Experiment 4: FREEZING POINT DEPRESSION

Purpose: An unknown solid is to be identified from a list of possible compounds by its molar mass, which is determined by freezing point depression.

Introduction: When a nonvolatile, nonelectrolytic solute is dissolved in a solvent, the freezing point of the solvent is lowered. The extent the freezing point is lowered is called the freezing point depression ($\Delta T_f$). It is found to be proportional to the molality (m) of dissolved solute particles in the solution. The proportionality constant ($K_f$) is characteristic of only the solvent and independent of the solute.

$$\Delta T_f = K_f m$$  \hspace{1cm} \text{Equation (1)}

where $\Delta T_f$ = freezing point depression = freezing point of pure solvent – freezing of solution

$$= T_f (\text{solvent}) - T_f (\text{solvent + solute})$$

$K_f$ = freezing point depression constant for the solvent

$m$ = molality of dissolved solute particles in the solution

(in units of moles of solute per kilogram of solvent)

Freezing point depression is a colligative property. The term, colligative property, refers to one that depends on the number of particles in a given volume of solvent, rather than on the chemical nature of the particles. However, for Equation (1) to hold true, the solute must be nonvolatile and nonelectrolytic. It must be nonvolatile because it must not alter the vapor pressure above the solvent. The second stipulation, that it must be nonelectrolytic is particularly relevant when the solvent is water. With water as the medium, the solute cannot be an ionic compound, which dissociates into ions when dissolved in water. The formation of ions would increase the number of particles and the molality of the solute would no longer represent the molality of the dissolved particles. Equation (1) would then take on the form shown below, where i is the van’t Hoff factor, and represents the number of particles formed per formula unit of the solute. For example, if the solute is MgCl$_2$, i would theoretically equal to three because one formula unit of MgCl$_2$ in water would exist as three particles: one Mg$^{2+}$ ion and two Cl$^-$ ions. The effect on the freezing point depression would theoretically be tripled.

$$\Delta T_f = i K_f m$$  \hspace{1cm} \text{Equation (2)}

An unknown nonvolatile nonelectrolyte is to be identified from a list of possible compounds by determining its molar mass. A known mass of the unknown is dissolved in a known mass of the solvent, cyclohexane, which has a freezing point depression constant of 20.0 °C m$^{-1}$. By measuring the freezing points of the solvent, before and after the unknown is added, the freezing point depression can be determined. Knowing $K_f$ and $\Delta T_f$, we can utilize Equation (1) to calculate the molality of the solution. From the molality and the mass of the solvent, the number of moles of unknown solute is determined. Since we know the mass of the unknown solute we can then calculate its molar mass. By comparing the molar mass with those of the compounds on the list, we can identify the unknown.
SAFETY PRECAUTIONS IN HANDLING CHEMICALS

Wear your goggles at all times. Wash your hands thoroughly if they come in contact with any of the chemicals in this experiment, especially before eating or drinking anything. Chemicals in Part I cannot go down the drain and are to be disposed of in a designated waste container.

**Cyclohexane:** Extremely flammable liquid and vapor. Keep away from open flame at all times. Vapor may cause flash fire. Harmful or fatal if swallowed or inhaled. It can affect the central nervous system and causes irritation to skin, eyes and respiratory tract.

**Unknowns:** Harmful if swallowed, inhaled or absorbed through skin. It causes irritation to skin, eyes and respiratory tract. It may affect liver, kidney, blood, central and peripheral nervous systems, and may cause allergic skin reaction.

Procedure

*Work with one partner. Remember to record your partner’s name in your lab notebook. Your lab notebook should have been prepared before you arrive to the lab.*

**Freezing Point of Pure Cyclohexane:**
1. Obtain an unknown from your instructor and record the unknown number in your lab notebook.
2. Obtain a stop-watch, a ceramic tile, a two-holed rubber stopper, a metal stirrer, two temperature probes (one for the ice bath and one for the cyclohexane), a 100- or 150-mL beaker and a clean and dry large test tube (25 mm in diameter and 150 mm in height). See your instructor if the test tube in your drawer does not have the proper dimensions. Set up a ring stand and utility clamp.
3. Place 12.0 mL of cyclohexane in a 50-mL graduated cylinder. Take it along with the large test tube, beaker, pen and lab notebook to the balance.
4. You are to determine the mass of cyclohexane in this manner: *Do not leave the balance until you are completely finished with Step 4!* Place the test tube in the beaker and tare it to zero. Remove the test tube from the balance and carefully transfer the cyclohexane into the test tube. Avoid letting the cyclohexane run down the outer surface of the test tube. Wipe the outside dry if it should get wet. Place the test tube back in the beaker and *WITHOUT ZEROING*, record the mass of the cyclohexane in your notebook.
5. Fill a 400-mL beaker about one-third full of tap water, and add ice until the beaker is three-fourths full. Place the ice bath on the ceramic tile and clamp the test tube to the ring stand at least 5 inches *above* the ice bath. Insert the metal stirrer, one of the temperature probes and 2-holed stopper into the test tube as shown in Fig. 4.1. Make sure the metal stirrer is shaped so that you can move it rapidly up and down without grinding bits of the rubber stopper into the test tube. Turn the stopwatch on, but do not press on START yet. Check to see it is reading zero. Press Reset if necessary.
6. Stir the ice bath with the second temperature probe for 2 to 3 minutes, until the temperature has stabilized, somewhere close to 0°C. There is no need to record this.
7. Review with your partner exactly what is to be done in this step. When both partners are ready, one partner will lower the test tube into the ice bath and quickly clamp it at a level such that the bottom of the test tube is not touching the bottom of the beaker. Immediately begin stirring the contents of the test tube in an up-and-down motion. Meanwhile, the other partner should press the START button of the stopwatch the moment the test tube is immersed in the ice bath and continue stirring the ice bath to ensure its temperature stays uniform.

8. One partner will stir the contents of the test tube, watch the stopwatch and call out the temperature (to 0.1 °C) of the cyclohexane (not the ice bath) at 10-second intervals, while the other partner records it in the lab notebook. You do not need to record the temperature at time zero. Begin recording at 10 seconds. The temperature will drop rapidly at first and then plateau off. Continue recording the temperature until the temperature has leveled off for 6 consecutive readings (around 150 seconds from time zero). If stirring was not thorough, you may get a dip in the curve as shown below. This is called supercooling. The lowest temperature in the dip does NOT represent the freezing point.

9. Before continuing, prepare an Excel plot with Time on the x-axis, and Temperature on the y-axis. Do not attempt to put a trendline or smooth curve through the points. Click on the Insert tab, Scatter, and then on Scatter with only markers. Remove
the “legend,” which is not necessary when there is only one series on the graph and takes up space. Title the graph “Temperature vs. Time of Pure Cyclohexane” and include your initials and your partner’s initials in the graph title. You can fix up the graph later on. For now, it is essential to examine the graph to see whether you need to repeat this part of the experiment. Consult with your instructor if you are not sure. **Save** your data and graph in the location designated by your instructor, under the file name “FP Depression Cyclohexane” followed by your last name and that of your partner’s.

Warm up the test tube and its contents to room temperature under warm running tap water. If you are dissatisfied with your data, repeat steps 5 –8 with a fresh ice bath. If you do more than one trial, label them as Trial 1 and Trial 2.

**Freezing Point of the Solution:**

10. Tare a weighing boat to zero and place 0.14 to 0.15 g of your unknown in it. Record the exact mass to 0.001 gram. Check to see that the cyclohexane has warmed back to room temperature. Try to transfer the unknown quantitatively and directly to the bottom of the test tube of cyclohexane. Avoid getting the unknown stuck to the sides of the test tube or to the upper portion of the temperature probe and stirrer. The idea is to get the entire unknown sample into the cyclohexane. If necessary, use the temperature probe to help get it to the bottom. Stir until the entire unknown sample has dissolved. Check carefully.

11. Follow Step 5 to prepare a fresh ice bath. Again stir for 2 to 3 minutes until the temperature has stabilized.

12. Repeat Steps 7 and 8 with the unknown solution, recording every 10 seconds until the temperature has leveled off, or is decreasing at a slow steady rate for at least one full minute. (After the entire sample has frozen, the temperature may continue to drop as the solid continues to cool down. You do not need to wait for the temperature to become constant.)

13. Again, prepare a graph with “**Scatter with only markers**” titled “Temperature vs. Time for Unknown in Cyclohexane Trial 1.” Again include your initials and that of your partner’s in the graph title. You will be doing a second trial. The plot for Trial 1 will help you decide whether you should take more or less data points in your Trial 2. Remember to remove the “Legend.” **Save** your data and graph, in the location designated by your instructor, under the file name “FP Depression Unknown Trial 1” followed by your last name and that of your partner’s.

14. Warm up the test tube and contents to room temperature with warm running tap water. Stir the content of the test tube until all of the solid has dissolved. Prepare a fresh ice bath and repeat steps 11–13.

15. Prepare a graph with “**Scatter with only markers**” titled “Temperature vs. Time for Unknown in Cyclohexane Trial 2.” **Save** your data and graph, in the location designated by your instructor, under the file name “FP Depression Unknown Trial 2” followed by your last name and that of your partner’s.

16. Discard all chemicals in the designated waste container in the hood. **NONE OF THE CHEMICALS IN PART I CAN GO DOWN THE DRAIN!** Rinse your test
tube, stirrer and temperature probes with the acetone provided in the hood. Rinses

go into the designated waste container. Dry all equipment with paper towels.

**FIXING UP THE GRAPHS**

You had to prepare the graphs very quickly during the experiment to see whether you have enough data points. Now you need to fix them up before printing them out and in order to obtain freezing points from them. Instructions here will be brief as you had already learned to prepare graphs with Excel in previous assignments. If necessary refer to the previous instructions in Experiment 3 and Appendix 2.

You should have at least 3 graphs: one of the pure cyclohexane and two of the unknown solutions. In all three cases, you should label both axes, but you do not need to do anything more to the x-axis in terms of adjusting the scale as we are interested only in reading the temperature off the y-axis. The x-axis should be labeled “Time in seconds” and the y-axis as “Temperature in deg C.”

1. After labeling the axes, the first adjustment is to expand the graph vertically so that the temperature can be read **precisely, to 0.1°C**. Highlight the graph by placing the cursor on the graph and click once. Go to **Page Layout, Orientation** and select **Portrait** mode. (*It is imperative that these graphs are in Portrait Mode.*)

2. Under **Chart Tools**, select **Layout, Axes, Primary Vertical Axis** and adjust the **Minimum** and **Maximum** to remove the top and bottom sections of the graph that do not have data points. (Minimum and maximum should be closer to your lowest and highest y-data).

3. Next, in the same window, change **Major Unit** to 1.0 and **Minor Unit** to 0.2. Click on **Close**. Go to **Gridlines**, select **Primary Horizontal Gridlines** and **Major & Minor Gridlines**. This will allow you to read the freezing point on the y-axis to the closest 0.1°C.

4. Have your instructor check your graphs before saving your changes and printing one copy of each graph for you and your partner.

With a ruler and sharp pencil, draw the lines as shown in Figure 4.2. The freezing point is the temperature at the intersection of the extrapolated lines. Record the freezing point on your graph as well as in your lab notebook.

**Calculations & Discussion**

*Show your calculations for all steps. WATCH YOUR SIGNIFICANT FIGURES and include units at each step.*

Do not confuse **freezing point** with **freezing point depression**

1. Calculate $\Delta T_f$ for your unknown solution for Trial 1 and Trial 2. WATCH YOUR SIGNIFICANT FIGURES!! Calculate the average $\Delta T_f$ from the two trials. Remember that the average cannot have more sig. fig. than the values themselves.

2. Using the average $\Delta T_f$, calculate the molality (m). See Equation 1.

3. Using the mass of the solvent and m, calculate the number of moles of unknown.
4. Using the mass and number of moles of unknown, calculate the molar mass of the unknown.
5. Identify the unknown from the list of possible compounds.

**POSSIBLE COMPOUNDS**

- benzene \((C_6H_6)\) 78 g/mol
- heptane \((C_7H_{16})\) 100 g/mol
- naphthalene \((C_{10}H_8)\) 128 g/mol
- biphenyl \((C_{12}H_{10})\) 154 g/mol
- anthracene \((C_{14}H_{10})\) 178 g/mol
- phenanthrene \((C_{14}H_{10})\) 178 g/mol

6. Complete the table and calculations on page 50.

Prepare this table in your lab notebook before arriving to the lab.

<table>
<thead>
<tr>
<th>Unknown # ____</th>
<th>Mass of Cyclohexane = ________________</th>
<th>Mass of Unknown = ________________</th>
</tr>
</thead>
<tbody>
<tr>
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</table>

<table>
<thead>
<tr>
<th>TIME</th>
<th>Pure Cyclohexane</th>
<th>Unknown Trial #1</th>
<th>Unknown Trial #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min:Sec</td>
<td>#of Seconds</td>
<td>Temp (°C)</td>
<td>Temp (°C)</td>
</tr>
<tr>
<td>0:10</td>
<td>10</td>
<td></td>
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<td>0:20</td>
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<tr>
<td>1:10</td>
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<tr>
<td>1:20</td>
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</tr>
<tr>
<td>1:30</td>
<td>90</td>
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<tr>
<td>etc.</td>
<td>etc.</td>
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</tbody>
</table>

(Prepare your table up to at least 5 minutes.)

**Preparation for Pre-Lab Quiz:**

1. Which temperature will you be recording in your lab notebook: the temperature of the ice bath? that of the sample in the test tube? or both?
2. What does \(T_f\) stand for? What does \(\Delta T_f\) stand for?
3. What are the units of molar mass?
4. A solution of urea dissolved in benzene freezes at 1.4°C. The freezing point of benzene is 5.45°C and has a freezing point depression constant of 5.07°C m\(^{-1}\).
   a) What is the \(\Delta T_f\) of the solution? Show your calculations and watch your sig. fig..
   b) What is the molality of the urea solution?
   c) If the benzene weighs 25.0 g, how many moles of urea is present in the solution.
Post-Lab Questions:

Answers must be typed.

1. (15 points) What is the identity of your unknown. Provide a thorough discussion as to how you can or cannot eliminate the other possibilities.

2. (5 points) Give an error analysis: Describe one of the largest unavoidable sources of error that cannot be totally eliminated. Do not include careless mistakes such as spillage or misreading a scale. Read over the procedure to refresh your memory. Explain how it might affect the molar mass of the unknown (would it be too high or too low, and why).

(15 points) The following questions relate to the experiments described on page 50.

3. Carefully explain why the $\Delta T_f$ of the two solutions described on page 50 are different keeping in mind the discussion that the freezing point depression is not supposed to be dependent on the type of solute. Note that urea and sodium chloride have about the same molar mass and therefore the molality was about the same for the two solutions.

4. Based on the data, if a solution of MgSO$_4$ of the same molality as the urea and sodium chloride solutions were used, what would you expect the $\Delta T_f$ to be? Explain.

5. What would you expect the van’t Hoff factor to be for an aqueous solution of each of the following: a) NaOH? b) CH$_3$OH? c) K$_2$CO$_3$? Include chemical equations to illustrate the explanation to each of your answers.

6. Benzene has a freezing point depression constant of 5.07 °C m$^{-1}$. For a 1.00 m solution of benzoic acid dissolved in benzene, the freezing point depression is only 2.5 °C. Use Equation 2 to calculate the van’t Hoff factor of benzoic acid. Provide an explanation for this unusual value for the van’t Hoff factor. (Hint: How is it unusual? If you are clueless, refer to textbook for an explanation.)
Calculations & Results: Name: ______________________________
CHEM 124 Sec: ____ Partner’s Name: ______________________________
(Be sure to show your setups at every step. Remember to include units at all times.)
Use pencil to keep it neat.
Part I:
1. Watch your significant figures!

<table>
<thead>
<tr>
<th></th>
<th>Trial 1</th>
<th>Trial 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_f$ of cyclohexane*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_f$ of unknown solution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta T_f$</td>
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</tbody>
</table>

*Use the same $T_f$ of cyclohexane if you did not need to do two trials.

Average $\Delta T_f$ of the two trials:

2. Using the average $\Delta T_f$, calculate the molality (m).

3. Using the mass of the solvent and m, calculate the number of moles of unknown.

4. Using the mass and number of moles of unknown, calculate the molar mass of the unknown.

5. Identify the unknown from the list of possible compounds: ______________

(continued on next page)
EXPERIMENT 4: FREEZING POINT DEPRESSION

Name: ______________________________

An ice/water mixture weighing 30.00 g is placed in an insulated double-nested Styrofoam cup and the temperature is recorded every 0.5 minute. At exactly 3.0 minutes, 1.00 g of urea is added. The mixture is stirred thoroughly and the urea dissolved immediately. Recording of the temperature is continued. See Figure 4.3A. This is repeated and 1.00 g of sodium chloride is used in place of the urea. See Figure 4.3B.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Urea</th>
<th>Sodium Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_f$ of water</td>
<td></td>
<td></td>
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<tr>
<td>$T_f$ of solution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta T_f$</td>
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</tbody>
</table>

By what factor (rounded to 1 sig. fig.) is one $\Delta T_f$ higher than the other?
Show calculations:

Ans. __________