Introduction

Some physical properties of solutions are different from those of the pure solvent. The size of the change in these physical properties is proportional to the number of solute particles contained in the solution. These physical properties are collectively called **colligative properties**. They include freezing point, boiling point, vapor pressure, and osmotic pressure.

The freezing point of a solution of low concentration is generally lower than the freezing point of the pure solvent. The change in freezing point, or the freezing point depression, ΔT_f, is defined as follows:

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

Since freezing point is a colligative property, the freezing point depression is proportional to the number of solute particles contained in solution. For nonelectrolytes, the number of solute particles contained in solution is proportional to the molality of solute. Therefore, the freezing point depression will be proportional to the molality of solute:

$$\Delta T_f = K_f m_{solute} \qquad (2)$$

The proportionality constant, K_f, is called the **molal freezing-point-depression constant**. Its value depends on the identity of the solvent. For water, the value of K_f is 1.86°C/m. For each mole of solute added per kilogram of pure water, the freezing point is lowered by 1.86°C.

The relationship between freezing point depression and molality can be used in several ways. For a solution of known molality, the freezing point depression may be measured experimentally to determine the value of K_f :

$$K_f = \frac{\Delta T_f}{m_{solute}} \qquad (3)$$

Freezing point depression may also be used to determine the molar mass of a solute. In order to do this, you need to know the masses of solute and solvent contained in the solution, the freezing point depression and the value of K_f. From this information, the molality of the solute may be calculated by solving the freezing point depression equation above for molality of solute:

$$m_{solute} = \frac{\Delta T_f}{K_f} \qquad (4)$$

Next, the number of moles of solute may calculated by multiplying the molality of the solute by the mass of solvent in kilograms:

$$\text{moles of solute} = m_{solute} \times (\text{mass of solvent in kg}) \qquad (5)$$

Please note that this equation has the mass of solvent only. The molar mass of the solute may then be calculated by dividing the mass of solute by the number of moles of solute:

$$\text{molar mass of solute} = \frac{\text{mass of solute in g}}{\text{moles of solute}} \qquad (6)$$

The freezing point of both the solvent and the solution will be determined by heating the substance to a temperature that is above the freezing point. Then, the substance will be allowed to cool. While it cools, the temperature of the substance will be measured every 30 seconds. A plot of temperature (vertical axis) versus time (horizontal axis) will be made from the data to give what is called a **cooling curve**. This curve is the opposite of a **heating curve** discussed in your textbook.

For a pure substance, the temperature does not change while the substance is undergoing a phase change. The heating curve in the textbook is flat during the phase changes (line BC and line DE). The same is true for the cooling curve of a pure substance like the solvent. While the solvent is freezing, the temperature should not change. For a solution, the temperature will change slightly during freezing but at a much slower rate than the liquid solution. Shown in Table 1 is temperature versus time data for the cooling of a solvent and a solution made from the solvent.

If you look at the temperature data, the temperature at the beginning drops a substantial amount between readings, more than 0.5°C. Later, the temperature drops much less between readings, less than 0.5°C. It is during the time that the temperature is dropping to a much lesser extent that the substance is freezing.

You will determine the freezing point by making a plot of temperature versus time and fitting two straight lines to the data. This is done by splitting the temperature data into two columns in Excel. The first column will be the temperature readings in which the difference between successive readings is greater than 0.5°C. The second column will be the temperature readings in which the difference between successive readings is less than 0.5°C. For the temperature data for the solvent, the spreadsheet would look like that shown in Table 2.

Table 1 Temperature vs. Time Data for the Cooling of a Solvent and a Solution

Time (seconds)	Temperature (°C) of a solvent	Temperature (°C) of a solution	Time (seconds)	Temperature (°C) of a solvent	Temperature (°C) of a solution
0	87.5	85.5	450	62.0	61.6
30	85.0	83.0	480	60.8	60.5
60	82.0	80.1	510	60.0	59.8
90	79.6	78.8	540	59.0	59.0
120	77.8	75.8	570	58.0	58.0
150	75.3	74.2	600	57.8	57.1
180	73.8	72.5	630	57.5	56.4
210	72.2	71.0	660	57.5	55.8
240	70.5	69.8	690	57.5	55.2
270	69.1	68.1	720	57.4	55.0
300	67.8	67.0	750	57.3	55.0
330	66.5	66.0	780	57.3	55.0
360	65.0	64.	810	57.2	55.0
390	64.0	63.6	840	57.2	55.0
420	63.0	62.6	870	57.2	55.0
			900	57.2	55.0

Table 2 Spreadsheet Example for Solvent Temperature vs. Time Data

Time	Temperature	Temperature
0	87.5	
30	85	
60	82	
90	79.6	
120	77.8	
150	75.3	
180	73.8	
210	72.2	
240	70.5	
270	69.1	
300	67.8	
330	66.5	
360	65	
390	64	
420	63	
450	62	
480	60.8	
510	60	
540	59	
570	58	
600		57.8
630		57.5
660		57.5
690		57.4
720		57.3
750		57.3
780		57.2
810		57.2
840		57.2
870		57.2
900		57.2

Construct a cooling curve plot by selecting all three columns (time plus the two temperatures) and proceeding to graph the data as described on pages xxxii - xxxiv. Choose "XY plot" for the type of plot and choose the sub-option with just the data points on it (the first sub-option on the left). When the plot is made, it should look like the following figure without the straight lines:

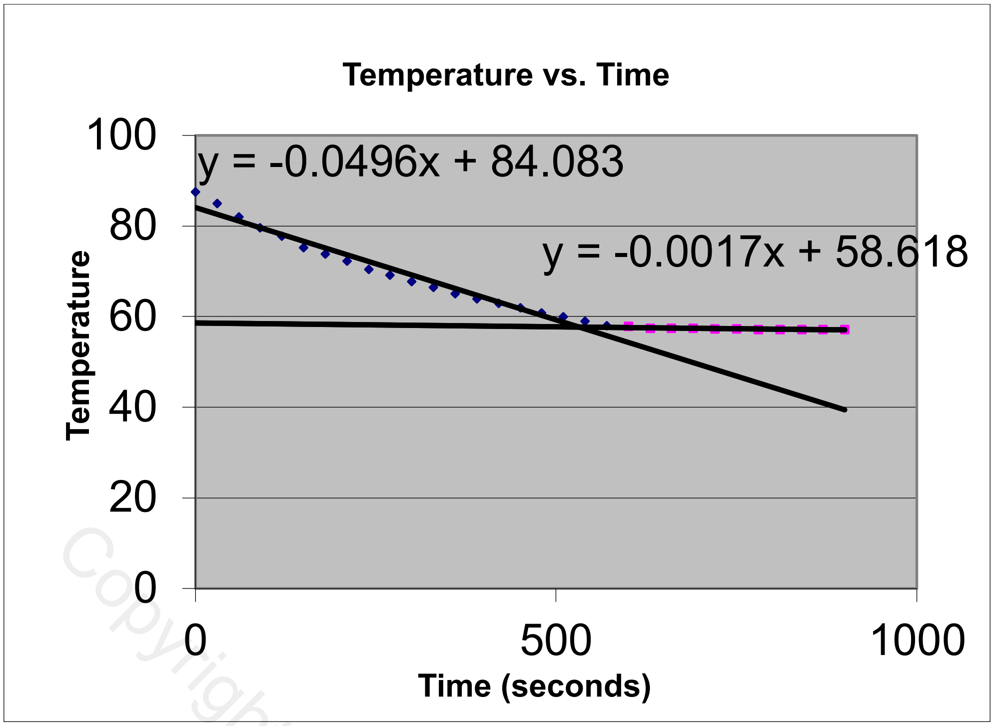

Figure 1 Typical Cooling Curve constructed from data in Table 2

Add trendlines to each set of data using the "Add trendline" option under the Chart menu. When you add the trendline, you will see two "Temperature's" under the "Based on series" box. Click on the first "Temperature". This is the set of data represented by the diamond shapes in Table 1. Go to the next page and click on "display equation" and click "OK". Then, add the second line by using the "Add trendline" option again. This time, choose the second "Temperature" under the "Based on series" box. Don't forget to click on "display equation." You should come up with a plot that looks like the plot in Figure 1. The freezing point will be determined by finding the temperature at which the two lines intersect. This can be done using algebra. Using the equations in Figure 1, the time at which the two equations meet can be determined by setting the two equations equal to each other and solving for *"x"*:

$$-0.0496x + 84.1 = -.0017x + 58.6$$
$$25.5 = 0.0479x$$
$$x = \frac{25.5}{0.0479} = 532 \text{ s}$$

Then, the temperature at which the two lines intersect can be determined by placing x = 532 s into either equation and calculating the value of y:

$$y = -0.0496(532) + 84.1$$
$$= 57.7^{\circ}\text{C}$$

The freezing point of the solvent is determined to be 57.7°C.

Equipment

The equipment needed for this experiment include a thermometer, a 400-mL beaker, a 250-mL beaker, and a 30-mL beaker from your desk. There should be large test tubes, stopwatches, copper wire stirring loops, and hot plates available in the lab for you to use.

Procedure

1. Fill your 400-mL beaker about 3/4 full with DI water. Place several boiling stones in the water and place the beaker with the water on a hot plate.
2. Start heating the water to boiling – about mid-scale.
3. While the water bath is heating, stand up a test tube in your 30 mL beaker and weigh both to the nearest 0.001 g. Record the weight on your data sheet.
4. Add about 9 grams of stearic acid to the test tube and weigh the test tube, stearic acid and beaker to the nearest 0.001 g. Record the weight on your data sheet.
5. Determine the mass of stearic acid using difference methods.
6. Place the test tube with the stearic acid in your water bath and heat it until it is a liquid at 85°C.
7. While you are waiting for the stearic acid to melt, crumple up 2 sheets of paper towels and place them in your 250-mL beaker for insulation while your molten stearic acid cools. There should be enough room in the beaker with paper towels for the test tube to fit snugly into.
8. When the temperature of the molten stearic acid reaches 85°C, take the test tube out of the water bath and place it in the 250-mL beaker with the paper towels. Take a temperature reading to the nearest 0.1°C while you start your stopwatch and record your reading as time 0 in the data table.
9. The molten stearic acid should be stirred gently with a wire loop while cooling to prevent supercooling. Continue to take a temperature reading to the nearest 0.1°C for about 15 minutes while you fill in the data table.
10. During the last 5 minutes, the temperature difference between readings should be less than 0.5°C and the substance should start freezing out (the solution will get cloudy). If the substance does not start freezing out in the first 15 minutes, you may need to cool for a longer period of time.
11. Obtain an unknown compound and record its number on your data sheet.
12. Weigh out approximately 1 gram to the nearest 0.01 g and record the mass on your data sheet.
13. Add the unknown compound to the test tube containing the stearic acid.
14. Place the mixture in the hot water bath and heat it until its temperature reaches 85°C.
15. Stir the molten mixture and repeat the above procedure used for pure stearic acid for the solution of the unknown and stearic acid.

Make 2 plots of cooling curves using Excel. Each cooling curve is a plot of temperature (vertical axis) versus time (horizontal axis). Follow the procedure gone over in the introduction. The first cooling curve will give you the freezing point of pure stearic acid. The second cooling curve will give the freezing point of the solution of the unknown plus stearic acid.

Determine the freezing point depression from the difference between the freezing point of pure stearic acid and the solution freezing point.

$$\Delta T_f = T_{f,solvent} - T_{f,solution} \tag{7}$$

Divide the freezing point depression by the K_f value of stearic acid, which is 4.5°C kg/mol, to obtain the molality of the solute in the solution.

$$m_{solute} = \frac{\Delta T_f}{4.5^{\circ}\mathrm{C{\cdot}kg/mol}} \tag{8}$$

Multiply the calculated molality by the number of kilograms of stearic acid to determine the moles of solute.

$$\text{moles of solute} = m_{solute} \times (\text{mass in kg of stearic acid}) \tag{9}$$

Divide the mass of solute in grams by the number of moles of solute to calculate the molar mass of the solute.

$$\text{molar mass of solute} = \frac{\text{mass of solute in g}}{\text{moles of solute}} \tag{10}$$

Name: ______________________________________ Section: _________

Partner: ____ Date: ___/___/___

Report Sheet: Molar Mass by Freezing Point Depression

Weight of test tube, beaker, and stearic acid ________________________

Weight of test tube and beaker ________________________

Weight of stearic acid ________________________

Unknown number ________________________

Weight of unknown used ________________________

The temperature data for the cooling curves must be recorded and plotted before proceeding with the rest of this page. (Data for cooling curves plotted on pages 8 and 9)

Freezing point of stearic acid ________________________

Freezing point of solution ________________________

Freezing point depression ________________________

Molality of unknown in solution ________________________

Calculation:

Moles of unknown in solution ________________________

Calculation:

Molar mass of unknown ________________________

Calculation:

Time and Temperature Data: 1st Cooling Curve

Time (seconds)	Temperature (°C)	Time (seconds)	Temperature (°C)	Time (seconds)	Temperature (°C)
0		330		660	
30		360		690	
60		390		720	
90		420		750	
120		450		780	
150		480		810	
180		510		840	
210		540		870	
240		570		900	
270		600			
300		630			

Attach the plot for the 1st cooling curve to the data sheet

Time at which 2 lines intersect ______________________

Show calculation:

Freezing point from 1st cooling curve ______________________

Show calculation:

Time and Temperature Data: 2nd Cooling Curve

Time (seconds)	Temperature (°C)	Time (seconds)	Temperature (°C)	Time (seconds)	Temperature (°C)
0		330		660	
30		360		690	
60		390		720	
90		420		750	
120		450		780	
150		480		810	
180		510		840	
210		540		870	
240		570		900	
270		600			
300		630			

Attach the plot for the 2nd cooling curve to the data sheet

Time at which 2 lines intersect ___________________________

Show calculation:

Freezing point from 2nd cooling curve ___________________________

Show calculation:

Name: ______________________________ Date: ___/___/___ Section: ________

Pre-Lab Exercise

The following cooling curve data was collected for a stearic acid sample:

Time (sec)	Temp (°C)
0	85.0
30	81.5
60	79.0
90	76.0
120	74.0
150	72.5
180	72.4
210	72.4
240	72.4
270	72.4
300	72.4

Following instructions in the Lab Manual, construct an excel plot showing the temperature change before and after the freezing point is reached. This plot should have axes properly labeled and show trend lines with their equations for the two portions of the graph. Print this graph and attach it to this sheet.

The actual freezing point is the intersection of the two trendlines. Show your calculations of the freezing point. Your calculated value was ______________.