**Experiment #4. Molar Mass by Freezing Point Depression**

**Introduction**

When a nonvolatile solute is dissolved in a solvent, the freezing point of the solution is lowered. This process is called Freezing Point Depression and is a colligative property of solutions. Colligative properties depend only on the amount and not the nature of the solute dissolved in the solvent. Sprinkling salt on icy roads to melt the ice is an example of Freezing Point Depression. One way to understand why the freezing point of a mixture is lower than that of the pure solvent is to consider the equilibria of freezing and melting.

In a pure solvent at its freezing point, there is some liquid and some solid, and they are both freezing and melting at the same time, and at the same speed. If it’s warmed, melting speeds up, and the solid melts. If it’s cooled, freezing speeds up, and the liquid freezes. However, when another substance is dissolved in the liquid, it is (in most cases) largely excluded from the freezing solid because it doesn’t fit into the solvent’s solid crystal structure. Now, when molecules approach the solid to freeze, some of them aren’t solvent anymore, and these solute molecules mostly bounce off without freezing. This slows the freezing process, but has little or no effect on the melting speed, and we must cool the mixture more than usual to freeze the solvent. Thus, the freezing point is lower.

Each solvent responds differently to the addition of a solute. This response is given by $K_f$, the molal freezing point depression constant. It is important that molality is used as the unit for concentration in temperature studies, as mass (used in molality calculations) is temperature independent while volume (used in molarity calculations) is not. The equation for freezing point depression is:

$$\Delta T_f = i m K_f$$

where:

- $\Delta T_f =$ the absolute decrease in temperature. This is always a positive value.
- $i =$ the van’t Hoff factor
  $$i = \frac{\text{moles of solute particles in solution}}{\text{moles of solute dissolved}}$$

(For a nonpolar organic solute such as our unknowns used in this experiment, $i$ is always 1, because nonpolar organic substances do not dissociate into multiple particles.)

- $m =$ molality of the solution = (moles of solute)/(mass of solvent in kg)
- $K_f =$ molal freezing point depression constant (this constant is solvent dependent)

$K_f$ (naphthalene) = 6.80 °C/molal

The aim of this experiment is to determine the molar mass and identity of an unknown compound by measuring the depression in freezing point. In this experiment, we will first measure the freezing point of pure naphthalene, then measure the freezing point again after adding an unknown solute. From the decrease in freezing point of the solution versus pure naphthalene, the molar mass of the unknown will be determined.

**Equipment:**
- analytical balance (measure to 0.001 g)
- 600 mL beaker
- 2 ring stands
- hot plate
- wide (fat) 6" test tube
- wide mouth “gas” bottle
- test tube clamp
- Venier with thermometer probe

**Chemicals:** Naphthalene

**Possible Unknowns:** p-dichlorobenzene, benzophenone, benzil
Procedure

Determining the Freezing Point of Naphthalene

1. Using a plastic weighing boat, weigh between 4.5 and 5.5 g of naphthalene to the nearest 0.001 g. Record this mass on the data sheet and place the naphthalene into a dry fat 6” test tube.

2. Place a hot plate on the base of the stand. Place a 600 mL (or a similar size) beaker on the hot plate. Add ~ 300 mL of water to the beaker and suspend the test tube in the beaker using a test tube clamp. Check that the water level in the beaker is above the level of the mixture in the test tube.

3. Now place the wire stirrer and a thermometer in the test tube, so that the loop of the stirrer surrounds the thermometer. Heat the water until the naphthalene melts (heat to at least 95°C). Do not stir until the naphthalene melts.

4. Measure the temperature of the melted naphthalene. This is the temperature at time zero. Start the stopwatch. Quickly remove the test tube from the hot water. Place the test tube into a wide mouth bottle. (Be sure to keep the water hot, since you will need it again.)

5. Gently stir the naphthalene with the wire stirrer and record the temperature (to the nearest 0.2 C) of the liquid every 30 seconds. Stir gently as you take your readings (be sure not to poke the bottom of the test tube, as it can break easily). Continue to take readings until about half the liquid has frozen/solidified. The naphthalene inside the test tube will be like ‘slush’.

Determining the Freezing Point of a Mixture

6. Using a plastic boat, weigh between 0.5 and 0.6 g of the unknown compound to the nearest 0.001 g. Your instructor may assign you the unknown. Follow your professor’s instructions. Record the mass and number or letter of the unknown on the data sheet and place the unknown in the test tube containing your original sample of naphthalene. Do not stir at this time.

7. Using the same sample, now with the unknown in it: melt and solidify the mixture, recording a second set of data with the same procedure as you used for the pure naphthalene.

8. When you have completed the experiment, carefully follow the...

Cleanup procedure as outlined below:

A. Warm the test tube in the hot water bath until all of the mixture has melted and all you have is a liquid in the test tube.
B. Remove the thermometer and stirrer and wipe them clean using a paper towel wetted with acetone. DO NOT THROW THIS PAPER TOWEL IN THE TRASH. Place the paper towel in plexiglass contaminated paper bin in the waste hood.
C. Pour the molten naphthalene mixture into the specified waste container. (lift the red lid before pouring) DO NOT POUR THE LIQUID INTO THE SINK !!!
D. Rinse the test tube with small amounts (2 mL) of acetone, pouring this waste solution into the appropriate waste container until the test tube is clean.

Have we mentioned that you will not pour anything from this lab down the sink?!!
9. Plot a graph of temperature versus time for each data set.

Guidelines for graphing:

- Use a scatter plot without lines in excel.
- **Do not add a trend line.** You will draw two lines by hand after printing.
- Give the graph a descriptive title. For example “Pressure versus Temperature of Gas in a Weather Balloon”, not just “Pressure vs Temperature”.
- Label the axes with the type of unit (ex: pressure, temperature, time) and the unit itself (ex: atm, °C, s)
- **Number the axes so that the data takes up most of the graph.** For most axes, it is not appropriate to start at zero.
- **Insert gridlines at least every 1°C** otherwise it will be difficult to interpret the temperature at the line intersection of your hand drawn lines.
- Print your graphs so that each one takes up at least a half a page. You will not be able to accurately interpret the freezing point on tiny graphs.

These plots are cooling curves – they show how temperature falls over time as the sample loses energy to the surroundings. During phase changes, the temperature will plateau. The phase change from liquid to solid is exothermic. As this phase change occurs, all energy loss goes to this transformation, not to changing the temperature. In an idealized sample, the temperature will not drop again until all the liquid has been converted to solid. Example 1 shows what this would look like, and this is also how cooling curves in your textbook will look. The freezing point of the sample is the temperature of the plateau.

However, in lab, some naphthalene evaporates as the experiment proceeds, so we do not get idealized graphs like Example 1, we get graphs that look like Example 2. The temperature stays relatively steady during the phase change, but it drops off at a slow rate.

**Determining the freezing point of a sample.**

- Determine which data points represent pure liquid cooling (the steeper part of the curve). Using a straight edge, draw an estimated best fit line for those data points.
- The rest of the data points (with the shallow slope) represent the liquid to solid phase change. Using a straight edge, draw an estimated best fit line for these data points.
- **The intersection of the two lines is your freezing point.** Estimate its value to the nearest 0.2°C.
### CHM112 Lab – Molar Mass by Freezing Point Depression – Grading Rubric

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Points possible</th>
<th>Points earned</th>
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<tbody>
<tr>
<td><strong>Lab Performance</strong></td>
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<tr>
<td>Printed lab handout and rubric was brought to lab</td>
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<td>Safety and proper waste disposal procedures observed</td>
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<td>Followed procedure correctly without depending too much on instructor or lab partner</td>
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<td>Work space and glassware was cleaned up</td>
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<tr>
<td><strong>Lab Report</strong></td>
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<tr>
<td>Calculations for molar mass shown clearly with units.</td>
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<tr>
<td>Graph 1 &amp; 2 (titled, axis labeled, gridlines every 1°, data takes up majority of graph, two lines hand drawn on each, freezing point clearly labeled.)</td>
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<tr>
<td>Question 1</td>
<td>1</td>
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<td>Question 2</td>
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<td>Question 3</td>
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<td><strong>Total</strong></td>
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Subject to additional penalties as per the instructor.
Molar Mass by FPD: Data Sheet

Name __________________________

Unknown letter _______  Mass of unknown compound _______  Mass of naphthalene _______

<table>
<thead>
<tr>
<th>Time</th>
<th>Temp: Naphthalene Run</th>
<th>Temp: Mixture Run</th>
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Graph your results.  Attach both graphs to the lab report.  Follow the graphing guidelines in the instructions.

Freezing point of naphthalene (from graph 1) _________  Freezing point of mixture (from graph 2) _________

Change in Freezing point ΔT: __________

Calculation for Molar mass (Show your work in detail with units.)
1. Look up the formulas and molar masses of all the possible unknowns (p-dichloro benzene, Benzophenone, Benzil) from a reliable source (CRC handbook or the NIST web book) and list them below. Based on your results, what is your unknown? Explain clearly the reason for your choice.

2. Find the structures of naphthalene and your unknown (based on your answer in 1). a) Draw the Lewis structures for each. Include all bonds and lone pairs. b) State which intermolecular forces are present in naphthalene and your unknown. c) Explain why your unknown dissolves in naphthalene based on your answer to b).

3. Compare the molar mass that you obtained from your experiment to the correct molar mass for your unknown. Calculate the percent error.

\[
\text{percent error} = \left( \frac{|\text{actual value}-\text{experimental value}|}{\text{actual value}} \right) \times 100\%
\]