

Experiment 13: Determination of Molecular Weight by Freezing Point Depression

Objective: In this experiment, you will determine the molecular weight of a compound by measuring the freezing point of a solution of the compound and then comparing the freezing point of that solution to that of the pure solvent.

Introduction

The properties of a solution differ from those of a pure solvent due to interactions that take place between the solute and solvent molecules. The properties that exhibit such changes are called the **colligative properties** and include vapor pressure lowering, boiling point elevation, freezing point depression and changes in osmotic pressure (see Tro, section 12.6-12.7 pp 535-550). These properties are dependent only upon the *number* of particles (ions or molecules) which are dissolved in the solvent and not on the identity of the particles. This experiment will examine the phenomenon of freezing point depression.

When a particular solute is dissolved in a solvent, the following expression holds true:

$$\Delta T = T_f^\circ - T_f = K_f m$$

The terms T_f° and T_f refer to the freezing-point temperatures of the pure solvent and the solution, respectively. The term “m” indicates the **molality** of the solution, which is defined as the *number of moles of solute per 1000 g of solvent*. This quantity is used, rather than molarity, because it is not temperature dependent. The constant, K_f , is referred to as the **freezing-point-depression constant** and is dependent only upon the solvent. The change in temperature is also dependent upon the number of solute particles in solution— the more particles that are present, the larger the change in temperature. For this reason, the above equation is sometimes written as: $T_f^\circ - T_f = K_f i m$, where i = the number of solute particles produced per formula unit that dissolves. In a solution containing an electrolyte, each *ion* is considered to be a particle. You will explore the influence of i on the freezing point depression in Part II of the experiment.

In Part I of the experiment, you will use cyclohexane, an organic compound that is a liquid at room temperature, as the solvent. You will be able to determine the molecular weight of an unknown compound by observing the freezing point of a solution of the compound in cyclohexane and comparing it to the freezing point of pure cyclohexane.

Calculations

1. The compound cyclohexane has a melting point (or freezing point) of about 6°C. You will obtain a series of temperatures of pure cyclohexane as it cools down from room temperature through its freezing point in an ice bath. These temperatures will be plotted as a function of time. Similarly, you will obtain temperatures of a solution of an unknown compound in cyclohexane as it cools down to the freezing point, which will also be plotted. The plots will look similar to those pictured in Figures 1a and 1b, and the T_f° and T_f values can be extrapolated from them as shown on [Figure Page 1, Expt. 13](#).

2. The molality of a solution can be expressed in terms of the molar mass of the solute:

$$\begin{aligned}
 m &= \frac{\text{moles of solute}}{1 \text{ kg of solvent}} \\
 &= \frac{(\text{g of solute}/\text{molar mass}_{\text{solute}}, \text{g/mol})}{(\text{g of solvent}) \cdot (\text{kg}/1000 \text{ g})} \\
 &= \frac{(1000 \text{ g/kg}) \cdot (\text{g of solute})}{(\text{molar mass}_{\text{solute}}, \text{g/mol}) \cdot (\text{g of solvent})}
 \end{aligned}$$

Substituting this expression into the equation for freezing-point depression we obtain:

$$\Delta T = T_f^{\circ} - T_f = \frac{(1000 \text{ g/kg}) \cdot (K_f) \cdot (\text{g of solute})}{(\text{molar mass}_{\text{solute}}, \text{g/mol}) \cdot (\text{g of solvent})}$$

Eq. 1

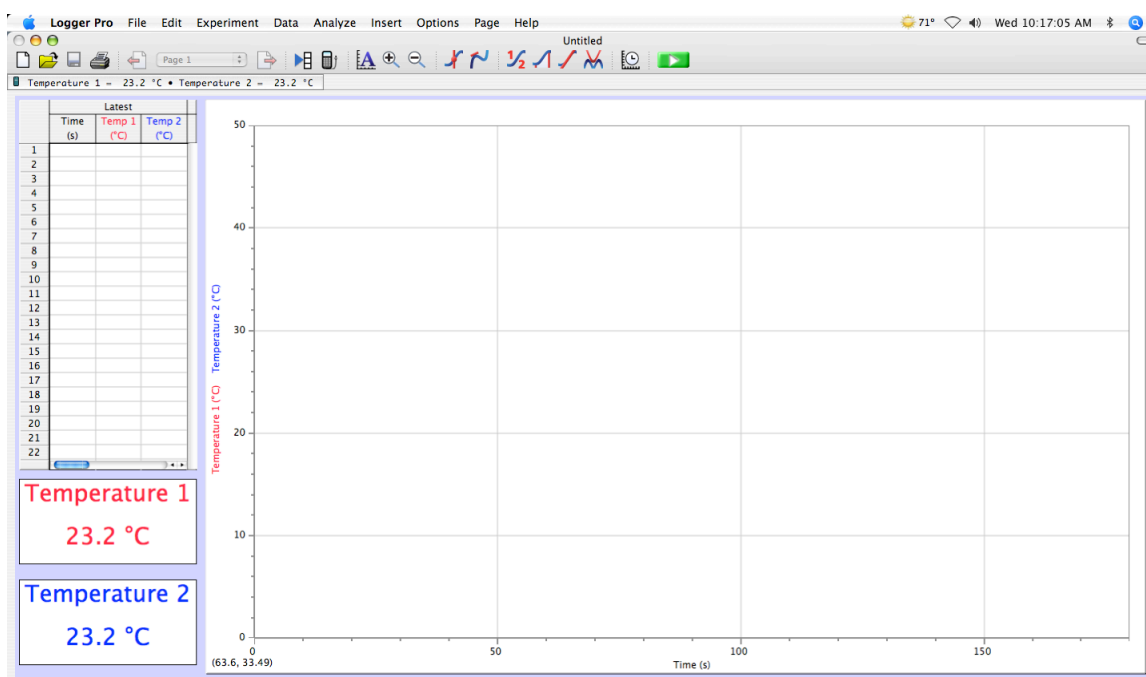
For cyclohexane, **$K_f = 20.2 \text{ deg} \cdot \text{kg}/\text{mole of solute}$** . Recall that the molecular weight (in amu) of a substance has the same numerical value as its molar mass.

In Part II of the experiment, you will measure the change in temperature when urea, CON_2H_4 , is added to a mixture of ice and water and compare it with the change in temperature observed when sodium chloride, NaCl , is added to an ice-water mixture.

Procedure (you do not need to outline instructions for using the LoggerPro software)

A temperature probe interfaced to a computer will be used to acquire the temperature readings in this experiment. Two students will use the same computer, but each student will have his/her own temperature probe and will obtain his/her own set of data to evaluate. Two temperature probes should already be plugged into the interface box. Choose a temperature probe and record the number of the channel into which it is plugged. You must use the *same* probe for all measurements. The temperature probes have an uncertainty of $\pm 0.1^\circ\text{C}$.

To log onto the computer, type “student” for the name and type “chemistry” for the password, then click on **Log In**. Click on the **Applications** folder at the bottom of the screen. In the window that opens, click on the button labeled **Logger Pro** to open the Logger Pro software. When two temperature probes are plugged into the interface box, the following picture should appear on the screen:



Pull down the **Experiment** menu and choose **Data Collection....** Change the length of the experiment to 800 seconds. The Sampling Rate should be set to 1 samples/second. Click on **Done**. Click once on the number at the very top of the y-axis. Type in 40 and press return. You are now ready to collect data.

Wear safety glasses at all times.

The computer will collect the data for both your and your partner's temperature probes simultaneously; therefore, you should carry out the steps of the experiment at approximately the same time.

Part I. Determining the Molecular Weight of an Unknown Compound

Wipe the temperature probe with a paper towel to be sure it is dry. Assemble your apparatus as in Figure 2, shown on [Figure Page 2, Expt. 13](#). A 16x150 mm test tube will be provided for you. The test tube **must** be *clean* and *dry*! Insert the stopper with

the temperature probe and wire stirrer into the test tube. The stopper should not extend further than halfway into the test tube. If it can be inserted further than halfway, you are using the wrong size test tube. Be sure that the temperature probe is pushed down *as far as possible*, and that it does not touch the sides or bottom of the test tube.

Part I.A. Measuring the Freezing Point of the Solvent

Caution! Cyclohexane is a flammable solvent. *Carefully* dispense 12.0 mL of cyclohexane into the 16x150 mm test tube from the dispensing bottle. Raise the piston of the bottletop dispenser slowly and evenly to the stop to fill the dispenser, then press down slowly and evenly to discharge the liquid into the test tube. Calculate the mass of cyclohexane which was dispensed (C_6H_{12} , density = 0.779 g/mL). Place the stopper with the temperature probe and stirrer in the test tube, and set the test tube in a test tube rack. Be sure that the wire stirrer moves freely in the test tube and that the tip of the probe is in the *center* of the volume of liquid.

Fill the largest beaker from your drawer about one-third full of water, and add ice until the beaker is three-fourths full. When both you and your partner are ready, click on the **green button** button, and the computer will begin to collect temperature readings. Move the test tube from the rack into the ice-water bath, and hold it such that the level of liquid in the test tube is *below* the level of water in the bath. Immediately begin stirring the liquid *continuously* and at a *constant* rate until the entire mass has solidified. Once freezing begins, as long as liquid and solid are *both* present, the temperature will remain constant until the entire mass has solidified. Agitation will prevent the "supercooling" which occurs just before crystals appear. Allow the computer to continue recording the temperature until the plot has leveled off at a constant temperature (see [Figure 1a](#)). Note: Once the cyclohexane has frozen solid, the temperature will start to decrease again.

When you have collected a sufficient amount of data, click on the **red button**. Remove the test tube from the ice-water bath and let it warm up to room temperature.

Important step! Saving your data:

- Save your data by pulling down the **File** menu and selecting **Save As...**
- In the dialog box that appears, the word **Documents** should be displayed in the drop down menu in the middle of the box. If it is not, scroll through the menu on the left, and choose Documents.
- Next to the words **Save as:**, type over the word "untitled" with the name of your file (example: FPcyclohexaneLAO). You should include your initials in the name you choose.
- Click on **Save**.
- To find your file later, you will have to go to the **Documents** folder. It should have the suffix .cmbl at the end of the file name.

You can now adjust the parameters on the graph. To view just one of the plots (yours or your partner's), click and hold on the y-axis label. Select Temperature 1 from the pop-up menu. Click on the **AutoScale** button in the Toolbar, which looks like this:



The computer will choose maximum and minimum values for the x - and y -axes such that the plot fills the graph completely. If you do not like the limits for the axes that the computer has chosen, it is possible to change them by simply clicking once on each of the numbers at the ends of the axes, typing in the desired limits and pressing return. It will be easier to determine the value for T_f later if the y -axis limits are whole numbers. Choose the maximum values to be slightly greater than the highest temperature or time

recorded, and choose a temperature minimum that is slightly lower than the lowest temperature. The minimum time recorded should be 0 seconds.

You can adjust other graph parameters in the **Graph Options...** found under the **Options** menu. Be sure that a check mark appears in the box next to Connect Points, and type in an appropriate title for the graph in the box under Title. Your initials should appear in parentheses at the end of the title (so you can identify your printout). Click on **OK**.

To print the graph, pull down the **File** menu and choose **Printing Options...** Click in the box next to Print Footer to make sure a check mark appears, then type in your name (and a comment about the plot, if desired). Now pull down the **File** menu and choose **Print Graph...** (*not Print...*). Click on **OK**. In the next dialog box, click on **Print**. The printer is located in the support room. Your name should appear at the bottom of the page.

Repeat the procedure for adjusting and printing the second plot, this time selecting Temperature 2 from the y-axis pop-up menu. Be sure to change the title, this time putting the second person's initials at the end.

It is possible to print the table of time and temperature readings that the computer collected, however, it is *not* necessary to do so for this experiment. If for some reason you would like a printout of the data, choose **Print Data Table...** from the **File** menu.

Part I.B. Measuring the Freezing Point of the Solution

Obtain from your instructor an unknown compound in a test tube and record its number. Accurately weigh about 0.14 g of this solid material onto a piece of weighing paper. The cyclohexane contained in the test tube should have re-melted by this time. Remove the stopper from the test tube and *carefully* add the unknown sample to the cyclohexane while avoiding the loss of any compound adhering to the sides of the test tube or stopper. Replace the stopper and re-weigh the paper to account for any crystals which remain on it. Return the test tube that contains unknown compound to your instructor.

Stir the solution in order to dissolve the solid. If necessary, place the test tube in warm water from the tap to aid in dissolving the solute. It is important that no crystals remain. **Do not use a hot plate or light a Bunsen burner! Cyclohexane is flammable!**

Make up a new ice-water bath, if necessary. Pull down the **Experiment** menu and select **Store Latest Run**. Under the **Data** menu, choose **Hide Data Set** followed by **Run 1**. You can now collect a new data set. Click once on the number at the end of the x-axis, type in 800 and press return. Click once on the number at the bottom of the y-axis, type 0 and return, then click on the upper limit, type 40 and return. Select **All of the Above** from the y-axis pop-up menu. When both you and your partner are ready, click on the **green button**. Place the test tube in the ice-water bath, as in Part I.A., and stir the solution continuously and at a constant rate. The temperature will not remain entirely constant as the solution freezes. The freezing point of the solution, however, is the point at which it first begins to freeze and is indicated graphically by a change in the slope of the temperature-time curve (see [Figure 1b](#)). You will need to collect data for 300-500 seconds in order to see this clearly.

When you have finished collecting data, click on the **red button**. *Now you must save your data immediately.*

Follow the procedures given above to **save, adjust, re-title** and **print** your plot.

Do not throw any cyclohexane or unknown compound down the sink. Pour the liquid mixture into the **Laboratory Byproducts Jar** provided by your instructor, then rinse your test tube and temperature probe with acetone to remove the last traces of any crystals, pouring the rinses in the Byproducts jar.

Part II. Comparison of Covalent and Ionic Compounds

Pull down the **Experiment** menu and select **Store Latest Run**. Under the **Data** menu, choose **Hide Data Set** followed by **Run 2**. Change the limits on the x-axis to 0 and 800, and change the limits on the y-axis to -10 and 10. Select **All of the Above** from the y-axis pop-up menu.

Weigh 1.0 g of urea onto weighing paper. Place approximately 20 g of ice in a 150 mL beaker, then add 10 mL of distilled water. Record the total weight of ice and water.

Place the temperature probe in the slush, and when both you and your partner are ready, click on the **green button**. Using the temperature probe, stir the slush continuously for 3 minutes. Add the 1.0 g of urea to the slush and continue to stir for another 5-6 minutes. Click on the **red button** to stop the data collection.

Save the data file, then choose **Store Latest Run** under the **Experiment** menu.

Weigh 1.0 g of sodium chloride. Pour the contents of the 150 mL beaker into the sink, then rinse the beaker and temperature probe thoroughly with water. Weigh 20 g of ice into the beaker, and add enough water such that the total weight equals the total weight of ice and water used above. Place the temperature probe in the slush, click on the **green button**, and stir the slush for 3 minutes. Add the 1.0 g of sodium chloride to the slush and continue to stir for 5-6 minutes. Click on the **red button**. **Save** the data, then choose **Store Latest Run** under the **Experiment** menu.

Print the graph with the two plots displayed simultaneously. Indicate on the printout which plot corresponds to which solid.

Pour the contents of the 150 mL beaker into the sink, then rinse the beaker and temperature probe thoroughly with water.

If you would like to view one of your earlier plots, simply pull down the **Data** menu and choose **Show Data Set** followed by the **Run #** that you wish to display. It is possible to have several sets of data displayed simultaneously. The Runs are numbered sequentially in the order in which they were acquired, with the most recent Run being called **Latest**. Simply use the **Hide Data Set** and **Show Data Set** commands to view the desired plot or plots. You may have to re-adjust the plot display parameters (such as axes scales, etc.). Use the y-axis label to display one or both temperature plots, as desired. Options also appear under the **Data** menu to delete one or more sets of data.

If at any point you have trouble displaying or printing the proper plot or axis limit, try the following:

1. Click on the y-axis label and select **More....**

2. In the window that appears, scroll through the list, clicking on the boxes until the box(es) corresponding only to the data that you wish to display has/have a check mark.

When you are ready to leave, pull down the **Logger Pro** menu and choose **Quit Logger Pro**.

You should leave the laboratory with printouts of all the necessary plots that you produced today. However, you should also store a copy of your data file(s) using either www.bc.edu/myfiles or by e-mailing the file(s) to yourself (see Storing and Retrieving Your Lab Files on page 14 of the notebook/manual). If you need to adjust any of your plots after your lab period is over, you can use the computers in the chemistry teaching labs when the rooms are not occupied (MWF 9:00-12:45 or TuTh 12:00-1:15).

Calculations

1. Determine T_f° for the pure cyclohexane and T_f for the unknown solution from the printouts of your plots as shown in Figures 1a and 1b on Figure Page 1, Expt. 13.
2. Calculate the molecular weight (in amu) of your unknown using **Eq. 1**.
3. Identify your unknown compound from the following list:
 Biphenyl; $(C_6H_5)_2$
 4-Bromochlorobenzene; $Br(C_6H_4)Cl$
 Naphthalene; $C_{10}H_8$

Calculate your percent error for the molecular weight of your unknown:

$$\% \text{ error} = \frac{|\text{accepted value} - \text{experimental value}|}{\text{accepted value}} \times 100$$

4. a) Calculate the molalities of the urea and sodium chloride solutions. To do this, use the mass of slush (ice plus water) and the mass of solute (urea or sodium chloride) that you measured.
- b) Determine the ΔT 's for the urea and sodium chloride solutions, using the lowest portion of the plots to determine T_f (see Figure 3 on [Figure Page 2, Expt. 13](#)).

Questions

1. What assumption is made regarding the solute and solvent in this experiment?
2. Why is molality *not* temperature dependent while molarity *is* temperature dependent?
3. a) Thoroughly discuss why the values of ΔT for the urea and sodium chloride solutions are different.
- b) A spike in temperature is often seen in the plots from Part II when the solid is first added to the water (Figure 3 on [Figure Page 2, Expt. 13](#)). Provide a possible explanation for this initial increase in temperature, and then describe an experiment that would allow you to test your theory.
4. List possible sources of error in Part I of this experiment and for each, indicate whether the effect would be an erroneously high or low value for the molecular weight of the unknown.