1. *A Molar Mass from Freezing-Point Depression*

Introduction

Solutions have many useful characteristics (Ebbing/Gammon, Chapter 12). Among these are the *colligative properties*. These properties, which include freezing-point depression, depend only on the number of solute molecules in a given quantity of solvent. They do not depend on the nature of the solute. As a consequence, colligative properties can be used to determine an unknown molar mass for a solute (Ebbing/Gammon, Section 12.6).

Purpose

You will measure the freezing-point depressions that occur with solutions containing a solute whose empirical formula is known. Your data and those of the entire class will be used to calculate the molar mass of the solute and its molecular formula.

Concept of the experiment

The apparatus you will use will probably resemble that shown in Figure 1.1. The solvent will be cyclohexane. The solute will be a substance whose empirical formula is C_3H_2Cl.

You will determine the freezing-point depression, ΔT_f. This quantity is proportional to c_m, the molal concentration of the solute:

$$\Delta T_f = K_f c_m$$

The proportionality constant is called the freezing-point-depression constant. It has a value of 20.5°C/m for cyclohexane. You can calculate the molar mass of a solute from ΔT_f, K_f, the mass of the solute, and the mass of the solvent (Ebbing/Gammon, Example 12.11).

In order to determine ΔT_f, you will measure the freezing point of pure cyclohexane and the freezing point of a solution of the solute in cyclohexane. You should use the following methods to obtain these temperatures.

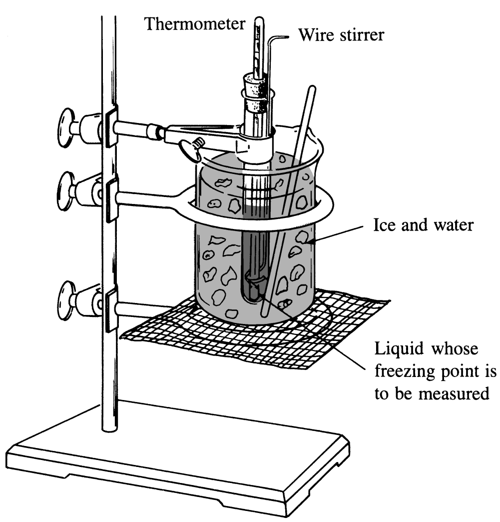
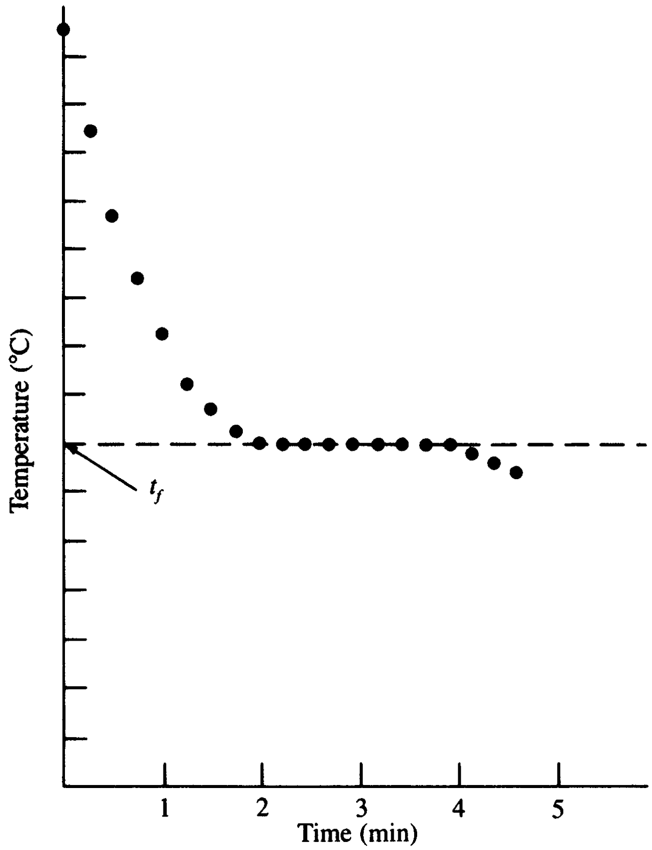


FIGURE 1.1
An apparatus suitable for determining the freezing point of a solvent or a solution.

To evaluate the freezing point of pure cyclohexane, you will cool a sample of this substance and measure the temperature as a function of time. The cooling curve in Figure 1.2 shows some typical results. As cooling begins, the temperature of the cyclohexane decreases rapidly. However, as soon as the solution begins to freeze, the temperature no longer decreases but remains constant until all the cyclohexane has frozen. When that has occurred, the temperature again decreases. The freezing point is the constant temperature that occurs while cyclohexane is freezing.

FIGURE 1.2
A typical cooling curve for pure cyclohexane. The freezing point is t_f, the constant temperature in the middle of the cooling curve.



The freezing point of a solution of solute in cyclohexane can be obtained in a similar way, but there is a difference. This difference can be seen in Figure 1.3. Cooling again results in an initial rapid decrease in the temperature until freezing begins. However, with the solution, unlike pure cyclohexane, the temperature does not remain constant until all the solvent has frozen. As the cyclohexane in the solution freezes, the solution becomes more concentrated because less liquid remains. The molal concentration of the solute must increase, and the freezing point must decrease still further. The result is a steadily decreasing freezing temperature. When all the solvent has frozen, the temperature decreases more rapidly.

The freezing point that you want is the initial freezing point because that is the only point at which you will know how much liquid solvent remains. You can obtain the initial freezing point by drawing two solid lines that best describe the data, as shown in Figure 1.3. The point at which these lines intersect corresponds to the initial freezing point.

FIGURE 1.3

A typical cooling curve for a solution composed of a solute dissolved in cyclohexane. Two straight lines have been drawn to describe the data immediately before and during freezing. The intersection of these lines occurs at t_f', the initial freezing point of the solution. Using the results from Figure 1.2, ΔT_f is given by $t_f - t_f'$.

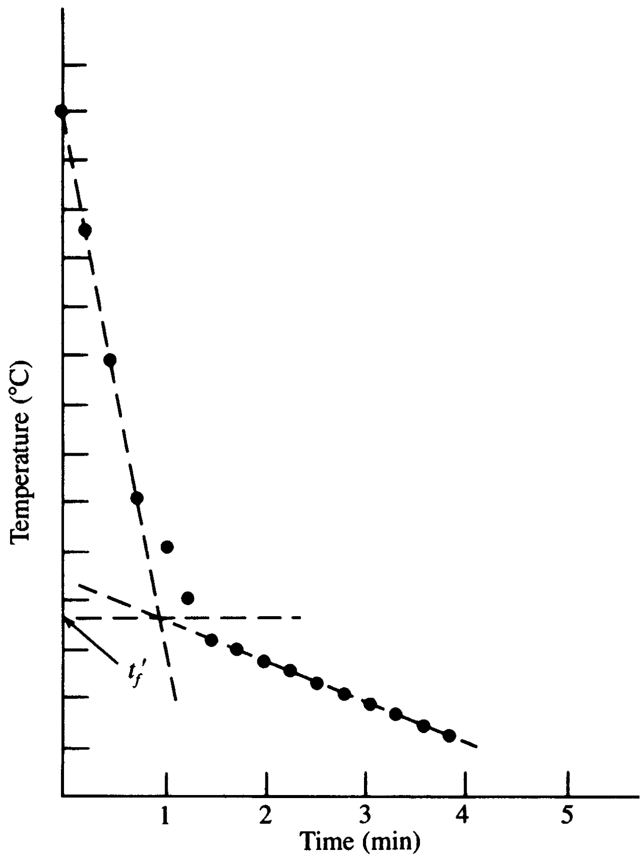
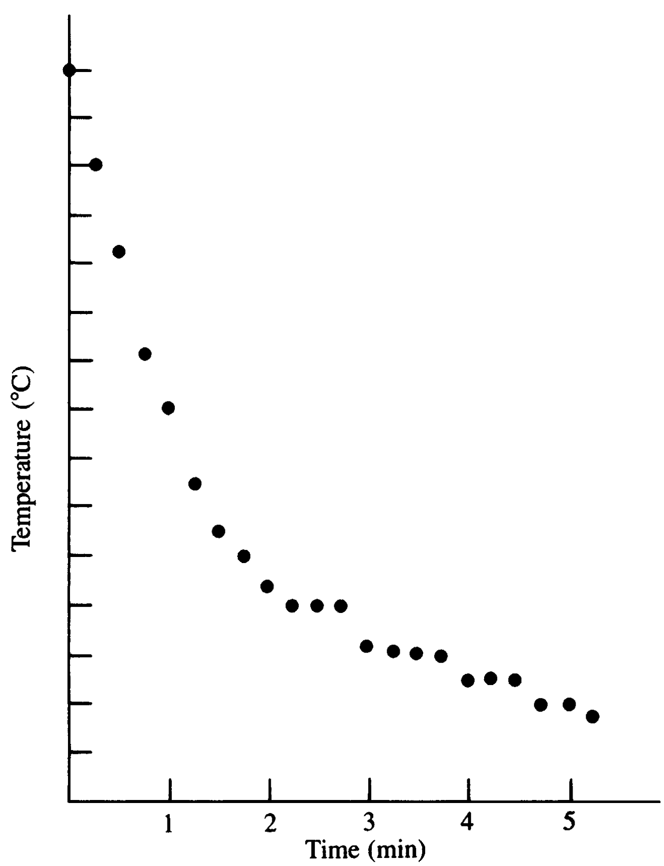


FIGURE 1.4

A cooling curve obtained from an inefficiently stirred solution. Compare this curve with the curve shown in Figure 1.3.



You will not obtain good cooling curves, such as those shown in Figures 1.2 and 1.3, unless you maintain efficient stirring. Otherwise, you will obtain a series of stair steps instead of a smooth decrease in the temperature. An example is shown in Figure 1.4. Drawing a line to describe this kind of data is very difficult, and the ultimate result is not very accurate.

Procedure

Getting started

1. Your laboratory instructor will probably ask you to work with a partner.
2. Obtain directions for discarding the cyclohexane solution that you will use in this experiment.
3. Obtain the apparatus required for this experiment. It will have been described or demonstrated by your laboratory instructor.
4. Make sure the apparatus is clean and dry.
5. Remember the following safety precaution whenever you use cyclohexane during this experiment:

CAUTION: Cyclohexane is flammable. No open flames are allowed during this experiment.

Measuring the freezing point of cyclohexane

1. Pipet exactly 20.0 mL of cyclohexane into the apparatus. Close it immediately. Evaporation of this volatile substance must be avoided for best results.

CAUTION: Never use your mouth to draw a liquid into the pipet. Use a rubber suction bulb or some other suction device.

2. Calculate and record the mass of cyclohexane. Use a density of 0.779 g/mL.
3. Place the apparatus in a beaker that contains crushed ice and water.
4. Stir the cyclohexane gently but constantly.
5. After the temperature has dropped to about 14–15°C, begin recording the temperature to the nearest 0.1°C every 15 s. A total time of 5–10 min will probably be required.
6. After the cyclohexane has frozen and the temperature has begun to decrease again, remove the apparatus from the beaker. Allow the cyclohexane to melt completely.
7. Repeat Steps 3 through 6.
8. Plot the data, find the freezing point in each case, and calculate the mean freezing point.
9. *Save* the cyclohexane for the next part of the experiment.

Measuring the freezing points of the solutions

1. Obtain 2 pieces of waxed weighing paper. Mark each one for recognition.
2. Obtain and record the mass of one of these, using your most precise balance. Place 0.24–0.25 g of the solute directly on the paper. Obtain and record the mass of the paper and solute. Calculate the mass of the solute.

3. Repeat for the other piece of weighing paper. However, use only 0.10–0.11 g of the solute on this paper.
4. Transfer the first sample into the apparatus.
5. Stir until you obtain a complete solution. All of the solid, including any on the walls of the apparatus, must dissolve before the measurement can begin.
6. Stir the solution gently but constantly.
7. Cool the solution to about 14–15°C, and then record the temperature at 15-s intervals. Continue cooling until the entire solution is frozen.
8. Remove the apparatus from the beaker and allow the solution to melt completely.
9. While you are waiting, scan your data. Has the temperature fallen smoothly? If you have a stair-step effect, repeat Steps 6 through 8 with faster stirring.
10. Add the second sample to the solution. The mass of the solute in solution will now be the combined masses of the first and second samples.
11. Repeat Steps 6 through 9.
12. Plot the data for each sample to find the freezing points.
13. Calculate each ΔT_f.
14. Calculate the molar mass (M_m) of the solute from each ΔT_f with due regard for significant figures.
15. Obtain the mean molar mass.
16. Share your results with the rest of the class and obtain their results. Calculate the grand average.
17. Calculate the molecular formula of the solute from the grand average and the empirical formula (C_3H_2Cl).

A Molar Mass from Freezing-Point Depression

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

Prelaboratory assignment

1. Provide definitions for the following terms:

   a. Solution

   b. Solute

   c. Solvent

   d. Colligative property

   e. Freezing-point depression

2. a. What is the objective of this experiment?

   b. How will that objective be achieved?

3. A 0.2436-g sample of an unknown substance was dissolved in 20.0 mL of cyclohexane. The density of cyclohexane is 0.779 g/mL. The freezing-point depression was 2.5°C. Calculate the molar mass of the unknown substance.

4. What safety rules must be observed during this experiment?

A Molar Mass from Freezing-Point Depression

Date: ....
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Instructor: ....

Student name: ....
Team members: ....
....
....

Results

1. Volume of cyclohexane: .... mL

   Mass of cyclohexane: .... g or .... kg

   Calculations:

2. *Freezing point of cyclohexane*

Trial 1		Trial 2	
Time	**Temperature (°C)**	**Time**	**Temperature (°C)**
....	....	....	....
....	....	....	....
....	....	....	....
....	....	....	....
....	....	....	....
....	....	....	....
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....	....	....	....
....	....	....	....
....	....	....	....

Freezing point of cyclohexane: .... First trial

.... Second trial

.... Mean

Student name: .... Course/Section: .... Date: ....

3. *Freezing points of the solutions*

Sample	1	2
Mass of paper + solute (g)	....	....
Mass of paper (g)	....	....
Mass of solute (g)	....	....

Sample 1		Samples 1 + 2	
Time	**Temperature (°C)**	**Time**	**Temperature (°C)**
....	....	....	....
....	....	....	....
....	....	....	....
....	....	....	....
....	....	....	....
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....	....	....	....
....	....	....	....
....	....	....	....

Freezing points of solutions:

Sample 1:

.... °C; $\Delta T_f =$ .... °C; $M_m =$ ....

Samples 1 + 2:

.... °C; $\Delta T_f =$ .... °C; $M_m =$ ....

Mean M_m: ....

Calculations:

Student name: .... Course/Section: .... Date: ....

Record M_m from your classmates (include your value).

Grand average: ....

Molecular formula:

Calculations:

Questions

1. What would be the effect of each of the following on the calculated molecular weight of the solute? Think carefully!

   a. Some cyclohexane evaporated while the freezing point of pure cyclohexane was being measured.

b. Some cyclohexane evaporated after the solute was added.

c. A foreign solute was already present in the cyclohexane.

d. The thermometer is not calibrated correctly. It gives a temperature that is 1.5°C too low at all temperatures.