Name_____Lab Day_____Lab Time_____

Experiment 5 · Freezing-point depression

Pre-lab questions
Answer these questions and hand them to the TF before beginning work.

(1) What is the purpose of this experiment?

_____

_____

(2) According to Figure 5-2 at what temperature does cyclohexane freeze at 1 atm pressure?

_____

_____

(3) What is the definition of "molality"?

_____

_____

(4) You will measure the temperature at which a sample of cyclohexane freezes. How will you know that the sample is at its freezing point?

_____

_____

(5) You will measure the temperature of a solution of an unknown dissolved in cyclohexane as the solution freezes. How will you know that the sample is in the process of freezing?

_____

_____

Freezing-point depression

Phase diagrams and phase transitions

A phase diagram such as Figure 5-1 indicates the most stable state of a substance (solid, liquid, or vapor) at any given temperature and pressure. Phase boundaries (solid lines) on a phase diagram indicate conditions at which two or more phases coexist in equilibrium.

When temperature and pressure change, a substance may undergo a phase transition, that is, a conversion from one state to another; the names of these phase transitions appear in Figure 5-1. Suppose that the substance whose phase diagram is given in Figure 5-1 is initially at 1 atm pressure and at a very low temperature; under these conditions, the most stable state of that substance is a solid. As the solid is heated at 1 atm pressure, the system moves to the right along the 1-atm pressure line in the phase diagram until it reaches the solid–liquid phase boundary, at which point the solid and the liquid coexist at equilibrium. In other words, the solid melts. The temperature at which melting of the solid (or freezing of the liquid if the phase boundary is approached from the right) occurs at 1 atm pressure is called the normal melting point (or the normal freezing point). Upon further heating at 1 atm, the system continues to move along the 1-atm pressure line until it reaches the liquid–vapor phase boundary, at which point the liquid

boils. The temperature at which boiling of the liquid takes place at 1 atm pressure is called the normal boiling point. Continued heating at 1 atm transforms the liquid to the vapor.

Although we are concerned with the conversion of a liquid to a solid (i.e., freezing) in this experiment, we must first discuss the conversion of a liquid to a vapor (i.e., boiling) because an understanding of the boiling process provides some theoretical ideas needed in the present experiment.

Vapor pressure and vapor-pressure lowering
Many liquids (e.g., water or alcohol) if left in a beaker that is open to the atmosphere will, in time, completely evaporate. However, if a beaker containing sufficient liquid is placed inside a closed box, a different result is obtained: some, but not all, of the liquid evaporates and the atmosphere within the box becomes permeated with vapor coming off the liquid. The end result of the experiment in the closed box corresponds to a situation in which the liquid and the vapor coexist in equilibrium with each other.

Figure 5-1 A phase diagram shows the most stable state of a substance at any given temperature and pressure. Phase boundaries (solid lines) indicate conditions at which two or more phases coexist in equilibrium. T_f denotes the normal freezing (or melting) point, T_b denotes the normal boiling point, and the triple point denotes conditions at which solid, liquid and vapor all coexist.
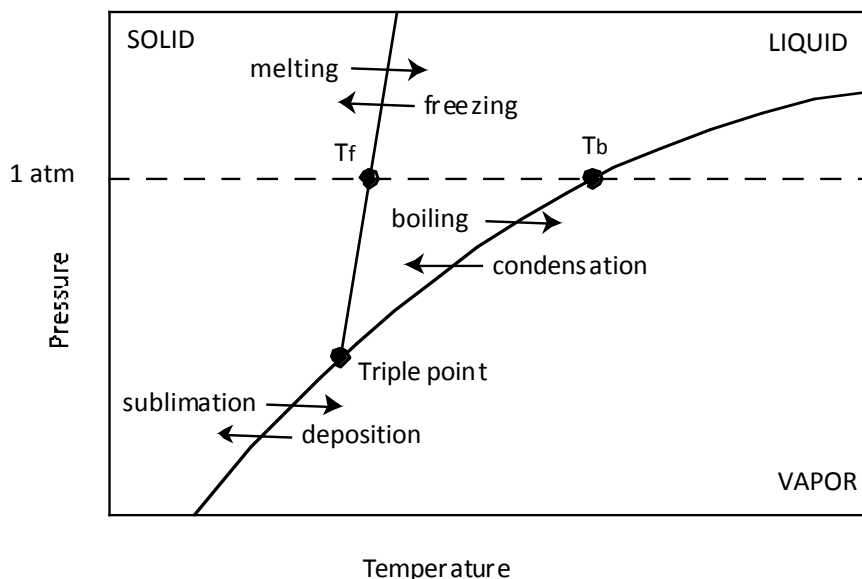
Because it is a gas, the vapor exerts a pressure on the interior walls of the box; this pressure is called the vapor pressure of the liquid. Liquids that have a high vapor pressure at room temperature are said to be volatile, that is, they evaporate readily, whereas liquids that have a low vapor pressure at room temperature are said to be non-volatile. Ether, whose vapor pressure is 0.703 atm at 25 °C, is an example of a volatile liquid. Water (vapor pressure = 0.0313 atm at 25 °C) is considered a moderately volatile liquid. Mercury (vapor pressure = 2.4×10^{-6} atm at 25 °C) is essentially a non-volatile liquid.

The vapor pressure of a liquid at a given temperature can be read off a phase diagram. Consider the phase diagram of cyclohexane shown in Figure 5-2. Suppose that a sample of cyclohexane is at 1 atm pressure and 20 °C; under these conditions, the most stable state of cyclohexane is the liquid. Its vapor pressure at 20 °C is found by following the 20 °C line until the liquid–vapor phase boundary is encountered: the figure shows that the vapor pressure of cyclohexane at 20 °C is 0.1 atm.

Boiling occurs when the vapor pressure of a liquid equals the pressure of the surrounding atmosphere. Cyclohexane boils

**Figure 5-2** Phase diagram of cyclohexane.
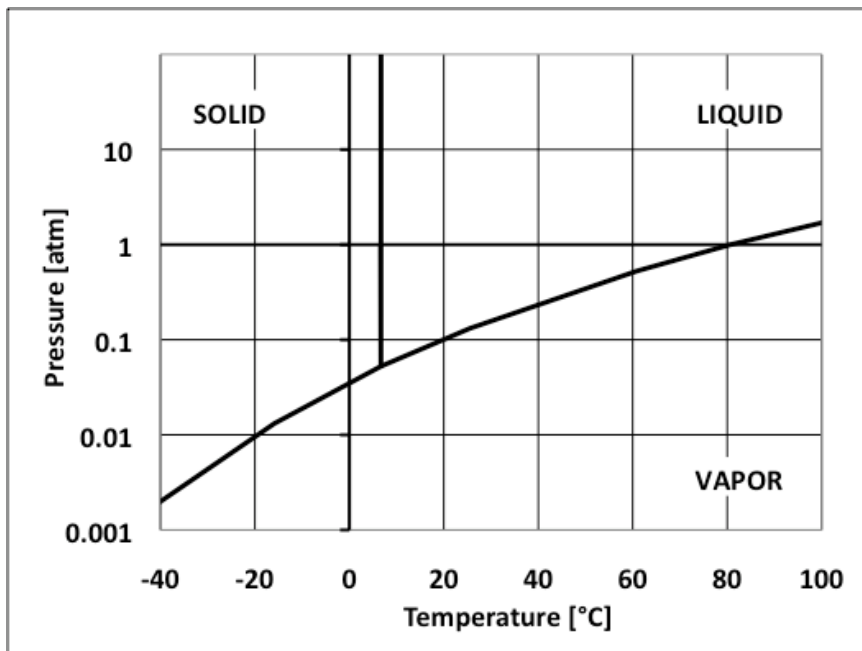
at 20 °C if the special arrangement is made so that the surrounding atmosphere is at 0.1 atm. However, in a beaker open to the atmosphere at the ordinary conditions of 1 atm, cyclohexane boils at 80 °C.

In the 1880s the French chemist François–Marie Raoult discovered that dissolving a substance (the solute) in a liquid (the solvent) lowers the vapor pressure of the liquid solvent. Raoult's observation can perhaps be best appreciated by looking at Figure 5-3 in which we have plotted the phase diagram of a pure substance (solid line) and the phase diagram of a solution in which that pure substance is the solvent (dotted line).

In accord with Raoult's findings, the liquid–vapor phase boundary belonging to the solution is lower at every point than the liquid–vapor phase boundary belonging to the pure liquid solvent. A consequence of this behavior is the phenomenon of boiling-point elevation: the solution boils at a higher temperature than the pure liquid solvent.

The requirement that the vapor pressure of the solution be

Figure 5-3 Phase diagram of a pure liquid (solid line) and of a solution (dotted line) in which the liquid is the solvent. Dissolving a substance (the solute) in the liquid lowers the vapor pressure of the liquid solvent. This effect results in boiling-point elevation and freezing-point depression.
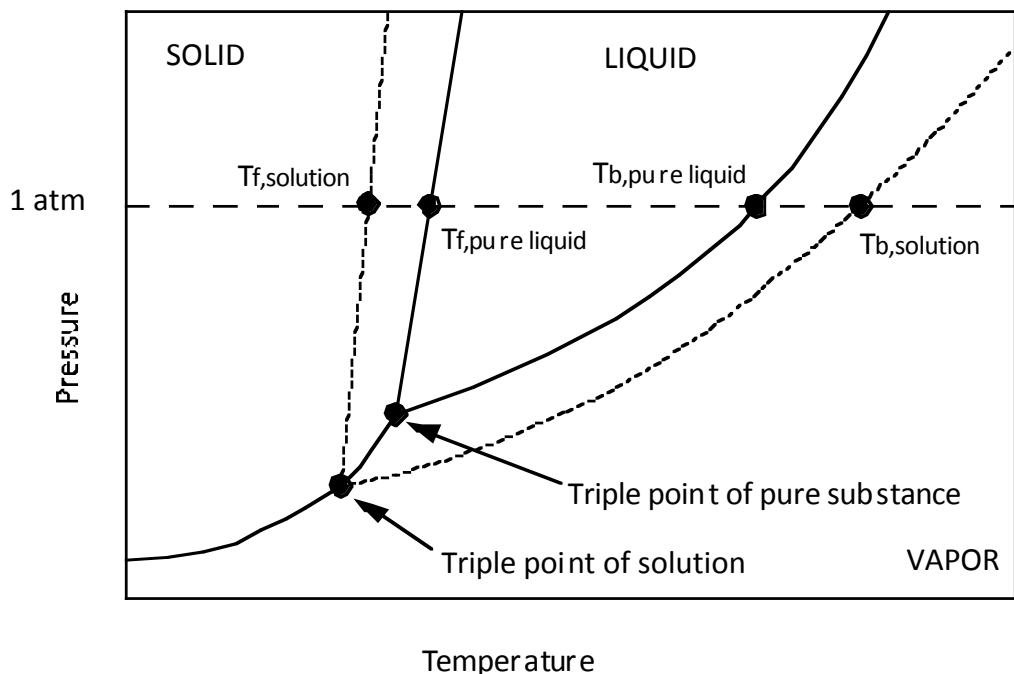
lower than that of the pure liquid solvent implies that the solution has a different triple point from that of the pure substance: the triple point of the solution is farther down the solid–vapor phase boundary. Because the solid–liquid phase boundary originates at the triple point, Figure 5-3 indicates that vapor-pressure lowering also results in the phenomenon of freezing-point depression: the solution freezes at a lower temperature than the pure liquid solvent.

Molar mass determinations from freezing-point depression data
The addition of antifreeze to the water in the radiator of a car is perhaps the most familiar practical application of freezing-point depression (see the post-lab questions).

Freezing-point depression data also allow us to determine the molar mass of a solute. The increment by which the freezing point of a solvent is lowered by the addition of a solute is proportional to the amount of solute present in the solvent. In equation form

$$\Delta T_f = T_{f,solvent} - T_{f,solution} = K_f \underline{m} \qquad \text{(Eqn. 5-1)}$$

where ΔT_f is the amount by which the freezing point of the solvent is lowered in units of degrees Celsius, $T_{f,solvent}$ is the freezing point of the solvent in units of degrees Celsius, $T_{f,solution}$ is the freezing point of the solution in units of degrees Celsius, K_f is the freezing-point depression constant of the solvent in units of degrees Celsius–kilogram of solvent per mole of solute, and $\underline{m}$ is the molality of the solution in units of moles of solute per kilogram of solvent. (The units in Eqn. 5-1 are awkward, but it's important to keep track of them in order to avoid making an error of several orders of magnitude.)

When we combine the definition of molality $\underline{m}$

$$\underline{m} = \frac{n_{solute}}{m_{solvent}}$$

where n_{solute} is the number of moles of solute in the solution and $m_{solvent}$ is the mass of the solvent in units of kilograms with the definition of the molar mass of the solute $\mathcal{M}_{solute}$

$$\mathcal{M}_{solute} = \frac{m_{solute}}{n_{solute}}$$

where m_{solute} is the mass of the solute in units of grams, we can rewrite the expression for molality $\underline{m}$ as

$$\underline{m} = \frac{m_{solute}}{\mathcal{M}_{solute}m_{solvent}}$$

Plugging this expression into Eqn. 5-1 and rearranging gives

$$\mathcal{M}_{solute} = \frac{K_f m_{solute}}{m_{solvent}\Delta T_f}$$

If the solvent is a liquid, we employ the substitution

$$m_{solvent} = \rho_{solvent}V_{solvent}$$

where $\rho_{solvent}$ is the density of the solvent in units of grams per milliliter and $V_{solvent}$ is the volume of solvent in units of milliliter. We at last arrive at a computational formula for determining the molar mass of the solute $\mathcal{M}_{solute}$ from freezing-point depression data:

$$\mathcal{M}_{solute} = \frac{K_f m_{solute}}{\rho_{solvent}V_{solvent}\Delta T_f} \qquad \text{(Eqn. 5-2)}$$

You will use Eqn. 5-2 to determine the molar mass of an unknown solute.

Procedure

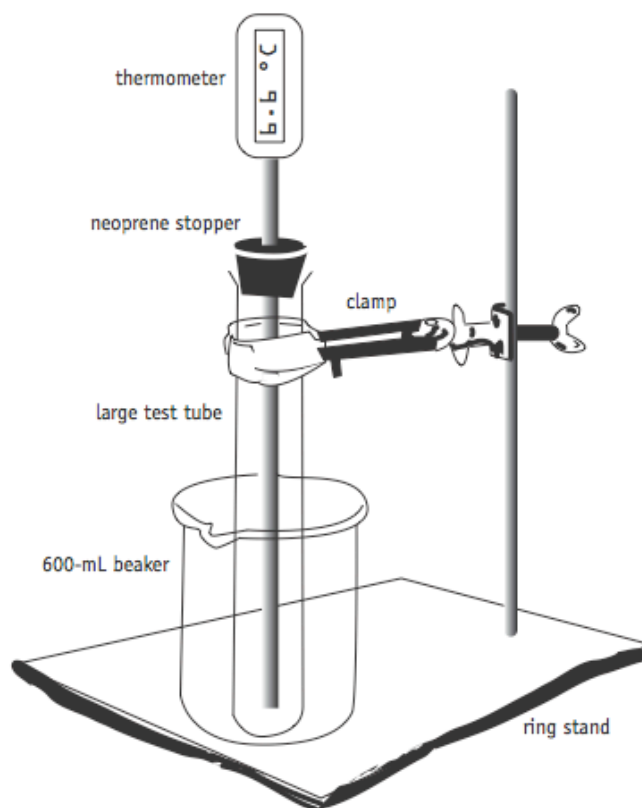**Determination of the freezing point of pure cyclohexane**
Obtain or assemble an apparatus for measuring freezing-point depression (see Figure 5-4). The apparatus consists of a large Pyrex test tube sealed off with a neoprene stopper that has been fitted with a thermometer. Clamp the apparatus to a ring stand. **Do not wash or rinse the test tube with water nor**

allow any wet object to come into contact with the inside of the test tube: water will contaminate the liquid you are about to pour into the test tube.

Using a graduated cylinder, measure out about 15 mL of cyclohexane. Record the volume you take in your notebook. Pour the cyclohexane into the test tube and reseal it with the stopper. Be sure that the tip of the thermometer is dipping into the middle of the cyclohexane and that the tip is not touching the sides or bottom of the test tube.

You will now prepare a cold bath. Obtain a second thermometer and a 600-mL beaker; place about 300 mL of ice in the beaker. Using a clean and dry 250 mL beaker, measure out about 50 mL of NaCl(s). Gradually add the NaCl(s) to the ice. Stir the mixture constantly using a spatula. After about a minute of constant stirring, the NaCl solution should get very cold. You can check its temperature using the second thermometer.

**Figure 5-4** Apparatus for measuring freezing-point depression.

Add another 300-mL portion of ice and another 50-mL portion of NaCl(s); stir the mixture constantly. You want the temperature of the NaCl solution to reach and stay at about –15 °C.

You are now ready to carry out your first determination of the freezing point of pure cyclohexane. Place the test tube containing the cyclohexane into the cold bath. Immediately record the temperature of the cyclohexane when you immerse it in the cold bath (call this $t = 0$ sec) and every 20 sec thereafter.

You should observe three separate régimes of cooling behavior (see Figure 5-5): (1) a rapid decrease in temperature as cylcohexane cools after its immersion in the cold bath; (2) a plateau as cyclohexane freezes; (3) a second decrease in temperature as cyclohexane(s) cools. The freezing point of cyclohexane ($T_{f,solvent}$ in Eqn. 5-1) corresponds to the temperature at the plateau. Continue taking time-versus-temperature data until you have positively identified the third régime of temperature decrease (the entire run from beginning to end should take no more than 10 min). Be aware of the possibility that there may be a significant wobble in the data: do not lose patience and abandon the run until you're sure that the system has come out of the plateau and that the temperature is really and truly decreasing. Success hinges in part on maintaining the temperature of the cold bath as close to –15 °C as possible: you may have to stir the cold bath throughout the run. In any event,

Figure 5-5 Cooling curve of a pure liquid undergoing freezing. The freezing point of the liquid Tf corresponds to the temperature at the plateau.
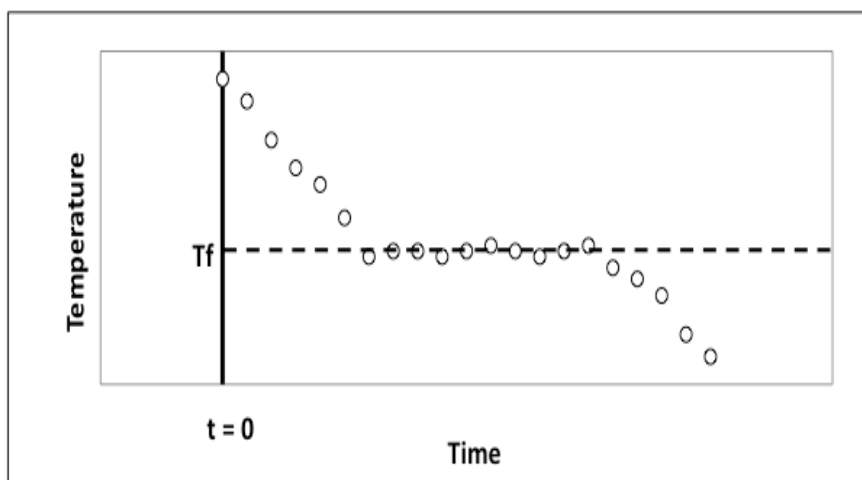
check the temperature of the cold bath between timed measurements using the second thermometer.

After the completion of the run, remove the test tube from the cold bath and gently heat it under a stream of warm tap water until the cyclohexane(s) melts. Remember that water will contaminate the cyclohexane: do not pour water near the top of the test tube and do not deluge the test tube in a raging torrent of hot water! Allow the cyclohexane to come to room temperature before continuing.

The results of your first run may be woefully inaccurate because you are just becoming familiar with the correct technique. Repeat the freezing-point determination at least once more: you want the average of at least two runs. You don't have to measure out new cyclohexane – just reuse the liquid already in the test tube. Before each run (1) be sure that the temperature of the cyclohexane has stabilized around room temperature, that is, do not begin the next run with hot or even warm cyclohexane; (2) check that the temperature of the cold bath is around −15 °C: if it is not, mix it again with a spatula or dispose of the cold bath in the sink and prepare a fresh cold bath if stirring does not bring the temperature back down to near −15 °C.

**Determination of the freezing point of a solution of an unknown dissolved in cyclohexane**

Weigh out about 0.5 g of unknown solid. Record the exact mass in your notebook. Transfer the solid to the cyclohexane in the test tube, being careful to avoid losses during the transfer. Shake the test tube gently to dissolve all the unknown and take care that no unknown sticks to the walls of the test tube. After all the unknown has dissolved, wait about 2 min for the temperature of the solution to stabilize.

Place the test tube containing the solution into the cold bath. Immediately record the temperature of the solution when you immerse it in the cold bath (call this $t = 0$ sec) and every 20 sec thereafter.

You should once again observe three separate régimes of cooling behavior, but the freezing of a solution is more complex than the freezing of a pure substance (see Figure 5-6). Immediately after its immersion in the cold bath, the temperature of the solution rapidly decreases. As the solution freezes, the rate at which the temperature decreases should slow down significantly, but it does not reach a temperature plateau in the way that pure cyclohexane does. After the solution is completely frozen, the temperature decrease resumes at a faster rate. The freezing point of the solution ($T_{f,solution}$ in Eqn. 5-1) is the temperature at which the solution just begins to freeze. The quantity $T_{f,solution}$ is best found by plotting the time-versus-temperature data, drawing a line through the data points corresponding to the initial rapid cooling stage and drawing a second line through the points collected during the quasi-plateau cooling stage: $T_{f,solution}$ is identified with the temperature at which the two lines intersect.

Ideally, you should continue taking time-versus-temperature data until you have positively identified the third régime of temperature decrease, but this is not always easy to

Figure 5-6 The cooling curve of a solution undergoing freezing exhibits three régimes of decreasing temperature: (1) an initial rapid rate of cooling followed by (2) a quasi-plateau over which the rate of cooling decreases but does not level off then (3) a second rapid rate of cooling. The freezing point of the solution T_f corresponds to the temperature at which a line drawn through the data points pertaining to the first cooling régime intersects a line drawn through the data points pertaining to the second cooling régime.
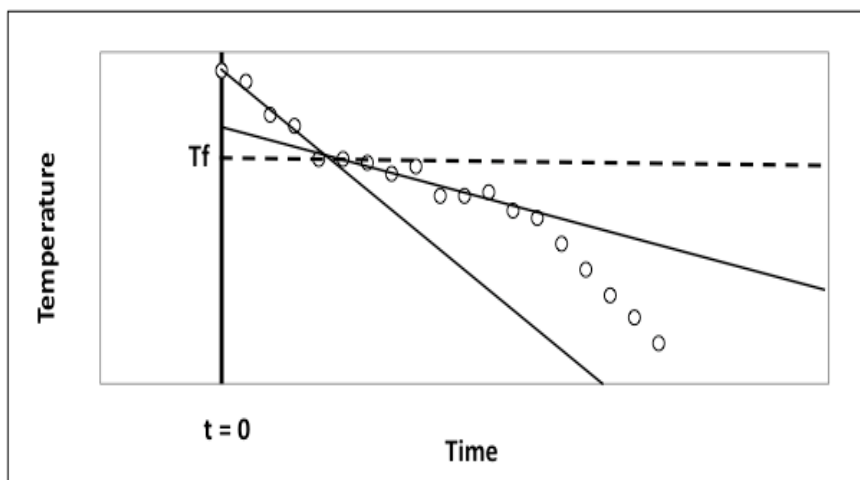
do because there can be significant wobble in the data. Check the temperature of the cold bath between timed measurements using the second thermometer: in order to successfully detect the third régime of temperature decrease, the cold bath must be as close to –15 °C as possible.

After the completion of the run, remove the test tube from the cold bath and gently heat it under a stream of warm tap water at the sink until the solution melts. Reusing the same solution, repeat the freezing-point determination twice more: you want the average of three runs.

It might be a good idea to plot the data collected in at least the first run immediately in order to get a better idea of how the solution is behaving; your plot should resemble Figure 5-6.

Clean-up

When you have finished all experimental work, dispose of the cyclohexane solution in a special container for organic waste. It goes without saying that the cyclohexane solution should not be poured down the drain.

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You are asked to submit several plots as part of this lab report. Prepare a separate plot for each run. Give each plot a truly informative title (i.e., don't just call it "Plot 1"), label the axes, and include appropriate units and divisions of those axes. Do not submit small plots: use a whole sheet of paper. Scale the horizontal and vertical axes so that the data points occupy most of the area of the plot.

(I.A) Prepare plots of the data collected in the measurement of the freezing point of pure cyclohexane $T_{f,solvent}$. Draw a line through the data points that correspond to the plateau in the cooling curve; $T_{f,solvent}$ corresponds to the temperature of the plateau.

(I.B) Prepare plots of the data collected in the measurement of the freezing point of the solution of the unknown in cyclohexane $T_{f,solution}$. Draw a line through the data points that correspond to the initial rapid rate of cooling and draw a line through the data points that correspond to the quasi-plateau over which the rate of cooling decreases; $T_{f,solution}$ corresponds to the temperature at which the two lines intersect.

(I.C) Report the results in the table below. Using the formulas given in Appendix A "Statistical Treatment of Data" of this lab manual, calculate the mean value of $T_{f,solvent}$, the mean value of $T_{f,solution}$, and the standard deviation of the means.

Run	$T_{f,solvent}$ [° C]	Run	$T_{f,solution}$ [° C]
1		1	
2		2	
		3	
mean [° C]		**mean [° C]**	
standard deviation [° C]		**standard deviation [° C]**	

(I.D) Report the freezing-point depression ΔT_f using Eqn. 5-1 and the mean values of $T_{f,solvent}$ and $T_{f,solution}$ reported in (I.C).

$$\Delta T_f = T_{f,solvent} - T_{f,solution} \qquad \text{(Eqn. 5-1)}$$

$\Delta T_f =$ _____ °C

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(II) The measurement of ΔT_f has an uncertainty $\sigma_{\Delta Tf}$ given by

$$\sigma_{\Delta Tf} = \sqrt{\left(\sigma_{Tf,solvent}\right)^2 + \left(\sigma_{Tf,solution}\right)^2}$$

where $\sigma_{Tf,solvent}$ is the standard deviation of the measurement of $T_{f,solvent}$ and $\sigma_{Tf,solution}$ is the standard deviation of the measurement of $T_{f,solution}$ reported in (I.C). Show the calculation of $\sigma_{\Delta Tf}$; include appropriate units in the final answer.

(III.A) Show the calculation of the molar mass $\mathcal{M}_{solute}$ of the unknown solute in units of gram per mole using Eqn. 5-2:

$$\mathcal{M}_{solute} = \frac{K_f m_{solute}}{\rho_{solvent} V_{solvent} \Delta T_f} \tag{Eqn. 5-2}$$

K_f represents the freezing-point depression constant of the solvent cyclohexane (20.0 °C-kg solvent/mol solute), m_{solute} is the mass of unknown solute taken, $\rho_{solvent}$ is the density of cyclohexane (0.799 g/mL), $V_{solvent}$ is the volume of cyclohexane taken, and ΔT_f is the freezing-point depression reported in (I.D). Pay careful attention to units.

Mass of unknown taken = _____ g

Volume of cyclohexane = _____ mL

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(III.B) The measurement of $\mathcal{M}_{solute}$ has an uncertainty $\sigma_\mathcal{M}$ given by

$$\sigma_\mathcal{M} = \frac{\mathcal{M}_{solute}\sigma_{\Delta T_f}}{\Delta T_f} \qquad \text{(Eqn. 5-3)}$$

where $\mathcal{M}_{solute}$ is the molar mass of the unknown reported in (III.A), ΔT_f is the freezing-point depression reported in (I.D), and $\sigma_{\Delta Tf}$ is the standard deviation reported in (II). Show the calculation of $\sigma_\mathcal{M}$. Include appropriate units in the final answer.

Post-lab questions
(1) Assume that the unknown has the formula C_nH_{2n}, that is, the unknown is a compound of carbon ($\mathcal{M}$ = 12.01 g/mol) and hydrogen ($\mathcal{M}$ = 1.01 g/mol) and there are twice as many hydrogens as carbons. What formulas fit your data? Explain your answer.

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(2) Use Eqn. 5-2 to calculate the mass of the antifreeze ethylene glycol ($\mathcal{M}_{solute}$ = 62 g/mol) that must be added to 1.000 L of water (K_f = 1.86 °C-kg solvent/mol solute, $\rho_{solvent}$ = 1.00 g/mL) to lower the freezing point of the solution by 6 °C. Show all calculations and pay attention to units.

(3) When the quantity A is calculated from the measured quantities x, y, z, etc., the uncertainty σ_A in A is given by

$$\sigma_A = \sqrt{\left(\frac{\partial A}{\partial x}\right)^2 \sigma_x^2 + \left(\frac{\partial A}{\partial y}\right)^2 \sigma_y^2 + \left(\frac{\partial A}{\partial z}\right)^2 \sigma_z^2 + \cdots} \qquad \text{(Eqn. 5-4)}$$

where σ_x is the uncertainty in x, σ_y is the uncertainty in y, σ_z is the uncertainty in z, and so on. Show the derivation of Eqn. 5-3 from Eqn. 5.2 and Eqn. 5-4 assuming that the uncertainty in $\mathcal{M}_{solute}$ is due only to uncertainty in ΔT_f.