EXPERIMENT 15
FREEZING POINT: A COLLIGATIVE PROPERTY OF SOLUTIONS

INTRODUCTION

Scientists seldom work alone today. Instead they work in teams on projects, sharing the labor of carrying out the experiments and of interpreting the results. In this experiment, your lab group will work together to collect and analyze data to determine the freezing points of a number of liquids, both pure solvent and solutions made from the solvent and several solutes. The freezing point data you and your lab partner collect will be combined with the data for your entire lab group, and your instructor will lead a discussion of what conclusions can be drawn from the data. Following this you will measure the freezing point of a solution containing an unknown solid. Using the information gathered above, you will determine the molar mass of the unknown solid.

TECHNIQUE

Determination of Freezing Points Using Cooling Curves

A cooling curve for a liquid shows graphically how the temperature varies with time as the liquid is cooled in a constant-temperature bath. The liquid is contained in a test tube and is stirred continuously to maintain thermal homogeneity. The rate of cooling is determined mainly by two factors. The first is the difference in temperature between the liquid and the bath. This factor causes the cooling curve to become gradually less steep (smaller negative slope) as the liquid temperature approaches that of the bath, eventually becoming zero, yielding a horizontal line at the bath temperature. The second factor is the extent to which the liquid is insulated from the bath. This factor does not control the overall shape of the cooling curve, but it does affect how long the experiment takes.

If the freezing point of the liquid is above the bath temperature, the cooling curve will not proceed in a smooth curve all the way to the bath temperature. It will instead show a discontinuity, i.e., a sudden decrease in slope, at the freezing point of the liquid. This slowing of the cooling occurs because the heat of fusion of the liquid is released as the liquid freezes, at least partially compensating for the heat being lost to the bath. It is occasionally observed that freezing does not begin immediately at the freezing point, but that supercooling occurs. When freezing does begin, the heat released will raise the temperature to the level that would have been observed in the absence of supercooling. Should supercooling occur in any of your samples, it will be obvious from the sudden, small rise in temperature after the supercooling “dip” in the cooling curve.

Cooling curves for pure liquids differ from those for solutions. The temperature remains constant as a pure liquid freezes, so a flat, horizontal region is expected in the cooling curve. If the cooling is continued until *all* of the liquid has frozen, the temperature will then decrease further as the solid is cooled, until it finally reaches the temperature of the bath. For a solution, on the other hand, the temperature continues to decrease as freezing occurs, although at a lower rate. This occurs because it is pure solvent that is freezing out of the solution, leaving the liquid solution more and more concentrated, continually decreasing the freezing point. If cooling is continued until all of the solution has frozen, the cooling curve will become steeper again, since no more heat of fusion is being released. It is important to note that it is the temperature at which the solution **begins** to freeze that is desired, since it is only there that the concentration is known.

An experimental cooling curve for a pure liquid is shown in **FIGURE 15-1** and for a solution in **FIGURE 15-2**. Careful examination shows that a small supercooling "dip" occurred in both curves. It is also apparent that the region after the onset of freezing in **FIGURE 15-1** isn't quite horizontal. The temperature continued to decrease slightly as the solvent froze. This *could* mean that the solvent wasn't 100% pure. It might, however, be due simply to a cooling rate that was too high. The temperature remains constant as a pure liquid freezes only if the solid and liquid are always essentially in equilibrium with each other. This may not be the case if the cooling is too rapid or if the stirring is not adequate. The solvent must freeze rapidly enough to produce heat (heat of fusion) at the rate at which heat is lost to the bath, and the stirring must be rapid and thorough enough to keep the temperature uniform throughout the sample.

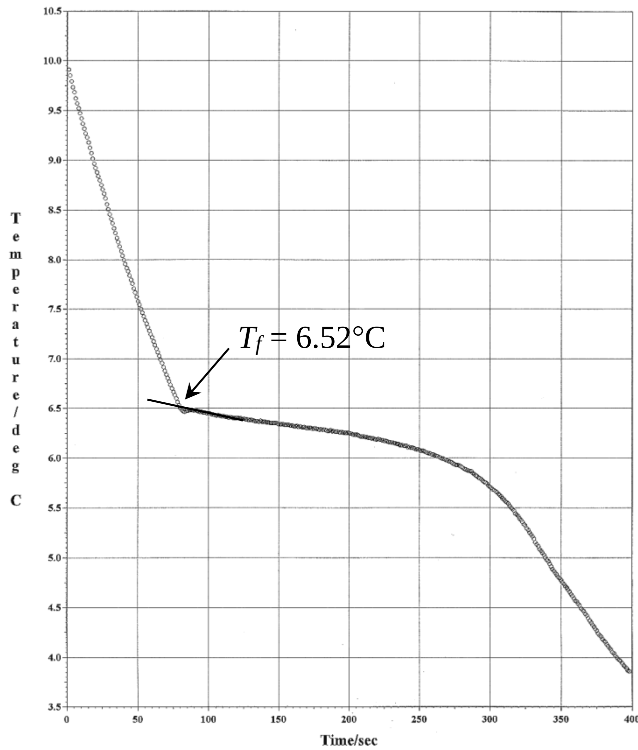

Figure 15-1. Cooling curve of a pure liquid.

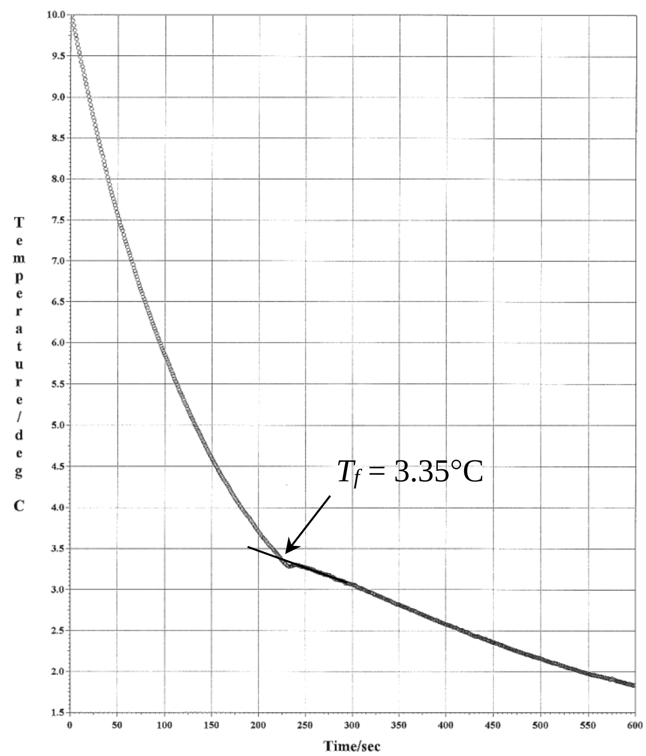

Figure 15-2. Cooling curve of a solution.

The cooling curve in **FIGURE 15-1** was followed much longer than necessary after the onset of freezing, in order to illustrate how the temperature drops quickly again after all of the liquid has frozen. Note how the freezing point, T_f, is determined in each case. A line is drawn to extrapolate the behavior just after freezing began back through the supercooling "dip" to the curve just before freezing began. The intersection of the extrapolated line with this curve is taken as the freezing point. If supercooling were not observed, the freezing point would be taken to be the point where the slope changes abruptly.

OBJECTIVES

- to determine the freezing points of several liquids
- to combine and discuss your data with the other students on your network
- to prepare a solution of an unknown solute and measure its freezing point
- to determine the molar mass of the unknown solute from the freezing point

EQUIPMENT NEEDED

beakers (150 mL and 800 mL)	medium test tube
ring stand and clamp	glass stirring rod
Styrofoam cups (2)	temperature probe
Kimwipe tissues	smaller test tube (supplied by stockroom)

CHEMICALS NEEDED

Note: Concentrations of solutions are expressed in units of *molality*.

cyclohexane, C_6H_{12}
naphthalene in cyclohexane (0.040 m, 0.080 m, 0.120 m, 0.160 m)
biphenyl in cyclohexane (0.040 m, 0.080 m, 0.120 m, 0.160 m)

PROCEDURE

A. Freezing Point Determination of Known Solutions and/or Pure Solvents

Each pair of students will be assigned at least three test liquids from the front of the lab room. Your instructor will give you an assignment sheet. One of the liquids you will investigate will be pure solvent (cyclohexane); the others will be solutions of a solute dissolved in cyclohexane. You will determine the freezing point of each of the liquids you have been assigned.

Calibration of the Temperature Probe and Setup of Workstation Display

Press **MAIN MENU** on the workstation, press the function key for **TEMPERATURE**, and then the function key for **TEMPERATURE V TIME**. Fill your 800-mL beaker with ice. Fill a Styrofoam cup approximately three-quarters full with ice and add enough ***distilled*** water to ***barely*** cover the ice. This ice/water mixture will be at 0.0°C. Press **CALIBRATE** and place the temperature probe in the ice water, using the temperature probe to continuously stir the ice water for at least two minutes. Follow the instructions on the display for the calibration of the temperature probe. **Since data from all of the students on your network will be combined in this exercise, it is particularly important to do a good job calibrating the temperature probe. Calibration errors will lead directly to disagreement among the values obtained by various group members.** When you have finished calibrating the temperature probe, remove it from the ice bath and carefully dry it. This is necessary in order to avoid contaminating one of the liquids to be studied by introducing water.

Press **SETUP** and set the graph limits for your workstation display. Set the minimum and maximum temperatures at 0°C and 10°C, respectively, and set the maximum time at 900 seconds. Press **DISPLAY** to accept the graph limits and begin monitoring the temperature.

Cooling Curve Measurements

Measuring a cooling curve experimentally would seem to be a very simple matter. However, in order to achieve results of comparable quality to those in **FIGURES 15-1** and **15-2**, you must pay surprisingly close attention to various details. Lack of careful technique in following the instructions below will be immediately apparent in your cooling curves.

Place the Styrofoam cup you used in the temperature probe calibration inside another Styrofoam cup. Use this *nested* pair of cups as the constant-temperature bath for each cooling curve measurement. Before **each** experiment fill the cup to the top with ice and add (or pour out) just enough water to bring its level to within a centimeter or so of the top. **You need to have ice all the way to the bottom of the cup. Be sure to stir the ice-water bath thoroughly before each experiment.**

Perform the cooling curve experiment on the pure solvent first. Attach the clamp to the ring stand and clamp a medium (18 mm × 150 mm) test tube near its open end. Obtain a KimWipe, tear~ ¼ of it off, roll the smaller piece into a ball, and place it in the medium test tube. To a smaller (15 mm x 125 mm) test tube (not in your drawer—obtain from the back bench), add a small amount of cyclohexane (just enough to fill the curved bottom of the test tube) and tilt the test tube so that the inner walls are rinsed, then pour the cyclohexane into the organic waste container Now fill the test tube ~1/4 full (no more!) with cyclohexane and place it inside the medium test tube. The KimWipe will hold the smaller test tube in the center of the larger one in such a way that they do not actually touch. The reason for this rather strange-sounding arrangement is that it conveniently limits the rate at which heat can be transferred from the smaller test tube to the bath around the larger one. If the cooling occurs too quickly, in addition to the resulting problems discussed above, the temperature probe may not be able to “keep up” and accurately show what is happening. The result would be a *smearing out* of the details around the onset of freezing, and that would make it difficult or impossible to determine just where freezing begins.

Loosen the clamp on the ring stand and slide it down to lower the test tubes into the ice bath in the Styrofoam cups. Wiggle the cups around as you insert the tube until it rests on the bottom. **Do not press down too hard, though, or you will break through the bottom of the cup.** Insert the temperature probe into the liquid in the smaller test tube and begin stirring the liquid. The best stirring technique is a regular, but gentle, up-and-down motion, about twice per second, in which the probe is raised about two centimeters and then returned to the bottom of the tube. **It is important that you keep stirring smoothly throughout the course of the measurements in order to maintain temperature homogeneity.** While you stir, monitor the temperature on the workstation screen. When it reaches 10°C, press **START/STOP** to begin collecting data. Continue stirring and monitor the plot of temperature *vs.* time on the workstation screen. **After** freezing begins, as seen in the a change in slope on the plot or from the numbers themselves, continue collecting data for about a minute more, then remove the smaller test tube from the larger test tube (do **not** press **START/STOP** yet). When the liquid in the test tube has warmed up to ~10ºC, place it back in the larger test tube and allow the liquid to cool down to its freezing point. In this manner, you will have two cooling curve experiments plotted on the workstation screen. When the second experiment is complete, press **START/STOP** to stop collecting data. Remove the smaller test tube from the ice bath (you can leave the larger one in the ice bath), remove the probe from the test tube, and wipe it off. (If the probe becomes stuck in the frozen liquid, warm the tube with your hand until the liquid melts and you can remove the probe.) Dispose of the liquid in the **non-halogenated liquid organic waste** container.

Print your temperature versus time plot. To do this, press **FILE OPTIONS**, press the function key for **PRINT standard**, and enter the number of copies to print, probably 2—one for you and one for your lab partner. As soon as you obtain your printout, label the plot with the name of the liquid being investigated (in this case, cyclohexane) . Show the printout to your instructor to make sure it is acceptable. To summarize, in order to obtain good-quality cooling curves, you must (1) keep the ice bath *filled* to the bottom with ice, (2) use a tissue to properly position the test tubes, (3) use the correct amount of liquid (no more than ¼ test tube full), and (4) stir smoothly and continuously as data are collected.

Press **DISPLAY** twice after printing your data to clear the plot on the workstation screen. Repeat the above procedure to obtain a cooling curve for each of your assigned solutions, adding more ice to the ice bath before the experiment if necessary. As you print out each plot, be sure to label it completely for later identification.

DATA ANALYSIS

Analyze your cooling curves as illustrated in **FIGURES 15-1** and **15-2** to determine the freezing points. If your freezing point curve for the pure solvent does not have a horizontal portion (indicating too-rapid cooling or the presence of an impurity in the solvent), analyze the curve as if it were for a solution. If the freezing points of your two trials differ, record the average of the two trials. Before proceeding to the next step, have your instructor verify that you are analyzing the data correctly.

Go to the computer connected to your network, be sure the program entitled "Freezing Point Plot" is running and visible, (select it from the task bar at the bottom of the computer screen if it is not), enter your data, and update the group plot.

When everyone has finished this part of the experiment, the freezing point data will be compiled into a single plot of freezing point *vs.* concentration. Your instructor will print and distribute this plot and lead a discussion of the results. In order to have this discussion in a timely fashion, you must have all of your freezing point data entered into the computer by the time announced. **After** the discussion, you may proceed to Part B.

B. Molar Mass Determination of an Unknown Solute

Weigh out ~0.10 to 0.15 g of your unknown solute on an analytical balance into a 150-mL beaker, recording the mass to the nearest 0.0001 g. Its molar mass is in the range from 100 to 200 g/mol. ***Be sure to record the unknown number!*** Measure out 10 mL of cyclohexane from a buret into the beaker. It is not important that you measure exactly 10 mL. **However, you should record the actual volume you use to the nearest 0.01 mL**. After the solute is completely dissolved in the cyclohexane, measure the freezing point of the solution by performing the cooling curve experiment as described in Part A.

Look up and record the density of cyclohexane, which will be used to calculate the mass of cyclohexane used.

Waste Disposal

Any unused solution should be poured into the Liquid Organic Waste container.

RESULTS

Part A. Freezing Points of Known Solutions

1. Include in your report the printouts of your cooling curves, showing how you determined the freezing points, and the group freezing point *vs*. concentration plot. Make sure all graphs are given appropriate titles.
2. Fill out the report sheet table summarizing the results of your freezing point measurements.

Part B. Molar Mass of Unknown Solute

1. Determine the freezing point, T_f, from the cooling curve of the solution containing your unknown solute. Show how you determined the freezing point, and be sure the graph is given an appropriate title.
2. Use the freezing point of your unknown solution and the equation of the best fit line drawn through the group plot data to determine the molality of your solution. Show how you obtained this value.
3. Calculate the mass of cyclohexane used in the experiment. Use the mass of cyclohexane and the solution molality determined above to calculate the molar mass of your unknown solute. Recall that molality is calculated by:

$$\text{molality} = \frac{\text{moles solute}}{\text{kg of solvent}} \qquad (15\text{-}1)$$

Record this information on the **REPORT SHEET.** Show all calculations.

DISCUSSION

Write a paragraph or two briefly describing the results and conclusions of the group experiment involving the freezing points of the known solutions. Be sure to cover the following topics:

1. How is the freezing point determined from a cooling curve graph?
2. What is the effect of the concentration of solute (expressed in molality, m) on the freezing point of the solution?
3. What is the effect of the chemical identity of the solute on the slope of the concentration vs. freezing point curve?
4. Explain how the data support the assertion that freezing point depression is a colligative property.

EXPERIMENT 15
REPORT SHEET

Name: ______________________________________ **Date:**__________

Partner:_____________________________________

PART A. FREEZING POINTS OF KNOWN SOLUTIONS

concentration	solute	freezing point
____	________	________
____	________	________
____	________	________
____	________	________

PART B. MOLAR MASS OF UNKNOWN SOLUTE

Unknown Number of Solute _______

Mass of Solute _____________________________________

Volume of Cyclohexane______________________________

Density of Cyclohexane______________________________

Mass of Cyclohexane, kg_____________________________

calculation:

Freezing Point of Solution ________________________________

Concentration of Solution ________________________________
(from freezing point curve)

Moles of Solute ____

calculation:

Molar Mass of Unknown _________________________________

calculation:

Lab Notes
Experiment 15
Freezing Point: A Colligative Property of Solutions

Procedure considerations

- Part A: You should perform three freezing point experiments: one with a pure solvent, two with solutions. Your assigned liquids are listed on the last page. Measure the freezing point of the pure liquid first.
- You should be able to do two cooling curve trials for a liquid without having to reset the workstation screen. Do not press 'Start/Stop' until after the second time the liquid has frozen.
- You will be following a timetable during this experiment in order to have a group discussion of the Part A data. The timetable will be as follows:

  First two hours   Collect freezing point data for Part A; analyze curves; enter data on computer

  At 2 hour mark   TA leads group discussion of compiled data

  After discussion   Complete Part B

- Be sure to take notes during this discussion! There will be topics discussed that will need to be included in your lab report.
- If you have completed Part A before the discussion you may begin Part B by preparing your unknown solution. You may perform the cooling curve trials for Part B if you are ready do so before the discussion; however, you should stop what you are doing when it is time for the group discussion.

Helpful Hints:

The two most important points to remember in this experiment are **stir the solution or solvent continually and make sure the ice bath is sufficiently cold**. The ice bath should be at least 3/4 filed with ice for each trial. Stir the ice water briefly before each trial to ensure that the temperature of the ice bath is relatively uniform. <u>Submerge the test tube in the ice bath as far as possible.</u>

Freezing Point Liquid Assignments

Station #	Liquid Assignment	Station #	Liquid Assignment
1, 9	1) Cyclohexane 2) 0.04 m biphenyl in cyclohexane 3) 0.16 m naphthalene in cyclohexane	5	1) Cyclohexane 2) 0.04 m biphenyl in cyclohexane 3) 0.16 m naphthalene in cyclohexane
2, 10	1) Cyclohexane 2) 0.08 m biphenyl in cyclohexane 3) 0.12 m naphthalene in cyclohexane	6	1) Cyclohexane 2) 0.08 m biphenyl in cyclohexane 3) 0.12 m naphthalene in cyclohexane
3, 11	1) Cyclohexane 2) 0.12 m biphenyl in cyclohexane 3) 0.08 m naphthalene in cyclohexane	7	1) Cyclohexane 2) 0.12 m biphenyl in cyclohexane 3) 0.08 m naphthalene in cyclohexane
4, 12	1) Cyclohexane 2) 0.16 m biphenyl in cyclohexane 3) 0.04 m naphthalene in cyclohexane	8	1) Cyclohexane 2) 0.16 m biphenyl in cyclohexane 3) 0.04 m naphthalene in cyclohexane