Freezing Point Depression

Introduction

In this experiment you will determine the molar mass of an unknown solute by measuring the freezing point depression of a solution of this solute in a solvent. The decrease in freezing point, ΔT_f (freezing point depression) for a near ideal solution can be described by the equation:

$$\Delta T_f = K_f \cdot m \qquad \text{Eq 1}$$

where K_f is the freezing point depression constant of the solvent and m is the molal concentration of the solute dissolved in the solvent (moles of solute/kg solvent).

Since the molar mass, $\mathscr{M}$, of a compound has units of g/mole, we can solve for moles and substitute the result into the molal concentration relationship, and then rearrange and solve for the molar mass, as is shown in Eq 2, below:

$$\mathscr{M} = (K_f \cdot g)/(\Delta T_f \cdot \text{kg solvent}) \qquad \text{Eq 2}$$

where $\mathscr{M}$ is the molar mass of the solute and g is the mass of that solute in the solution. If we add a known mass of the unknown compound to a known mass of solvent and determine the change in freezing point of the solution, we can use Eq 2 to determine the molar mass of the unknown compound.

At the freezing point of any substance, an equilibrium exists in which both liquid and solid are present. The temperature at which this equilibrium exists is the freezing point of the substance. Sometimes this temperature is difficult to determine, so the use of cooling curves is required. To construct a cooling-curve a sample is warmed to well above its melting point, then allowed to cool. As the sample cools the temperature of the sample is monitored as a function of time. As the sample begins to solidify the change in temperature will slow, and at equilibrium the temperature will be constant until all of the sample has solidified. A graph is made by plotting the temperature vs. time. An example of a cooling curve is shown below in Figure 1.

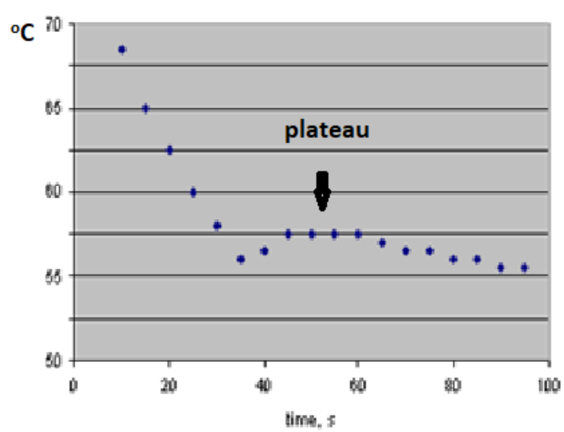
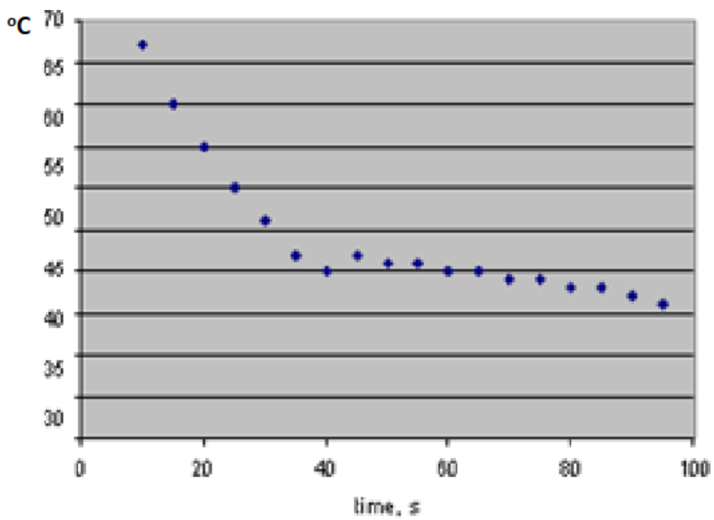


Figure 1: Cooling curve for a pure solvent

In this cooling curve you see a steady decrease in temperature followed by a dip which is followed by a slight rise in the temperature. This dip is not unusual and results from supercooling during the early stages of the freezing process. In this example the dip is followed by a short plateau in the temperature. **This plateau (57.5ºC in the above graph) is at the freezing point of the pure solvent as shown in Figure 1.**

When solute is added to the solvent, the shape of the cooling curve sometimes changes so that we don't see a clear horizontal plateau as the example shown in Figure 1.



In Figure 2 we don't see a clear horizontal plateau. In this case we must draw a trend line through the data points corresponding to the cooling of the liquid and a trend line through the data points corresponding to the freezing of the liquid. **The temperature at the point where those two lines intersect is the freezing point of the solution.**

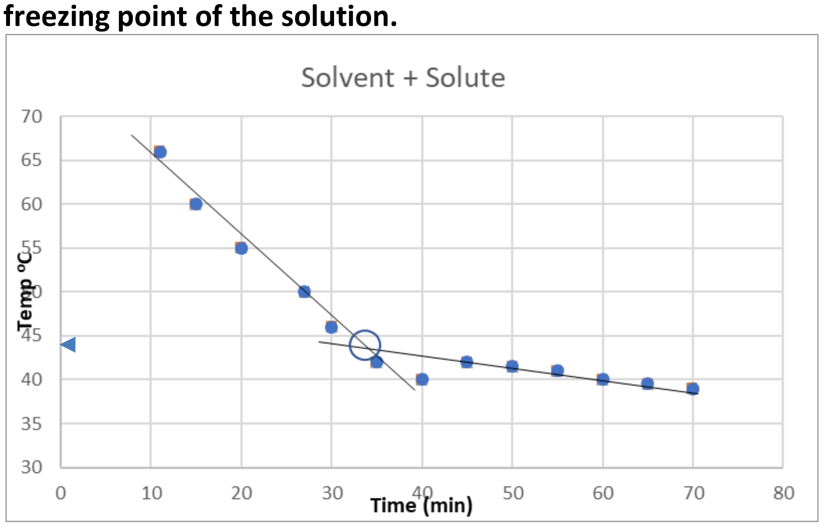


Figure 3: Solution cooling curve showing best fit straight lines through the two portions of the data.

Figure 3 shows an example with the trend lines drawn in and the intersection of the lines. In the example shown in Figure 3 the freezing point would be measured as about 44 °C. If we continue to record and plot the temperature of the solid, the data points may start to deviate from the trend line shown in Figure 3 corresponding to the freezing of the liquid. <u>In this case you would not include those points in the trend line.</u>

In this experiment you will determine the freezing point of pure tertiary butyl alcohol (*t*-butanol) then the freezing point of *t*-butanol with an unknown solute dissolved in it. From these freezing point measurements, you will be able to calculate the molar mass of the unknown solute. The *t*-butanol is a good solvent choice for this experiment. Its transition state from solid to liquid occurs near room temperature, so it has a relatively low melting point, thus a low freezing point. It also has a relatively large K_f, 9.10 °C/m, which is good for estimating the molar mass of a solute because it will allow us to see a greater ΔT_f relative to a solvent with a lower K_f.

EXPERIMENTAL

1. Freezing point of pure *t*-butanol:

At your bench you have a 16 x 150 mm test tube (the fp tube), a 25 x 150 mm tube (a tube to use as an air jacket) and a tube containing t-butyl alcohol. If the t-butyl alcohol is a solid, you will have to warm it in a beaker of warm water from the water bath.

Place a test tube rack on a balance and then tare the balance. Place the 16 x 150 mm test tube in the rack and record the mass. Using a plastic transfer pipet, add t-butyl alcohol to the test tube to a height equal to one third of the tube. Do not get any water into your tube. Record the mass.

Place about 250 mL of hot water obtained from the hot water bath in a 400 mL beaker and place the test tube containing the *t*- butanol you just weighed into the hot water. Insert the stirring loop into the test tube and then insert the thermometer so that the loop of the stirrer surrounds the thermometer. Warm the t-butanol to about 32 °C. Periodically stir the t-butanol with the stirring loop with an up and down motion while warming it.

Figure 4

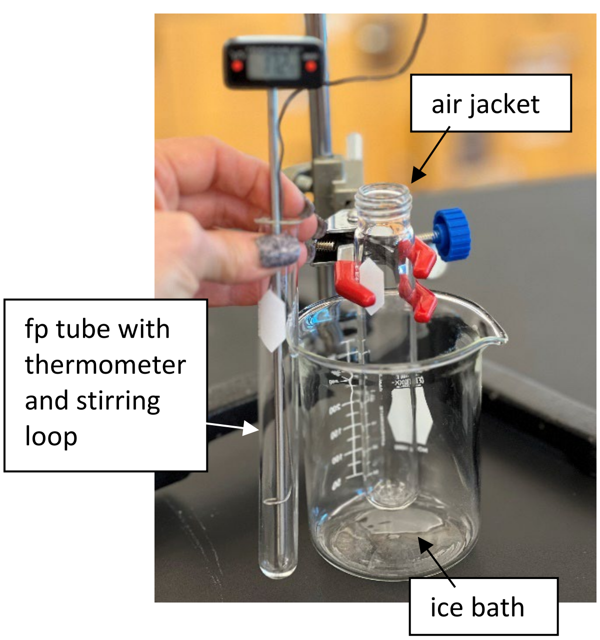


Figure 4 shows the set up for the cooling step. The fp tube with thermometer will be placed into larger tube (air jacket), which is clamped in a beaker containing the ice bath.

Place about 250 mL of ice in a 400-mL beaker and add enough tap water to just cover the ice. Clamp the 25 x 150 mm air-jacket tube to a ring stand (Fig. 2) and lower the tube into the beaker of ice water. Once the temperature of the *t*-butanol has warmed to about 32 °C, slide the fp tube containing the t-butyl alcohol, stirring loop and thermometer into the larger, air-jacket tube in the ice-water bath, making sure that most of the *t*-butanol is below the surface of the ice bath. Add more ice if needed. Immediately begin to take temperature readings and record them in the table every 15 seconds, while continually stirring the t-butanol with the stirring loop in an up and down motion.

Continue to stir and take temperature readings every 15 seconds until the *t*-butanol has solidified. When the t-butanol has solidified so that the stirring loop will no longer move, stop trying to stir, but continue to record the temperature every 15 seconds for one more minute. Do not try to pull the thermometer and stirrer from the frozen t-butanol! Doing so may break the thermometer.

2. Freezing point of t-butanol with unknown:

Place the test tube from Part 1 back in the warm water bath to melt the solid. Remove the thermometer and stirring loop. Place the test tube rack on the balance and tare. Place the test tube with the t-butanol into the rack and record the mass of the test tube and t-butanol on line 2 of your data table. While the test tube is on the balance, use a disposable pipet with graduated markings to add about 0.2 mL of your unknown to the test tube. Record the mass of the test tube, t-butanol and the unknown on line 4 of your data table. Reheat the test tube as before to about 27°C. If you need fresh hot water in which to warm your sample, get it. Check to see if you need more ice for your ice- water bath. As before, once the temperature is about 27 °C, transfer the test tube to the air jacket tube which is in the ice-water bath. Begin stirring and take temperature readings every 15 seconds until the solution has solidified. Stop stirring once the solution has solidified, but continue to record the temperature every 15 seconds for one more minute.

3. Clean-Up:

Place the test tube back in the warm water bath to melt the solid. Remove the thermometer and stirring loop. Pour the t-butanol solutions into the waste beaker under the fume hood. Wash the thermometer, stirring loop and test tube in the sink with soap and water and dry them. Empty all beakers and other glassware you used and return them to your drawer.

Data: *Use correct significant figures throughout.*

1) Mass of test tube: ____________________

2) Mass of test tube and t-butanol: ____________________

3) a. Calculate the mass of t-butanol in the tube: ____________________
Show work:

b. Convert the mass of t-butanol to kilograms: _____________________
Show work:

4) Mass test tube, t-butanol and unknown: ____________________

5) Calculate the mass of the unknown added (g): ______________________
Show work:

<u>Data Table</u>:

pure *t*-butanol		***t*-butanol + unknown solute**	
time (s)	temp (°C)	time (s)	temp (°C)

Graphing, Calculations and Questions:

Using Microsoft Excel, plot temperature vs. time for the pure *t*-butanol and for the solution by making and printing one page with two curves on it. (See the following page for Excel instructions.)

Use the discussion in the background section above as a guide (draw lines by hand) to determine the freezing point, T_f, of *t*-butanol for the unknown solution. Attach the graph to your report.

Using correct significant figures, determine the ΔT_f by subtracting the T_f of the unknown solution from the T_f of pure *t*-butanol.

ΔT_f : ________________________

Show work:

Calculation of Molar Mass:

Calculate the molar mass, $\mathcal{M}$, of your unknown compound by substituting the ΔT_f, the mass of unknown solute in grams (line 5), the mass of *t*-butanol solvent in kilograms (line 3b), and the K_f of t-butanol (9.10 °C/m) into Equation 2.

$\mathcal{M}$: ________________________

Show work:

Directions for Graphing with Excel

1. Open Microsoft Excel using the Task Bar or Start Menu.

2. Start a column with the word Time in the top cell and enter the time in seconds in the cells below that.

3. In a column to the right of the time data, head the column with Temperature and add the values that correspond to the temperatures for the given time.

4. Highlight the 2 columns (and titles) of data. Open ***Insert*** (next to Home). Under Charts move until you see ***Insert Scatter Chart*** and click on it and choose the top left option.

5. Change the title of the graph by typing in the title area, using a reasonable title for your graph.

6. If you click on the graph you should see a plus sign on the top right. Click on the plus sign and check ***Axis Titles*** and ***trendline***. Type in axis titles and units for both.

7. Once your instructor approves your graph, select the graph and then print two copies. Check with your instructor to see if you also need to print the data along with your graph.

8. After you graph is printed, you will need to draw by-hand the two trend lines to determine where the temperature where they intersect. See Figure 3 for an example.

<u>Post-Lab</u>:

1. Once you have your molar mass calculated, your instructor will provide the correct molar mass for your unknown. Calculate the percent error for your value.

$$\text{percent error} = \frac{|\text{measured - reference}|}{\text{reference}} \times 100$$

2. List three possible sources of error in your data.

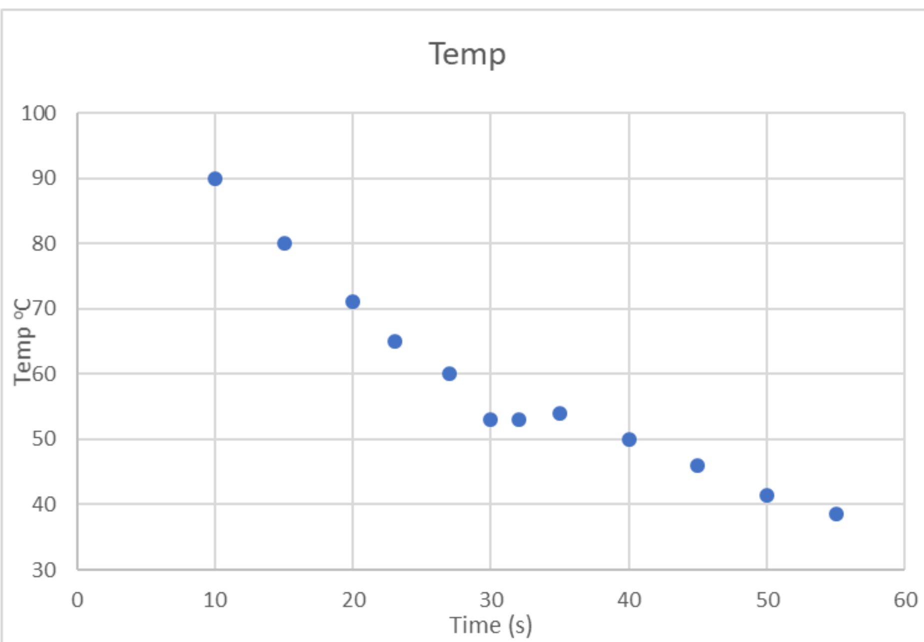
2. Write a brief summary/conclusion for the work you completed in this lab.

Pre-lab Assignment

1. Write the purpose of today's procedure. What data will you obtain and what will you calculate from that data?

2. Briefly describe the procedure and explain what you will graph.

3. Using the following graph, draw lines to determine the freezing point for this solution. See Figure 3 for an example. Record the value you determined here: _______________



Reference: Microsoft Word - CHEM110 Lab Manual Fall 2010.doc (ulm.edu)