Chemistry 101 15-MOLECULAR WEIGHT BY FREEZING POINT DEPRESSION

Investigations into the nature of solutions have shown that certain properties are different for the solution compared to the pure solvent. Foremost among these is a lower vapor pressure for the solution compared to the pure solvent. As a result of this effect, the freezing point of a solution is lower than the pure solvent, its boiling point is higher, and the solution exhibits osmotic pressure. These properties are called the **colligative** properties. These depend only on the total concentration of all dissolved species in the solution and not on their molecular or ionic nature. Thus, if 1.00 mole of glucose ($C_6H_{12}O_6$) is dissolved in 1000 g of water, it will exhibit the same colligative properties as 0.50 mole of NaCl since the NaCl dissociates into 0.50 mole of Na^+ and 0.50 mole of Cl^- for a total concentration of species equal to 1.00 mole in 1000 g of water.

In this experiment, the freezing point depression of an aqueous solution of a solute will be compared to the freezing point of pure water. The depression of the freezing point can be used to calculate the molecular weight of the solute. If ΔT_f represents the depression of the freezing point, then:

$$\Delta \mathbf{T_f = T_f^\circ - T_f}$$

where T_f° is the freezing point of pure water and T_f is the freezing point of the solution. The value of T_f is related to the concentration by the equation:

$$\Delta \mathbf{T_f = K_f m}$$

where m is the molality of the solution, equal to (moles solute)/(kg solvent) and K_f is the molal freezing point depression constant which, for water, is 1.86°C/molal. Other solvents can also be used and each will have its own value of K_f. Tables of K_f values can be found in most general chemistry textbooks or chemistry handbooks. Regardless of the solvent, however, the equation $\Delta T_f = K_f m$ applies well only to dilute solutions.

The molecular weight of a solute can be calculated from the freezing point and molality data. This can be seen if the equation is rearranged, making the indicated substitutions:

$$\Delta \mathbf{T_f = K_f m \text{ where } m = (\text{moles solute})/(\text{kg solvent})}$$

since (moles solute) equals (g solute)/(MW solute), then:

$$\Delta T_f = K_f \text{ x } \frac{\frac{\text{g solute}}{\text{MW solute}}}{\text{kg solvent}} \quad \text{so,} \quad \text{MW solute} = K_f \text{ x } \frac{\text{g solute}}{\Delta T_f \text{ x kg solvent}}$$

Thus, by first determining the freezing point of pure water, then by carefully weighing out both a sample of solute and a sample of solvent water and determining the freezing point of the solution, the molecular weight of the solute can be calculated.

To determine the freezing point depression, pure water will be placed in a test tube and immersed in an ice-salt bath. The temperature of the solution will be followed as a function of time and then graphed. A typical graph is shown in Figure 10:

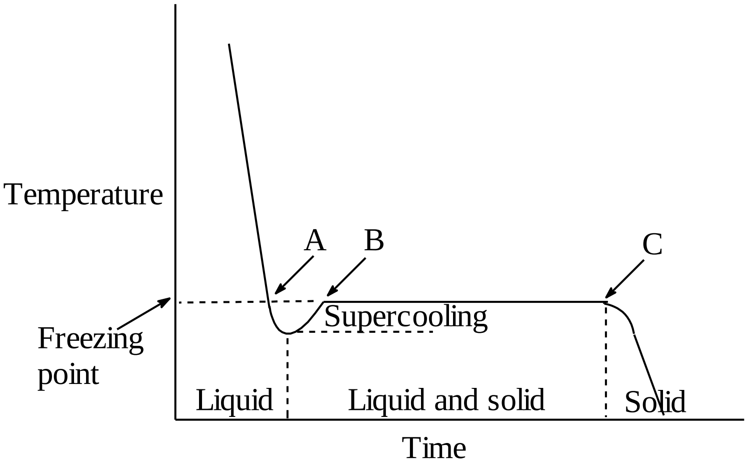

Figure 10: The Cooling Curve for a Pure Liquid

The temperature represented by the level portion of the graph (slope=0) is the freezing point of pure water. At this temperature, the water is freezing (both liquid and solid are present) and the temperature will not begin to decrease again until the water is completely frozen (point C). It is often observed that the temperature initially drops below the usual freezing point (point A) before freezing actually begins and then rises back to the freezing point (point B). This is called **supercooling.**

A plot can also be made for the solution, as shown in Figure 11:

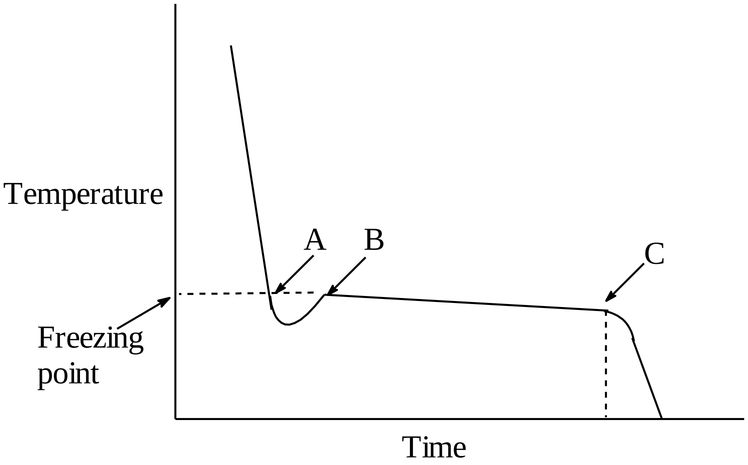

Figure 11: The Cooling Curve for a Solution

For the solution, the graph may not level off completely while the solution is freezing and may have a slope less than zero. If this happens, the T_f of the solution can be determined by extrapolation of the data, as shown in the figure above. If the temperature does level off, then the freezing point is determined as in the first graph. ΔT_f can then be calculated and the molecular weight of the solute determined.

PROCEDURE

Wear your **safety glasses** while doing this experiment.

Obtain from the stockroom a freezing point depressing apparatus, which consists of an inner test tube and outer plastic jacket (preferably 18x200 mm test tubes), a wire stirrer, the Venier LabQuest, temperature probe (also known as thermocouple), and a 400 mL beaker. Record the number inscribed on the LabQuest equipment so that you can use the same equipment during the second period. Clean the test tube and then add approximately 20 mL of deionized water. Insert the stopper which holds the thermometer and wire stirrer. The bulb of the thermometer must be completely immersed in the water, but not touching the sides or bottom of the test tube.

Prepare an ice-salt bath in the 400 mL beaker by placing a layer of crushed ice about 4 cm deep in the beaker, sprinkling a thin layer of rock salt over the ice, and then continuing the alternation of layers of crushed ice and salt until the beaker is full. Then stir the ice and salt until they are well mixed.

Figure 1, below, shows the apparatus set-up.

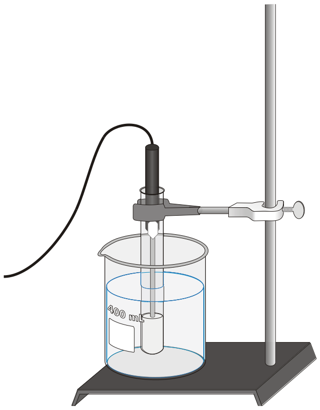

Figure 1: Freezing Point Depression Apparatus

Immerse the test tube into the ice-salt bath. Connect the Temperature Probe to LabQuest (top) and choose **New** from the **File menu**. You may either use it as a thermocouple at this point by simply recording in your lab notebook the numbers of the front screen. Or if you would like to retain the graph and data points follow the directions given at the end of the procedure. Take temperature readings once the temperature has dropped to about 3°C. Begin stirring the water and continue to stir constantly. Take temperature readings every 30 seconds and read the temperature to the nearest 0.01°C. Record the time-temperature data in your lab notebook and continue taking readings through any supercooling that may occur until you have four or five essentially constant readings after the supercooling (point B on the sample graph). At this point, remove the test tube set-up from the bath and allow the ice to melt.

DO NOT REMOVE THE THERMOCOUPLE FROM THE TEST TUBE WHILE IT IS STILL FROZEN IN ICE. Any attempt to remove it while it is still frozen in ice will probably break it.

Repeat the determination with a fresh sample of deionized water.

Determination of the Freezing Point of a Solution

Use the same set-up as in the first part of the experiment.

Obtain an unknown from the instructor, who will tell you the approximate sample weight necessary for the determination. This will eliminate the need for any trial runs.

Dry the test tube thoroughly, place it in a beaker or flask for support and then place them on the analytical balance. Add approximately 20 mL of deionized water and determine the weight of the water, then add the approximate amount of unknown and determine its weight. Insert the stopper containing the thermocouple and stirrer and **thoroughly stir** the mixture with the wire stirrer until the solute has **completely dissolved**. Place the test tube in the ice-salt bath and begin taking readings as before, beginning at about 3°C. Be sure to stir the solution constantly while the temperature readings are being taken. Continue to record the data as before, taking about five readings past point B of the graph.

Remove the test tube assembly from the bath, taking all precautions as before to avoid breaking the thermocouple. Clean and dry the test tube and repeat the determination a second time.

After completing the experiment, graph the data, either in your lab notebook or print the graph saved on LabQuest, as indicated by your instructor. You may place more than one graph on a sheet of paper, if you wish. However, the temperature axis must be such that the entire range of data fills as best as possible the entire axis. Once all of the freezing points have been determined, use the equation in the introduction to calculate the molecular weight of the unknown.

Using the Venier LabQuest to collect your data:

1. Connect the Temperature Probe to LabQuest and choose **New** from the **File menu**.
2. On the **Meter** screen, tap **Rate**. Change the **data-collection rate** to 1 sample/second and the **data-collection length** to 3000 seconds.
3. Once you ready to start data collection: Press the bottom green left-hand “start” button. Press the same button, now red, to stop.
4. The freezing temperature can be determined by finding the mean temperature in the portion of the graph with nearly constant temperature.
    a. Select the data point at the beginning of the flat portion of the graph and drag across the flat portion to select the region.
    b. Choose **Statistics** from the **Analyze** menu.
    c. Record the mean (average) temperature as the freezing temperature.
    d. Store the data from the first run by tapping the **File Cabinet icon**.

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Section______________ Name______________________

Report Sheet

Unknown Number___________ LabQuest Number____________

	Trial #1	Trial #2
Mass of water, g	______	______
Mass of water, kg	______	______
Mass of unknown, g	______	______
Freezing point of water, °C	______	______
Mean freezing point of water, °C	______	
Freezing point of sol'n of unknown, °C	______	______
Freezing point depression, ΔT_f, °C	______	______
Molality of the solution of unknown	______	______
Molecular weight of unknown	______	______
Mean molecular weight of unknown	______	

Show your calculations below:

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Questions

1. Calculate the freezing point of a solution of 1.25 g of aniline (C_6H_7N, a nonionizing solute) dissolved in 26.3 g of benzene. (See your text for solvent data.)

2. When 0.72 g of acetic acid is dissolved in 25.0 g of benzene, the freezing point of the solution is 4.25°C.

    a. Calculate the apparent molecular weight of acetic acid in benzene.
    b. Your answer to part "a" should be different from normal molecular weight of acetic acid. Explain the cause of this difference.

3. Give three sources of error in this experiment that will cause the calculated molecular weight to be too low.

Chemistry 101 **15-MOLECULAR WEIGHT BY FREEZING POINT DEPRESSION**

Section_____________ Name_____________________

Pre-Laboratory Assignment

1. When 0.593 g of an unknown solute is dissolved in 14.9 g of water, the freezing point is depressed by 1.74°C. Calculate the molecular weight of the unknown solute, assuming that it is a nonelectrolyte.

2. Calculate the freezing point of 0.10 m solutions of $(NH_4)_2CO_3$ and $HClO_4$. Both are completely ionized in water.

3. When a solution freezes, the solid that forms is essentially pure, frozen solvent, without any solute contaminating it. Given this information, why does the freezing point of a solution continue to decrease with time, i.e., the graph has a slope less than zero, rather than stays constant, as in the case of the pure solvent?