

Experiment 1: Colligative Properties

Determination of the Molar Mass of a Compound by Freezing Point Depression.

Objective: The objective of this experiment is to determine the molar mass of an unknown solute by measuring the freezing point depression of a solution of this solute in a solvent as compared to the freezing point of the pure solvent.

Background: **Colligative properties** are properties of a solvent, such as freezing point depression and boiling point elevation, which depend on the concentration of solute particles dissolved in the solvent. The decrease in freezing point, ΔT_f (freezing point depression) for a near ideal solution can be described by the equation:

$$\Delta T_f = k_f \cdot m \quad \text{Eq 1}$$

where k_f is the **molal freezing point depression constant** of the solvent with units $^{\circ}\text{C} \cdot \text{kg}$ solvent/mole solute. m is the molal concentration of the solute dissolved in the solvent expressed as moles of solute/kg solvent.

Since the molar mass \mathcal{M} (traditionally and often, but erroneously called the molecular weight) of a compound has units g/mole, we can solve for moles and substitute the result into the molal concentration relationship, and then into Eq 1 as is shown below.

$$\mathcal{M} = \text{g/ mole} \quad \text{Eq 2}$$

Rearranging Eq 2 gives

$$\text{moles} = \text{g}/\mathcal{M} \quad \text{Eq 3}$$

Now substituting Eq 3 into the unit definition of molality yields

$$m = \text{g}/(\mathcal{M} \cdot \text{kg solvent}) \quad \text{Eq 4}$$

And substituting Eq 4 into Eq 1 gives

$$\Delta T_f = (k_f \cdot \text{g})/(\mathcal{M} \cdot \text{kg solvent}) \quad \text{Eq 5}$$

We can rearrange Eq 5 and solve for the molar mass, mol wt, as is shown in Eq 6, below.

$$\mathcal{M} = (k_f \cdot \text{g})/(\Delta T_f \cdot \text{kg solvent}) \quad \text{Eq 6}$$

Therefore, if we know the mass of unknown compound added to a known mass of solvent and determine the change in freezing point of the solution, relative to pure solvent, we can use Eq 6 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 one would warm their sample, pure solvent or solution, to well above its melting point, then allow it 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 the equilibrium shown by Eq 7 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.

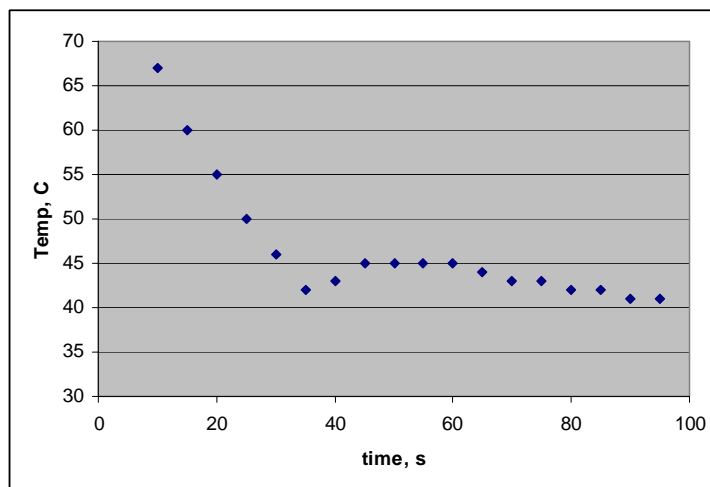


Figure 1: Cooling curve for a pure solvent.

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 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.

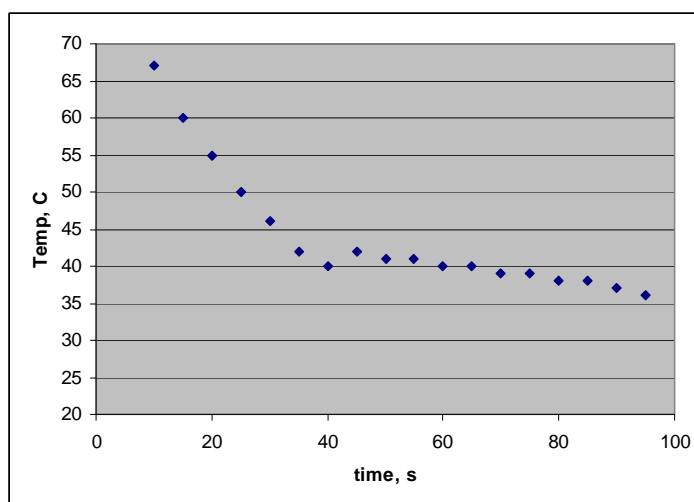


Figure 2: Cooling curve for a solution.

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.

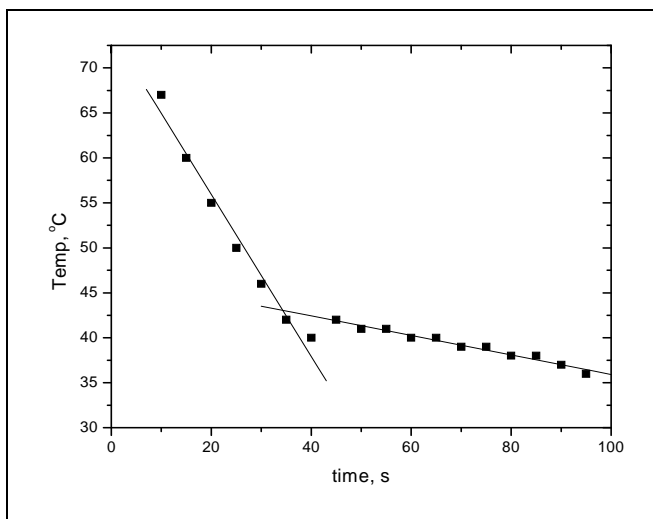


Figure 3: Solution cooling curve showing best fit straight lines through the two portions of the curve discussed in the text.

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 43 °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. In this case you would not include those points in the trend line.

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·kg solvent/mol solute, 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 .

Procedure: For this experiment you will need a 150 ml beaker, two 400 ml beakers, a large test tube (25 x 150 mm), a tripod stand with wire mesh, a thermometer, a stirring loop and a Bunsen burner.

Freezing point of pure *t*-butanol:

Place a 150 ml beaker on a top loader balance and tare it. Place a clean, dry 25 x 150 mm test tube in the beaker and record the mass in the data table, line 1. Fill the test tube about half full with *t*-butanol, reweigh and record this mass in the data table, line 2. Place the beaker and test tube aside for now.

Place about 250 ml of hot tap water in one 400 ml beaker and place the test tube containing the *t*-butanol in the hot water; we want to warm the *t*-butanol to about 40 °C. You may use a tripod and Bunsen burner to warm the *t*-butanol in the water bath if needed. **(Do not heat the test tube with a**

direct flame!) Insert the stirring loop into the test tube and then insert the thermometer so that the loop of the stirrer surrounds the thermometer. Periodically stir the *t*-butanol with the stirring loop by an up and down motion while warming it.

Place about 250-300 ml of ice in the other 400 ml beaker and enough cold tap water to just cover the ice. Once the temperature of the *t*-butanol has warmed to about 40 °C, transfer the test tube to the ice-water bath making sure that most of the *t*-butanol is below the surface of the ice-water 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.

Freezing point of solutions:

Place the test tube in the 150 ml beaker, the test tube may now be top heavy, so use caution, or use a 250 ml beaker. Place the beaker with test tube on a top loader balance and tare the balance. With a disposable pipette add about 0.5 g of our unknown to the test tube and record the mass, line 4. Reheat the test tube as before to about 40 °C, this is sample solution 1. If you need fresh hot tap water in which to warm your sample, get it. Try to make sure all your unknown is dissolved in the *t*-butanol. Use the stirring loop to aid the dissolution of the solute, if needed. If you need more ice for your ice-water bath get it. As before, once the temperature is about 40 °C, transfer the test tube to the ice-water bath. Begin stirring and take temperature readings every 15 seconds until the solution has solidified. When the solution has solidified so that you can no longer stir it, stop trying to stir, but continue to record the temperature every 15 seconds for one more minute.

Return the test tube to the 150 ml beaker and place the beaker with test tube on a top loader balance and tare the balance. With a disposable pipette add about another 0.5 g of the unknown to the test tube and record the mass, line 5 (this is sample solution 2). Repeat the melting and temperature recording steps outlined in the previous paragraph.

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, dry and return them to the side shelf. Empty all beakers and other glassware you used and return them to your drawer.

Data:

- 1) Mass of test tube: _____
- 2) Mass of test tube and *t*-butanol: _____
- 3) a) Mass of *t*-butanol (line 2 – line 1): _____
 b) Mass of *t*-butanol in kgs: _____
- 4) Mass of first sample of unknown: _____
- 5) Mass of second sample of unknown: _____
- 6) Total mass of unknown in second solution freezing point
determination (line 4 + line 5): _____

Data Table:

<i>t</i> -butanol, pure solvent		<i>t</i> -butanol plus first sample portion, solution 1		<i>t</i> -butanol plus second sample portion, solution 2	
time	temperature	time	temperature	time	temperature

Data Handling, Calculations and Questions:

Use graph paper and plot temperature vs. time for the pure *t*-butanol and for each solution analyzed; make 3 different graphs. Use the discussion in the background section above as a guide and determine the freezing point, T_f , of *t*-butanol and of each solution. Clearly mark on each graph all your data points and the best fit lines you used to determine each freezing point. Determine the ΔT_f of solution 1 by subtracting the T_f of solution 1 from the T_f of pure *t*-butanol. Determine the ΔT_f of solution 2 by subtracting the T_f of solution 2 from the T_f of pure *t*-butanol.

Use the ΔT_f for solution 1 along with the mass of unknown in solution 1, line 4 of the data table, the mass of solvent, *t*-butanol, line 3b of the data table, and the k_f of *t*-butanol, $9.10\text{ }^\circ\text{C}\cdot\text{kg solvent/mol solute}$, in Eq 6 to determine the molar mass, \mathcal{M} , of your unknown compound.

Repeat the calculation above for solution 2 remembering to use the total mass of solute, line 6 of the data table, and the ΔT_f for solution 2.

Report:

In your lab report briefly discuss the theory behind why the freezing point of a solution is typically lower than the freezing point of pure solvent.

Reproduce the data from the Data page and the Data Table, pages 5 and 6, and turn in with your report, along with all three graphs.

Make a data and calculations page to report the T_f of pure *t*-butanol and for each solution. Show all calculations and report the molar mass of unknown as determined in each of the two solutions.

Average the two molar masses you determined and calculate the percent difference for each determination vs. the average. This should give you about a 6 or 7 page lab report, not all pages will be full of text.

Reference:

Some information at the following lab experiment was used for this experiment.

<http://infohost.nmt.edu/~jaltig/FreezingPtDep.pdf>