

**CHEMISTRY 206****Experiment 3: DETERMINATION OF MOLAR MASS BY FREEZING-POINT DEPRESSION**

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**Instructor's Informal Preamble**

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One of the several problems of fundamental importance in chemistry is the determination of previously unknown compounds' molecular formulae. This information is generally determined by combining information gained from experiments designed to determine a compound's empirical formula, and others designed to determine its molecular weight (*i.e.*, molar mass or molecular mass). As an example, by burning an unknown hydrocarbon with oxygen and weighing the amounts of water and carbon dioxide produced, it is possible to determine its empirical formula, which perhaps might be  $\text{CH}_2$ . The compound's real molecular formula could be any multiple of this, for example,  $\text{C}_2\text{H}_4$ , or  $\text{C}_5\text{H}_{10}$ , or  $\text{C}_{17}\text{H}_{34}$ . To determine the molecular formula of the compound, the molecular mass is needed. In this experiment, we will perform one of the dozen or so methods for determining the molecular mass of an unknown compound: freezing-point depression.

Freezing-point depression measurement is one of several methods that depend on the so-called *colligative properties* of solutions. Similar methods involve measurement of the elevation of a solvent's boiling point or measurement of osmotic pressure. These methods are all based on the fact that individual *solute particles* (molecules or ions) interfere with the interactions between solvent molecules and the ability of the solvent molecules to move from one phase to another (or, more specifically for osmosis, through a membrane). The magnitude of this effect depends only on the quantity of solute particles present, not on their identities. For example, any solute added to a solvent will cause the freezing point of the solvent to be lowered by an amount proportional to the concentration of solute particles in the solution. Different solvents are affected to different extents, but for any given solvent, the freezing point changes by a predictable (and constant) number of degrees per unit concentration of dissolved solute particles.

Freezing-point depression and boiling-point elevation experiments both involve making measurements over a range of temperatures. Because volumes of substances often change dramatically with temperature (especially near phase changes), if we want to get meaningful data, then we must express the concentrations of our solutions in units that are not based on the solution volume – remember, chemists' typical unit of concentration is molarity, moles of solute per litre of solution. Thus, for the present type of experiment, concentrations are presented in *molality* ( $m$ , moles of solute dissolved in 1 kg of solvent), because the solvent's *mass* does not vary with temperature.

## CHEMISTRY 206

## Experiment 3: DETERMINATION OF MOLAR MASS BY FREEZING-POINT DEPRESSION

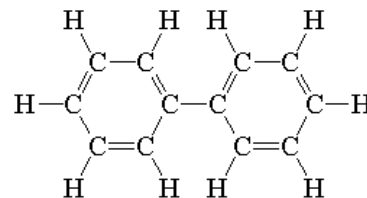
### Introduction

In this experiment, we will be taking advantage of the fact that the presence of a solute lowers the freezing point of the solvent in which it is dissolved. The solvent we will be using is an organic compound called biphenyl. Its freezing-point depression constant is  $8.0\text{ }^{\circ}\text{C } m^{-1}$ , where  $m$  = molality (moles solute per kg solvent). Based on the units of this constant, we can see that the following mathematical relationship will hold:

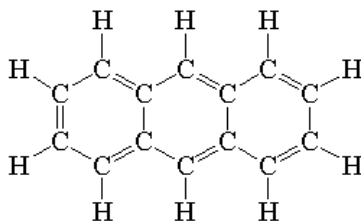
$$\Delta T = m K_f \quad \text{where } \Delta T \text{ is the depression of the freezing point (in } ^{\circ}\text{C)} \\ \text{and } m \text{ is the concentration of solute particles (in molality)}$$

Biphenyl (shown at right) is a nonpolar substance and is therefore well suited to dissolving nonpolar solutes. We will be studying an unknown nonpolar solute, one of four compounds (shown below) with similar chemical structures but different molecular masses.

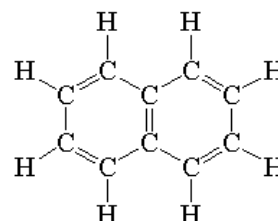
Biphenyl



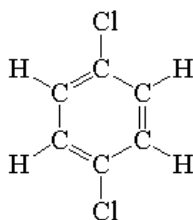
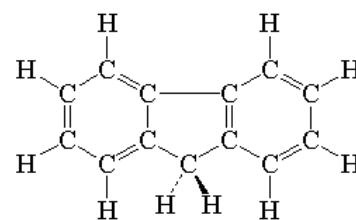
Anthracene



Naphthalene



p-dichlorobenzene

Fluorene  
(Not fluorine!)

Measuring the depression of the freezing point of a well-defined solution of “unknown” in biphenyl compared to pure biphenyl will allow us to calculate the molal concentration of unknown in the sample. Because the mass of unknown in the solution will be known, we will be able to calculate the unknown’s molar mass and therefore identify the compound.

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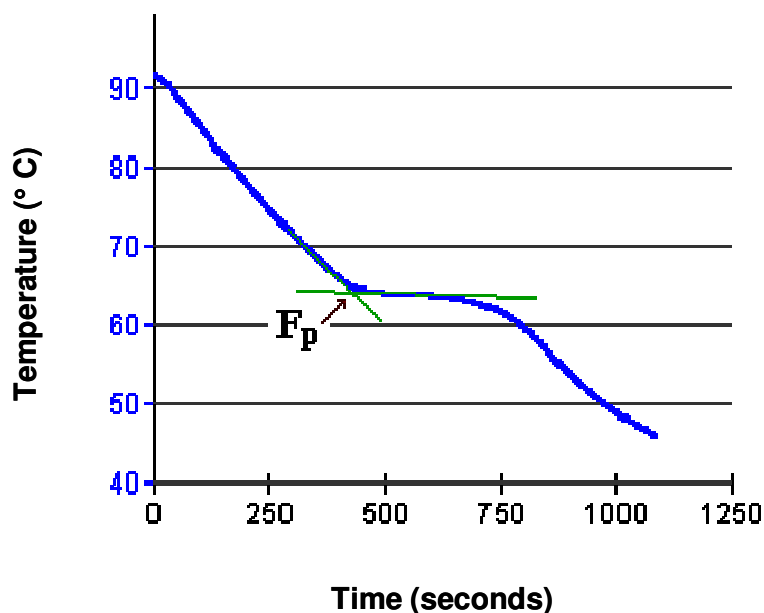
## Experiment Summary

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You will plot cooling curves (temperature *vs.* time) for pure biphenyl and for a solution of an unknown organic compound dissolved in biphenyl. The freezing points will be deduced from the shapes of the curves (see the diagram below). From the amount by which the freezing point is depressed, you will be able to calculate the molecular mass of the unknown substance.

Cooling curves typically show a steep cooling portion, due to loss of heat to the surroundings, which is sometimes followed by a dip where the solvent supercools, and then a gentler downward slope when the solvent is freezing. The temperature remains approximately constant during the phase change, because loss of heat to the surroundings is nearly balanced by the release of heat due to the solidification process. Once the entire solution has solidified, the steep cooling trend resumes.

To interpret the data, a straight line is drawn through the points of steep initial slope and extended until it intersects the straight line drawn through the more gently sloping portion. The point where the two lines meet,  $F_p$ , yields the experimentally determined freezing point.



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## Prelaboratory Assignment

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Read the procedure and answer the preliminary questions before coming to the lab. Your demonstrator will inspect and collect in your prelab before you are permitted to begin the experiment - keep a copy of it for yourself, and have the TA sign your receipt record.

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## Materials

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### Apparatus

- Computer running Logger Pro 3 (equipped with temperature probe)
- Hot plate
- Stand and three clamps (2 with two jaws and 1 small three-jaw clamp)
- 6-inch test tube
- Stirring wire with loop on one end
- 2 sample vials (straight-walled, with minimal lip at top)
- 1× 30 mL beaker, 1× 250 mL beaker

### Reagents and Materials

- Biphenyl
- Unknown
- Wash bottle with acetone for clean up

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## Procedure

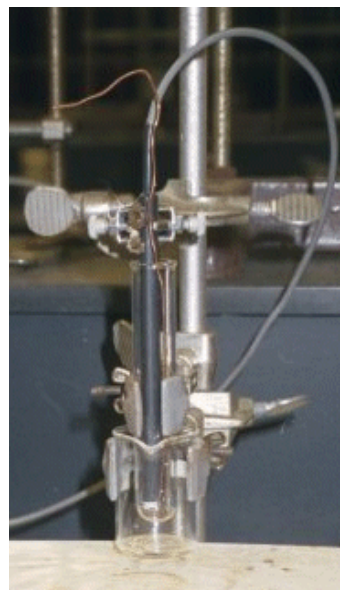
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**Important:** In the steps that follow, *do not attempt to pull the temperature probe out of the solidified biphenyl under any circumstances* - you may break it.

### Part 1: Measuring the Freezing Point of Pure Biphenyl

#### a) Preparing to Measure the Freezing Point

1. Weigh out about 2 g of biphenyl into a sample vial (weigh the empty vial first!). Carefully transfer the biphenyl to the test tube, then reweigh the vial to determine the exact mass of biphenyl used (*a little may stick to the vial.*) Note the mass in your report.
2. Place about 15 – 20 mL of water in the 30 mL beaker and clamp it so it just touches the hot plate. [*You will need to slide the hot plate away later.*]
3. Clamp the test tube in the centre of the 30 mL beaker (*this is easiest if both clamps are the same type*). The tube should not touch the beaker, and the biphenyl should be well below the water level.
4. With the hot plate on medium, heat the water to ~ 80 °C. The biphenyl will melt.
5. Put the stirring wire in the test tube (loop end down). Plug the temperature probe's cord into either one of the USB ports located on the front of the computer (the probe plugs directly into the computer; no other interface is required). Use the small clamp to secure the probe inside the test tube, with the tip positioned in the centre of the biphenyl sample. The loop of the stirrer should fit around the bottom of the probe and slide up and down easily to provide stirring.



**b) Acquiring the Freezing-Point Curve**

6. On the computer, double click on the icon "CHEM 206 Experiment 3" to bring up the data acquisition window. The program will automatically identify the temperature probe, and then you are ready to collect data.
7. With the temperature probe inside the liquefied biphenyl sample, you are able to see the current temperature of the sample on the screen.
8. Continue slowly heating the sample, stirring gently so the liquid doesn't go far up the walls of the tube (*i.e.*, keep it below the level of the water bath).
9. When the temperature reaches 85-90 °C, carefully slide away the hot plate. Continue stirring gently. When you see the temperature dropping below 80 °C, click COLLECT to start recording the cooling trend data.
10. Continue gently stirring the biphenyl until you see it begin to freeze (at ~ 68 °C). Take note of the time on the data screen, and stop stirring the sample.
11. After 800 - 1000 seconds, a good freezing-point curve should have formed (similar to the sample curve, with a well-defined second steep region). Click on STOP to stop data acquisition.
12. *Important:* Click on FILE, then SAVE AS, and save the file under a logical file name onto the computer's Desktop into the folder called *Chem 206 Expt 3 Data*. (If a folder like this does not yet exist: right click inside the Save As window, choose New, then Folder, then name the new folder as specified above).
13. To start a new acquisition, click on COLLECT while you still have the old run on the screen. A message will follow; choose "Erase and Continue".
14. Replace the hot plate and repeat steps (7) – (12) twice more on the same sample to get a total of three cooling curves. When finished, keep this sample for Part 2.

**Part 2: Determining the Freezing Point of the Solution of the Unknown**

15. Accurately weigh out 0.18 – 0.20 g of your unknown substance into a clean sample vial (weigh empty vial first). [*Note: using too much unknown will make your cooling curves hard to interpret!*] Note the unknown number and the mass used.
16. Remelt the same sample of biphenyl as you used in Part 1. When it is completely liquid, gently raise the probe and swing it clear of the test tube. [*Try not to lose any drops of biphenyl.*]
17. Carefully pour the unknown from the sample vial into the test tube so that as little as possible is lost on the sides. Reweigh the sample vial to determine the exact amount of unknown that has actually been added to the test tube.
18. Stir the mixture until the unknown has dissolved. Replace the probe. Continue stirring until Schlieren lines (wavy lines seen during mixing, caused by differences in refractive index of materials with different density) are no longer visible at the bottom.
19. Perform steps (7) – (13) to acquire a cooling curve, then remelt the sample and repeat this procedure to get a total of three cooling curves for the same sample.

### Cleaning up

20. Melt the mixture again completely.
21. Remove the probe and stirrer and wipe them with a piece of paper towel. Dispose of the soiled towel in the solid waste container. To remove the residual material from the probe and stirrer, wash them several times with a little acetone. Put all washings in the organic waste disposal container.
22. To clean the test tube, quickly pour the melted mixture into organic waste container. This will not remove all the biphenyl, as will be seen after a few seconds when it solidifies on the walls of the tube. Rinse it several times with a little acetone. Put all washings in the organic waste disposal container.

### Analysis of the Data

#### a) Printing the Graphs

You should now have six data files, three for the freezing point of biphenyl and three for the freezing point of biphenyl containing a known amount of unknown. For each file, do the following:

- Select the file to be opened, and open it.
- Click on ANALYZE in the top menu, then AUTOSCALE, then AUTOSCALE.
- Print out the resulting graph by clicking on FILE in the menu bar, then PRINT GRAPH and OK. [*Print it twice so each partner gets a copy.*]
- After the graph is printed out, close the file by clicking on FILE and EXIT. When prompted to save the data, click on YES.
- Print out the graphs for the other five files in the same manner.
- Manually label each of your graphs in detail (name, experiment, part, run, description, etc.)

#### b) Extracting the Freezing Points from the Cooling Curves

Extend the initial steep part of the cooling curve. Draw a straight line through the more gently sloping plateau. Extend the two lines so they intersect. From the point of intersection, determine the freezing point,  $F_p$ , as precisely as you can.

On all curves, note the time at which you visually observed the onset of freezing, for comparison with your graphical value of  $F_p$ . For curves that were still quite steeply sloping throughout the freezing process, you may need to use your visual observation of the time at which freezing began to help you interpret the data.

Enter your freezing point data in Table 2. Hand in the printouts of all your graphs with your report.

Name: \_\_\_\_\_ Section: \_\_\_\_\_ Date: \_\_\_\_\_

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#### Prelaboratory Questions

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1. (2 marks) Write a brief summary, in your own words, describing the purpose of this experiment and the steps you will follow. One page - maximum.
2. (1 mark) Derive a formula for the molar mass of the solute in terms of the freezing point depression,  $\Delta T$ , the freezing-point depression constant,  $K_f$ , and the masses of solvent,  $m_{\text{solvent}}$ , and solute,  $m_{\text{solute}}$ , used in an experiment like this one. Show your work, and include all units in your final formula.
3. (1 mark) Define enthalpy of fusion, and explain why the cooling curve flattens out while a pure solvent is freezing.
4. (1 mark) Explain why the cooling curves of solutions are more steeply sloping during the freezing process than the curve for same pure solvent. Hint: refer to the figures (and their captions!) from the Kotz textbook's freezing point depression section.

### **Exp.3** FREEZING POINT DEPRESSION

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Name: \_\_\_\_\_ Section: \_\_\_\_\_ Date: \_\_\_\_\_

## CHEMISTRY 206

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#### Laboratory Report

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#### Observations and Data

**(1 mark) Table 1: Masses of solvent and solute used**

Mass of sample vial and biphenyl	_____
Mass of sample vial emptied	_____
Mass of biphenyl	_____
Unknown number	_____
Mass of sample vial and unknown	_____
Mass of emptied sample vial	_____
Mass of unknown added to the biphenyl	_____

**(5 marks: for the interpretation of graphs and the data in Table 2)**

**Table 2: Freezing point data and freezing point depression by unknown**

Freezing point of pure biphenyl from run 1	_____
Freezing point of pure biphenyl from run 2	_____
Freezing point of pure biphenyl from run 3	_____
Average freezing-point of pure biphenyl	_____
Freezing point of solution of unknown in biphenyl from run 1	_____
Freezing point of solution of unknown in biphenyl from run 2	_____
Freezing point of solution of unknown in biphenyl from run 3	_____
Average freezing point of solution of unknown in biphenyl	_____
Freezing point depression	_____

