

# 1. Colligative Properties of Solutions

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## Objective

Colligative properties of solutions depend on the *quantity* of solute dissolved in the solvent rather than the *identity* of the solute. The phenomenon of freezing point lowering will be examined quantitatively as an example of a colligative property in Choice I. The phenomena of osmosis and dialysis will be investigated qualitatively in Choice II.

## Choice I. Freezing Point Depression and Molar Mass Determination

### Introduction

When a solute is dissolved in a solvent, the properties of the solvent are *changed* by the presence of the solute. The magnitude of the change generally is *proportional to* the amount of solute added. Some properties of the solvent are changed only by the *number* of solute particles present, without regard to the particular *nature* of the solute. Such properties are called **colligative properties** of the solution. Colligative properties include changes in vapor pressure, boiling point, freezing point, and osmotic pressure.

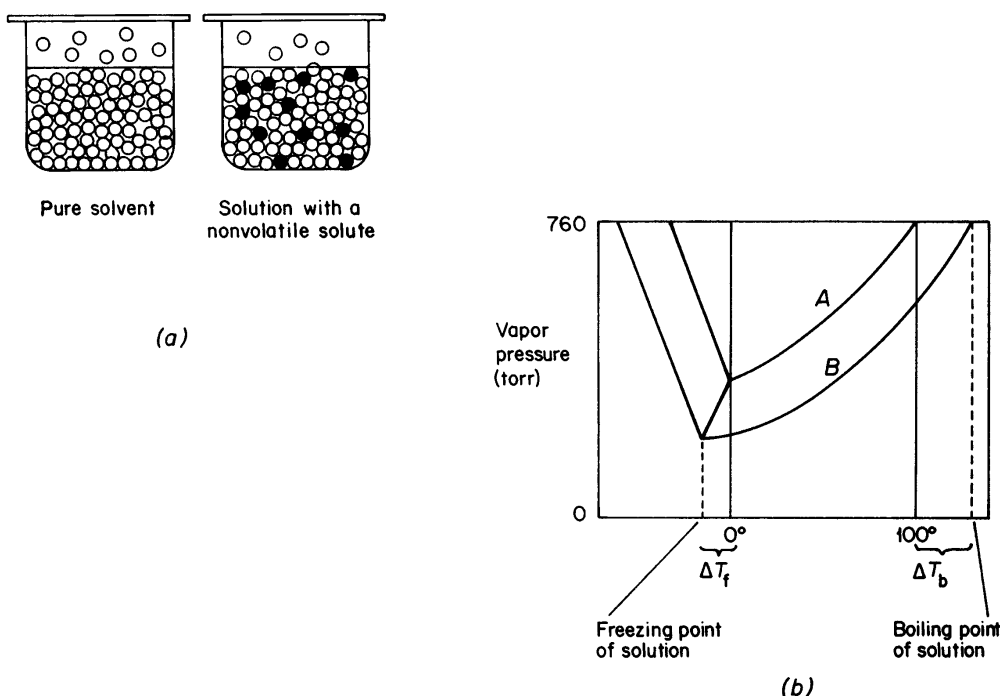
For example, if a nonvolatile, nonionizing solute is added to a volatile solvent (such as water), the amount of solvent that can escape from the surface of the liquid at a given temperature is lowered, relative to the case where only the pure solvent is present. The vapor pressure above such a solution will be lower than the vapor pressure above a sample of the pure solvent under the same conditions. Molecules of nonvolatile solute physically *block* the surface of the solvent, thereby preventing as many molecules from evaporating at a given temperature. (See Figure 1-1.) As shown in the figure, if the vapor pressure of the solution is lowered, there is an increase in the boiling point of the solution as well as a decrease in the freezing point.

In this experiment, you will determine the freezing points of a pure solvent (naphthalene), a solution of a known solute (1,4-dichlorobenzene,  $C_6H_4Cl_2$ ) dissolved in naphthalene, and an unknown solution of sulfur in naphthalene. The sulfur is considered to be an unknown solute because you will be determining the molar mass of sulfur (and the formula of elemental sulfur). It may turn out to be rather surprising.

The decrease in freezing point ( $\Delta T_f$ ) when a nonvolatile, nonionizing solute is dissolved in a solvent is proportional to the molal concentration ( $m$ ) of solute present in the solvent:

$$\Delta T_f = K_f m \quad (1-1)$$

FIGURE 1-1  
 (a) The presence of a nonvolatile solute lowers the vapor pressure of the solvent by blocking the surface.  
 (b) Plot of vapor pressure vs. temperature for a pure solvent and a solution. Note that the presence of a solute changes the properties of the solvent.



$K_f$  is a constant for a given solvent (called the molal freezing point depression constant) and represents by how many degrees the freezing point will change when 1.00 mol of solute is dissolved per kilogram of solvent. For example,  $K_f$  for water is  $1.86^\circ\text{C kg/mol}$ , whereas  $K_f$  for the solvent benzene is  $5.12^\circ\text{C kg/mol}$ .

The molal concentration of a solution represents how many moles of solute are dissolved per kilogram of the solvent. For example, if 0.50 mol of the sugar sucrose were dissolved in 100 g of water, this would be equivalent to 5.0 mol of sugar per kilogram of solvent, and the solution would be 5.0 molal. The molality of a solution is defined as

$$\text{molality, } m = \frac{\text{moles of solute}}{\text{kilograms of solvent}} \quad (1-2)$$

The measurement of freezing point lowering is routinely used for the determination of the molar masses of unknown solutes. If Equations 1-1 and 1-2 are combined, it can be derived that the molar mass of a solute is related to the freezing point lowering experienced by the solution and to the composition of the solution. Consider the following example:

The molal freezing point depression constant  $K_f$  for the solvent benzene is  $5.12^\circ\text{C kg/mol}$ . A solution of 1.08 g of an unknown in 10.02 g of benzene freezes  $4.60^\circ\text{C}$  lower than pure benzene. Calculate the molar mass of the unknown.

The molality of the solution can be obtained using Equation 1-1:

$$m = \Delta T_f / K_f = 4.60^\circ\text{C} / 5.12^\circ\text{C kg/mol} = 0.898 \text{ mol/kg}$$

Using the definition of molality from Equation 1-2, the number of moles of unknown present can be calculated

$$m = 0.898 \text{ mol/kg} = \text{mol unknown}/0.01002 \text{ kg solvent}$$

$$\text{moles of unknown} = 0.00898 \text{ mol}$$

Thus, 0.00898 mol of the unknown weighs 1.08 g, and the molar mass of the unknown is given by

$$\text{molar mass} = 1.08 \text{ g}/0.00898 \text{ mol} = 120. \text{ g/mol}$$

In the preceding discussion, we considered the effect of a *nonionizing* solute on the freezing point of a solution. If the solute does indeed ionize, the effect on the freezing point will be *larger*. The depression of the freezing point of a solvent is related to the number of particles of solute present in the solvent. If the solute ionizes as it dissolves, the total number of moles of all particles present in the solvent will be larger than the formal concentration indicates. For example, a 0.1 *m* solution of NaCl is effectively 0.1 *m* in *both* Na<sup>+</sup> and Cl<sup>-</sup> ions.

## SAFETY PRECAUTIONS

- **Wear safety glasses at all times while in the laboratory.**
- **Naphthalene and 1,4-dichlorobenzene are toxic, and their vapors are harmful. Do not handle these substances. Work in an exhaust hood. Wear disposable gloves.**
- **Use glycerine when inserting the thermometer through the rubber stopper. Protect your hands with a towel.**
- **Acetone is highly flammable. Use acetone only in the exhaust hood.**
- **Dispose of the naphthalene solutions as directed by the instructor.**

## Apparatus/Reagents Required

8-inch test tube with two-hole stopper to fit, thermometer, stirring wire, beaker tongs, naphthalene, 1,4-dichlorobenzene, sulfur, acetone, disposable gloves

## Procedure

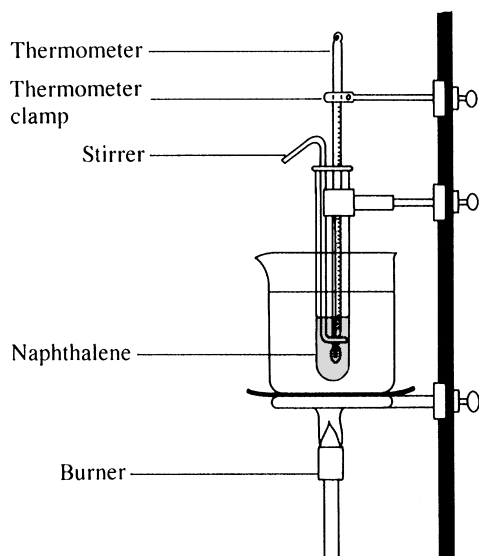
Record all data and observations directly in your notebook in ink.

### A. *Determination of the Freezing Point of Naphthalene*

Set up a 600-mL beaker about three-fourths full of water in an exhaust hood, and heat the water to boiling.

Using glycerine as a lubricant and protecting your hands with a towel, insert your thermometer through a two-hole stopper so that the temperature can still be read from 60–90°C. Equip the second hole of the stopper with a length of copper wire, coiled at the bottom into a ring that will fit around the thermometer. The copper wire will be used to *stir* the solution. (See Figure 1-2.)

FIGURE 1-2  
Apparatus for  
freezing point  
determination.  
Be certain the  
thermometer  
can be read  
from 60–90°C.



Weigh a clean, dry 8-inch test tube to the nearest 0.01 g.

Add approximately 10 g of naphthalene to the test tube, and reweigh precisely, to the nearest 0.01 g.

Use a clamp to set the test tube vertically in the boiling water bath. Allow the naphthalene to melt completely.

When the naphthalene has melted completely, insert the rubber stopper containing the thermometer and copper wire into the test tube. See Figure 1-2. Make certain that the bulb of the thermometer is immersed in the molten naphthalene and that the copper stirring wire can be agitated freely.

Continue to heat the test tube to remelt any naphthalene that might have crystallized on the thermometer or stirring wire. Move the stirring wire up and down to make certain the temperature is uniform throughout the naphthalene sample.

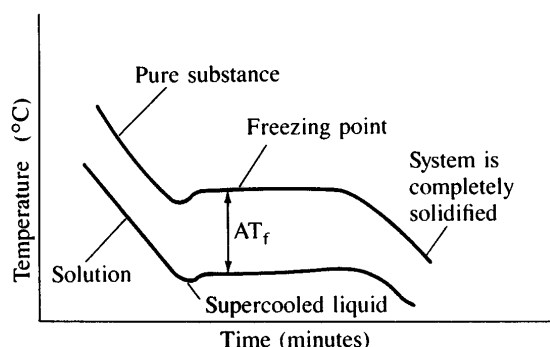
When the naphthalene has remelted completely (generally the temperature will be above 95°C), remove the beaker of hot water from under the test tube (*Caution!*) using tongs or a towel to protect your hands from the heat.

Ensure that the thermometer is immersed in the center of the molten naphthalene and does *not* touch the walls of the test tube. When the temperature of the molten naphthalene has dropped to 90°C, begin recording the temperature of the naphthalene every 30 seconds. Record the temperatures to the nearest 0.1°C.

Continue taking the temperature of the naphthalene until the temperature has dropped to around 60–65°C. The naphthalene will freeze in this temperature range.

On graph paper, plot a **cooling curve** for naphthalene: graph the *temperature* of the naphthalene as it cools versus the *time* in minutes. You will notice that the naphthalene *remains* at the same temperature for several minutes; this results in a horizontal, flat region in the cooling curve. This temperature represents the freezing point of pure naphthalene. (See Figure 1-3.)

FIGURE 1-3  
Cooling curve for a pure solvent and of a solution involving the solvent. The flat portions of the curves represent freezing.



Use the boiling water bath to remelt the naphthalene in the test tube, and remove the thermometer and wire stirrer. In the exhaust hood, rinse any adhering naphthalene from the thermometer/stirrer with acetone (*Caution: Flammable!*). Allow the thermometer/stirrer to remain in the hood until all acetone has evaporated.

### B. Determination of $K_f$ for Naphthalene

Reweigh the test tube containing the naphthalene to the nearest 0.01 g. Some of the naphthalene may have been lost on the thermometer/stirrer apparatus or vaporized.

Add approximately 1 g of 1,4-dichlorobenzene crystals to the test tube containing the naphthalene, and reweigh the test tube to the nearest 0.01 g.

Melt the naphthalene/dichlorobenzene mixture in boiling water.

Make certain that all acetone has evaporated from the thermometer/stirrer apparatus (any remaining acetone would *also* lower the freezing point of naphthalene).

Insert the thermometer/stirrer apparatus into the test tube containing the molten naphthalene/dichlorobenzene mixture. Stir the mixture for several minutes while it is in the boiling water bath to make certain that the solution is completely homogeneous.

Following the same procedure as in Part A, determine the cooling curve and the freezing point of the 1,4-dichlorobenzene/naphthalene solution.

From the freezing point depression of the naphthalene/dichlorobenzene solution and the composition of the solution, calculate the molal freezing point depression constant,  $K_f$ , for naphthalene. The molecular formula of 1,4-dichlorobenzene is  $C_6H_4Cl_2$ .

Use the boiling water bath to remelt the naphthalene mixture in the test tube, and remove the thermometer and wire stirrer. In the exhaust hood, rinse any adhering naphthalene from the thermometer/stirrer with acetone (*Caution: Flammable!*). Allow the thermometer/stirrer to remain in the hood until all acetone has evaporated. Dispose of the naphthalene/dichlorobenzene mixture as directed by the instructor.

### ***C. Determination of the Freezing Point of a Sulfur Solution***

Clean and dry an 8-inch test tube, and weigh it to the nearest 0.01 g.

Add approximately 10 g of naphthalene to the test tube, and reweigh the test tube and contents to the nearest 0.01 g.

Add approximately 0.5 g of powdered sulfur to the naphthalene in the test tube and reweigh again to the nearest 0.01 g.

Make certain that all acetone has evaporated from the thermometer/stirrer apparatus (any remaining acetone would also lower the freezing point of naphthalene).

Melt the mixture in the boiling water bath (following the procedure described earlier) and insert the thermometer/stirrer apparatus. Stir thoroughly to make certain that the sulfur is completely dissolved. Determine the cooling curve and freezing point of the sulfur/naphthalene solution.

From the freezing point depression of the sulfur/naphthalene solution and  $K_f$  for naphthalene as determined in Part B, calculate the molar mass of sulfur. Determine the number of sulfur atoms that must be present in a molecule of elemental sulfur to give rise to this molar mass

Attach your three graphs to the laboratory report.

## **Choice II. Osmosis and Dialysis**

### **Introduction**

Plant and animal cell membranes must provide some mechanism for the transfer of materials across the membrane without the wholesale loss of the cell's fluid contents or microstructures. Although there are several mechanisms by which molecules are passed through cell walls, perhaps the simplest to understand and demonstrate are the processes of *osmosis* and *dialysis*.

Cell membranes are said to be **semipermeable**: such membranes contain pores that are of a sufficient size that they permit the passage of ions and

small molecules, while *not* allowing the passage of most macromolecules or cell organelles. Osmosis represents the passage of *solvent* through a semipermeable membrane, whereas dialysis refers to the passage of *solute* molecules as well. Both osmosis and dialysis occur whenever a concentration gradient (difference) exists between the solutions on either side of a membrane. Osmosis and dialysis occur in an attempt to *equalize* the concentrations of the solutions on either side of the membrane.

For example, suppose you had just eaten a sugary snack after a few hours without food. After digestion of the snack takes place, your bloodstream would have a relatively high concentration of carbohydrates, whereas in the interior of your cells, the concentration of carbohydrates would be expected to be lower (since whatever sugars had been present would have been metabolized during the period without food). Dialysis of sugar molecules from the region of high concentration in the bloodstream to the region of low concentration inside the cells would take place until the concentrations on either side of the cell membrane were similar. Osmosis of water from the cell interior into the bloodstream will also take place.

Osmosis and dialysis are special examples of the process of diffusion: Molecules of solute and solvent diffuse across a membrane separating two solutions in an effort to equalize the concentrations of the solutions, which is very nearly the same as would happen between the two solutions if the membrane were not present.

The *force* with which osmosis/dialysis takes place—that is, how strongly solvent or solute flows through the membrane—depends on the degree of difference in concentration across the membrane. If the two solutions separated by the membrane are of very nearly the same concentration, the osmosis/dialysis that takes place will be very gentle. If a *large* difference in concentration exists across the membrane, however, the osmosis/dialysis will be very strong (perhaps so forceful as to rupture the membrane). For this reason, solutions to be injected into the bloodstream, such as the dextrose solutions used for intravenous feeding in hospitals, have their concentrations adjusted to be very nearly that of normal bodily fluids: Such solutions are said to be *isotonic* with the normal fluids of the body.

The force with which osmosis takes place is measured in terms of the **osmotic pressure** that exists between a solution and a sample of the pure solvent. The osmotic pressure represents the pressure that would have to be applied to the solution to just *prevent* osmosis of the solvent across a membrane. Osmotic pressure ( $\Pi$ ) is a colligative property of solutions and is dependent on the molarity of solute present in the solution:

$$\Pi = MRT \quad (1-3)$$

Accurate osmotic pressures are not conveniently measurable in the general chemistry laboratory, and so this experiment will only investigate the processes of osmosis and dialysis on a qualitative basis. Osmosis into both a concentrated and a dilute solution of the same solute will be examined to determine into which solution osmosis occurs with the greater force. Dialysis of sodium chloride (an ionic solute), dextrose (a molecular carbohydrate solute), and starch (a colloidal macromolecular solute) will be investigated, and the relative *time* required for dialysis determined.

## SAFETY PRECAUTIONS

- Wear safety glasses at all times while in the laboratory.
- Silver nitrate solutions will discolor the skin if spilled. Nitrates are strong oxidizing agents and are toxic. Wash your hands after handling.
- Benedict's and Fehling's solutions are toxic. Wash your hands after handling.

## Apparatus/Reagents Required

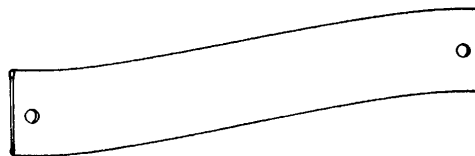
Cellophane dialysis tubing, paper punch, 5% NaCl, 25% NaCl, 5% glucose, 1% starch solution, 0.1 M silver nitrate, Benedict's or Fehling's reagents, 0.1 M I<sub>2</sub>/KI reagent, 600 mL beakers, graduated cylinder

## Procedure

### A. Demonstration of Osmotic Pressure

Cut two strips of cellophane dialysis tubing each 10–12 inches long. With a paper punch, make a small hole through each piece of tubing about 1 inch from each end. See Figure 1-4.

FIGURE 1-4  
Preparation  
of dialysis  
tubing. Note  
the location of  
the punch  
holes.



Soak the strips of tubing in water until they become soft and the tubing walls can be spread apart.

Set up two 600-mL beakers in a location where they will not be a disturbed. Place 450–500 mL of distilled water in each beaker.

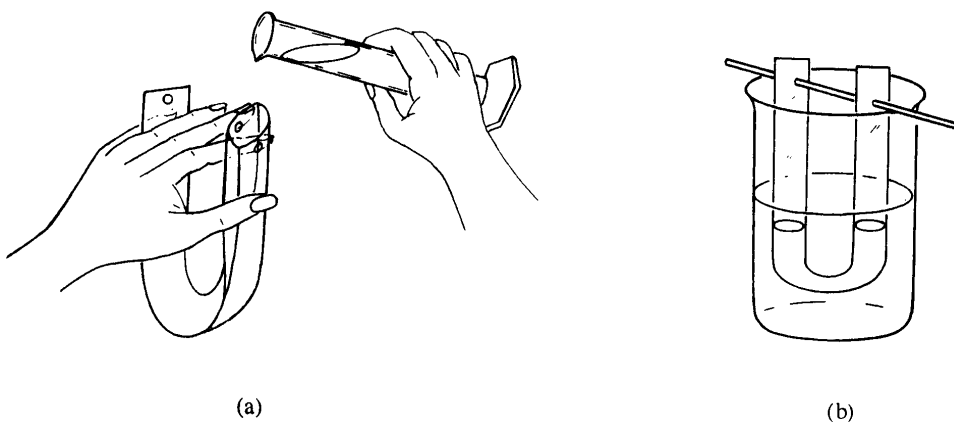
Obtain 30–40 mL of 5% NaCl solution in a clean beaker, and then transfer exactly 25 mL of this solution to a graduated cylinder.

Holding one of the pieces of dialysis tubing by both ends to prevent spillage, transfer the 25 mL of 5% NaCl solution to the tubing. See Figure 1-5(a).

Insert a stirring rod through the holes in the end of the dialysis tubing, and suspend the tubing containing 5% NaCl solution in one of the beakers of distilled water. If the solution in the tubing is not covered by the water in the beaker, add additional water to the beaker. See Figure 1-5(b).

FIGURE 1-5

(a) Make a “sling” with a length of dialysis tubing containing the NaCl solution. (b) Suspend the solution in the tubing so that it lies beneath the water’s surface.



Repeat the process using the second length of dialysis tubing and the other beaker, using 25% NaCl in place of the 5% solution.

Allow the two beakers to stand for approximately one hour.

At the end of this time, carefully determine the volume of the solutions in the dialysis tubing lengths by pouring the solutions separately into a graduated cylinder.

Determine the volume of water that has entered each length of tubing by osmosis. Did more water diffuse into the concentrated or the dilute NaCl solution?

## **B. Dialysis**

In separate clean beakers, obtain 15–18 mL each of 5% NaCl solution, 5% dextrose solution, and 1% starch.

Transfer about 1 mL of each solution to separate clean test tubes. These test-tube samples will be used for a *preliminary* test for each of the three solutes to be used for dialysis.

To the test tube containing 5% NaCl solution, add 5–6 drops of 0.1 M silver nitrate (*Caution!*). The appearance of a white precipitate of AgCl upon treatment with silver nitrate during the dialysis experiment will confirm the presence of chloride ion.

To the test tube containing starch, add 5–6 drops of 0.1 M I<sub>2</sub>/KI reagent. The appearance of a blue-black color upon treatment with iodine reagent during the dialysis experiment will confirm the presence of starch.

To the test tube containing dextrose, add approximately 5 mL of Benedict’s or Fehling’s reagent, and heat briefly in a boiling water bath. The appearance of a green or orange precipitate upon similar treatment will confirm the presence of dextrose during the dialysis.

Obtain a 10–12-inch length of dialysis tubing and punch a hole about 1 inch from either end. Soak the tubing in water until the walls can be spread apart.

Set up a 600-mL beaker containing 450–500 mL of distilled water in a place where the beaker will not be disturbed.

Holding the dialysis tubing by both ends to prevent spillage, transfer approximately 10 mL of the 5% NaCl, 5% dextrose, and 1% starch solutions to the tubing.

Insert a stirring rod through the holes in the dialysis tubing, rinse the outside of the tubing with a stream of distilled water from a wash bottle, and suspend the tubing in the beaker of distilled water [see Figure 1-5(b)]. Add additional water if necessary to cover the solution in the dialysis tubing.

*Immediately* after placing the dialysis tubing in the distilled water, remove approximately 3–4 mL of water from the beaker and perform the tests for NaCl, dextrose, and starch described earlier.

At *10-minute intervals* for the next hour, remove small portions of distilled water from the beaker and repeat the tests for the three solutes.

In what *order* were the solutes able to dialyze through the membrane? How is this order related to the size of the particles involved?





# ***Colligative Properties of Solutions***

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Date: ..... Student name: .....  
Course: ..... Team members: .....  
Section: .....  
Instructor: .....

## **Results/Observations**

### **Choice I. Freezing Point Depression and Molar Mass**

#### **A. Determination of the Freezing Point of Naphthalene**

Mass empty test tube .....  
Mass test tube plus naphthalene .....  
Mass naphthalene taken .....  
Freezing point of naphthalene (from graph) .....

#### **B. Determination of $K_f$ for Naphthalene**

Mass test tube plus naphthalene .....  
Mass naphthalene in test tube .....  
Mass test tube/naphthalene plus dichlorobenzene .....  
Mass 1,4-dichlorobenzene taken .....  
Freezing point naphthalene/dichlorobenzene solution .....  
Molality of dichlorobenzene solution .....  
 $K_f$  for naphthalene .....

#### **C. Determination of the Freezing Point of a Sulfur Solution**

Mass empty test tube .....  
Mass test tube with naphthalene .....  
Mass of naphthalene taken .....  
Mass of test tube after adding sulfur .....  
Mass of sulfur added .....  
Freezing point of naphthalene/sulfur solution .....

Molality of sulfur in the solution .....

Molar mass of sulfur .....

Number of sulfur atoms per molecule .....

## Questions

1. A phenomenon called **supercooling** is frequently encountered in this experiment. In supercooling, a solution momentarily drops below its freezing point, and then warms up again, before solidification begins. What event is likely to give rise to supercooling?
2. The molal freezing point constant,  $K_f$ , is a property of the solvent, not the solute. What does this say about the fact that freezing point depends on the amount of solute, rather than on the solute's nature?
3. Look up the freezing point constant,  $K_f$ , for naphthalene in a handbook. How closely does your value for  $K_f$  compare? What might have led to your obtaining a different value?
4. A phenomenon that happens sometimes during freezing point depression experiments is that the solute is affected in some manner by the solvent. One common occurrence is for a solute to dimerize; that is, two solvent molecules combine to produce a single double molecule (a dimer). What effect would there be on a molar mass determination if the solute were to dimerize?

# ***Colligative Properties of Solutions***

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Date: ..... Student name: .....  
Course: ..... Team members: .....  
Section: .....  
Instructor: .....

## **Results/Observations**

### **Choice II. Osmosis and Dialysis**

#### **A. Demonstration of Osmotic Pressure**

Volume of 5% sodium chloride solution taken .....

Volume measured after osmosis .....

Volume of water that passed through membrane .....

Volume of 25% sodium chloride solution taken .....

Volume measured after osmosis .....

Volume of water that passed through membrane .....

Into which NaCl solution was the osmosis stronger? .....

Why?

#### **B. Dialysis**

Observation of  $\text{AgNO}_3$  test for  $\text{Cl}^-$  .....

Observation of  $\text{I}_2$  test for starch .....

Observation of Benedict's test for dextrose .....

After approximately what time intervals were the solutes detectable by dialysis from the tube into the beaker of water?

NaCl ..... dextrose ..... starch .....

