORE VOLATILE COMPONENTS

- Solutions sometimes have 2 or more volatile components. For example, gasoline is a complex solution containing several volatile substances.

- Assuming ideal behavior, we used Raoult’s law to calculate the vapor pressure of the mixture based on mole fraction of each component and the vapor pressure of each in the pure state.

- These calculations indicated that the vapor in equilibrium above each mixture is richer in the more volatile component. Therefore, we can generalize the following statement:

  The vapor in equilibrium above an ideal solution is richer in the more volatile component compared to the original mixture.

- This fact forms the basis of an important technique, called distillation. Distillation is used to separate (or partially separate) mixtures containing several volatile components.

- Distillation is the procedure by which a moonshiner obtains whiskey using a still, and by which petrochemical plants achieve the separation of crude petroleum into gasoline, diesel, lubricating oil and so on. Shown below are laboratory and industrial uses of this technique.
VAPOR PRESSURE OF SOLUTIONS CONTAINING STRONG ELECTROLYTES

- Just as the freezing point depression and boiling point elevation of solutions containing an electrolyte solute are greater than that of a solution containing the same concentration of a nonelectrolyte solute, so is the vapor pressure lowering (and for the same reason).

- For example, the vapor pressure of a sodium chloride solution is lowered about twice as much as it is for a nonelectrolyte solution of the same concentration. To calculate the vapor pressure of a solution containing an ionic solute, we need to account for the dissociation of the solute when we calculate the mole fraction of the solvent, as shown in the example below:

**Examples:**

1. A solution contains 0.102 mol Ca(NO$_3$)$_2$ and 0.937 mol H$_2$O. Calculate the vapor pressure of the solution at 55°C. The vapor pressure of pure water at 55°C is 118.1 mmHg. (Assume the solute completely dissociates)

2. Calculate the vapor pressure at 25°C of an aqueous solution that is 5.50% NaCl by mass. The vapor pressure of pure water at 25°C is 23.8 mmHg. (Assume complete dissociation of the solute)
COLLIGATIVE PROPERTIES OF STRONG ELECTROLYTES

VAN’T HOFF FACTOR

- We have already discussed that when determining the colligative properties of solutions containing an ionic solid, one must consider the total concentration of dissolved particles. Earlier we used the term \((i)\) to designate the number of particles formed in solution when an ionic solid dissolves.

- The ratio of the moles of dissolved particles in solution to the moles of formula units dissolved \((i)\) is called the Van’t Hoff factor:

\[
i = \frac{\text{moles of particles in solution}}{\text{moles of formula units dissolved}}
\]

- Since 1 mol of NaCl produces 2 mol of particles in solution, we expect the van’t Hoff factor for NaCl to be exactly 2. In reality, this expected factor occurs only in very dilute solutions. For example, the van’t Hoff factor for 0.10 m NaCl is 1.87 and that for 0.010 m NaCl is 1.94. The van’t Hoff factor approaches the expected value at infinite dilution.

- The table below shows the actual and the expected van’t Hoff factors for a number of solutes:

<table>
<thead>
<tr>
<th>Solute</th>
<th>(i) Expected</th>
<th>(i) Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonelectrolyte</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>NaCl</td>
<td>2</td>
<td>1.9</td>
</tr>
<tr>
<td>MgSO(_4)</td>
<td>2</td>
<td>1.3</td>
</tr>
<tr>
<td>MgCl(_2)</td>
<td>3</td>
<td>2.7</td>
</tr>
<tr>
<td>K(_2)SO(_4)</td>
<td>3</td>
<td>2.6</td>
</tr>
<tr>
<td>FeCl(_3)</td>
<td>4</td>
<td>3.4</td>
</tr>
</tbody>
</table>

- The reason the van’t Hoff factors do not exactly equal expected values is that some ions effectively pair in solution, slightly reducing the number of particles in solution.

- The diagram to the right shows how some hydrated anions and cations can get close enough to effectively pair and reduced the number of particles in solution.
Examples:

1. The freezing point of an aqueous 0.050 m CaCl₂ solution is –0.27°C. What is the van’t Hoff factor for CaCl₂ at this concentration? (K_f for water = 1.86°C/m)

2. Calculate the freezing point of an aqueous 0.10 m FeCl₃ solution using a van’t Hoff factor of 3.2.

3. A solution is prepared from 4.5701 g of magnesium chloride and 43.238 g of water. The vapor pressure of water above this solution is 0.3624 atm at 348 K. The vapor pressure of pure water at this temperature is 0.3804 atm. Find the value of the van’t Hoff factor for magnesium chloride in this solution.
### ANSWERS TO IN-CHAPTER PROBLEMS:

<table>
<thead>
<tr>
<th>Page</th>
<th>Example No.</th>
<th>Answer</th>
</tr>
</thead>
</table>
| 2    | 1           | a) Molarity = 0.538 M  
b) Molality = 0.554 m  
c) Mass percent of solute = 3.33%  
d) Mole fraction of solute = 0.0989 |
| 3    | 2           | Molarity = 0.375 M |
|      | 3           | Molality = 0.651 m |
| 5    | 1           | $T_f = -8.11 \, ^\circ C$ |
|      | 2           | $T_b = 102.23 \, ^\circ C$ |
|      | 3           | $T_f = -15.6 \, ^\circ C$ |
|      | 4           | 610 g |
| 6    | 1           | $T_f = -0.093 \, ^\circ C$ |
|      | 2           | 0.10 m Fe(NO$_3$)$_3$ |
| 8    | 1           | $P_{\text{soln}} = 23.4 \, \text{mmHg}$ |
|      | 2           | $P_{\text{soln}} = 22.5 \, \text{mmHg}$ |
|      | 3           | $X_{\text{EG}} = 0.144$ |
| 10   | 1           | a) $X_A = 0.55\overline{3}5; \; X_B = 0.44\overline{6}5$  
b) $P_A = 285 \, \text{mmHg}; \; P_B = 148 \, \text{mmHg}$  
c) $P_{\text{tot}} = 433 \, \text{mmHg}$ |
| 11   | 2           | a) $P_A = 26.6 \, \text{mmHg}; \; P_B = 20.4 \, \text{mmHg}$  
b) $P_{\text{tot}} = 47.0 \, \text{mmHg}$  
c) $\% \, A = 52.5\% ; \; \% \, B = 47.5\%$ |
|      | 3           | $X_{\text{pentane}} = 0.391; \; X_{\text{hexane}} = 0.609$ |
| 13   | 1           | $P_{\text{soln}} = 88.8 \, \text{mmHg}$ |
|      | 2           | $P_{\text{soln}} = 23.0 \, \text{mmHg}$ |
| 15   | 1           | $i = 2.9$ |
|      | 2           | $T_f = -0.60 \, ^\circ C$ |
|      | 3           | $i = 2.484$ |