Determination of Molar Mass by Freezing Point Depression

INTRODUCTION: The vapor pressure of a pure liquid at a given temperature is a characteristic property of that liquid. However, when a nonvolatile solute is dissolved in the liquid, the vapor pressure of the liquid is reduced. This lowering of the vapor pressure causes a change in the melting point, boiling point, and osmotic pressure of the liquid. The magnitude of the change in these properties depends upon the number of solute particles dissolved in a given amount of the solvent, but not upon the nature of the particles (their identity). Such properties are called **colligative properties**. The addition of ethylene glycol to the water in a car radiator in order to raise its boiling point or the use of salt to lower the melting point of ice on a sidewalk are some everyday applications of colligative properties.

In this experiment we will investigate the phenomenon of freezing-point depression and determine the molar mass of an unknown solute. The relationship between the lowering of the freezing point and the concentration of a solution is given by the following:

$$\Delta T_f = T_f(\text{pure solvent}) - T_f(\text{solution}) = K_f \cdot m \qquad (1)$$

where T_f is the freezing temperature, K_f is the molal freezing-point depression constant (a property of a given solvent), and m is the **molality** of solute in the solution. Molality of a solute is defined as follows:

$$m = \text{moles of solute / kg of solvent} \qquad (2)$$

One application of freezing-point depression is in the determination of the molar mass of an unknown solute. A weighed amount of the solute is dissolved in a known mass of solvent. The freezing point of the solvent (the temperature at which solid and liquid phases are in equilibrium) is determined by cooling the solution and plotting a graph of temperature as a function of time. A horizontal portion of the graph indicates that a pure liquid will freeze at a constant temperature. However, a solution will freeze over a range of temperatures and will not exhibit the constant freezing point of the pure liquid; instead of exhibiting a horizontal portion, the plot will show a change of slope when solid solvent begins to form. The concentration of dissolved solute then steadily increases as the solvent freezes, causing the freezing point to continually decrease. (The solid forming is pure solvent.) The temperature at which freezing begins is determined by the intersection of the two extrapolated straight lines. In practice, it is necessary to first determine the freezing point of the solvent alone, since the solvent may not be pure. This step also makes prior calibration of the thermometer unnecessary. With the change in freezing point and the value of K_f, it is then possible to calculate the approximate molar mass of the solute.

The phenomenon of **supercooling** occurs when a liquid cools below its freezing point without crystallizing. A supercooled liquid is in an unstable condition, and any disturbance such as vibration will cause crystallization to begin, with a consequent rise in temperature to the actual freezing point. The dip in the graph due to supercooling should be ignored and the two straight portions extrapolated to their intersection to find the freezing point.

PRE-LAB EXERCISE:

1. A solution containing 15.00 g of glucose in 100.0 g of water was found to freeze at 1.53°C. Use these data to determine the molar mass of glucose.

2. What is the expected freezing temperature of a solution of 2.00 g of CCl_4 in 100 g of benzene?

USEFUL INFORMATION:

Table I. Freezing temperatures and constants for some common solvents.

Solvent	Formula	T_f, °C	K_f, °C*kg/mol
Water	H_2O	0.0	1.86
Acetic acid	CH_3COOH	16.6	3.90
Benzene	C_6H_6	5.5	5.12
tert-Butanol	C_4H_9OH	25.5	9.10
Cyclohexane	C_6H_{12}	6.5	20.00
para-Dichlorobenzene	$C_6H_4Cl_2$	53.1	7.10

EQUIPMENT: Large test tube with two-hole stopper and wire stirrer, large rubber stopper drilled to fit around test tube, 250-mL wide-mouth Erlenmeyer flask, powder funnel, large beaker for water bath, 100º thermometer, 2 wire test tube clamps, spatula, ring stand, iron ring, wire gauze, 3-finger clamp, burner, flint lighter, computer, interface, and temperature probe.

PROCEDURE: For data collection using the computer and Logger Pro software, after starting Logger Pro, find the Setup tab on the menu bar and open it. Check to make sure that the stainless temperature probe on channel 1 is designated as the sensor. On the data sampling tab, set the time of sampling to 12 minutes and the sampling rate as 12 samples per minute. On the View tab of the menu bar, you can set the axis limits under Graph Options. The x-axis should run from zero to 12 minutes. Suggested values for the y-axis are from 50 to 65 degrees for solvent runs and from 40 to 60 degrees for solution runs. You can modify these after the run so that the data fill the entire graph as much as possible.

The solvent to be used is paradichlorobenzene, $C_6H_4Cl_2$, (DCB). You may recognize from the odor that this is the substance found in mothballs. This solvent freezes at 53.1°C if pure. Since we can not be assured of its purity, we will measure the freezing point twice and average the values.

Weigh to the nearest 0.001 g about 30 grams of DCB and quantitatively (completely) transfer it to the test tube.

Fill a large beaker almost full with hot water from the faucet. In the hood, heat the water to about 70-75°C, but no hotter. Immerse the test tube in the water bath until most of the DCB has melted. Insert the stopper-stirrer assembly and stir to complete the melting of the DCB. After the sample is completely liquefied, continue heating and stirring for an addition five minutes.

Remove the test tube from the water bath and dry the outside. Insert the temperature probe through the second hole of the stopper. Click the Start button on the computer screen to begin data collection. Begin stirring the sample slowly but continuously. Continue to stir at a steady rate until the recording of data ends. At this point there should be a significant amount of solid present in the test tube, but it does not have to be completely solidified. Adjust the graph scales such that the data fill the page as much as possible and the print the data screen to the network printer.

Remelt the sample and repeat the freezing point determination.

Record the code number of your unknown solute. Weigh out about 2 grams (to the nearest 0.001 g) of your unknown and record the mass. Melt the DCB in the test tube using the hot water bath, then carefully add the weighed sample to the test tube without losing any of either the solute or the solvent. Heat and stir to dissolve all of the unknown. As before, continue heating for five minutes after the solution is homogeneous. Remove and dry the tube. Insert the temperature probe and record time-temperature data as above (you may wish to reset the y-axis limits beforehand). Remelt the solution and repeat the determination.

When finished, remelt the solution, then pour it into the labeled waste jar in the hood. Do not pour the solution down the drain. Use a small amount of toluene (FLAMMABLE) to rinse the test tube, stirrer, and probe; discard these rinsings in the waste solvent can. Obtain the name of your unknown compound from the instructor and write it in your lab notebook.

CALCULATIONS: For each of the four determinations, use the data table and graph from Logger Pro output to determine the freezing temperatures of the pure solvent and the solution as explained in the prelab lecture (the leveling-off point or the break in slope). Determine the average of your two trials in each case, then use these to calculate the change in freezing point. Calculate the molar mass of your unknown solute. Obtain the identity of your unknown from the instructor and look up the formula to determine the correct value of the molar mass (reference your source). Possible sources include the *Handbook of Chemistry and Physics* (organic compounds section), *Merck Index*, *Lange's Handbook of Chemistry*, or find the MSDS for the compound. Calculate the absolute and relative errors (see the section on measurements and error in the introduction section of the lab manual) in your result.

REPORT: Today you will write an abstract describing the experiment and your results in 100 words or less. Use past-tense passive voice in your abstract. Your report should also include the data and observations from your experiment, calculations of molar mass and a brief discussion of possible sources of error.

QUESTIONS (to be included in report)

1. Explain the effect of each of the following errors upon your calculated molar mass. Be specific as to whether the result would be high or low and explain why.

   a. Some solvent is lost by evaporation.
   b. Some of the unknown is lost during transfer to the test tube.
   c. The thermometer consistently reads one degree too low.
   d. Part of the solute does not dissolve.

2. Is it necessary that the solvent be absolutely pure? Explain your answer clearly.

3. Many ionic compounds, e.g., NaCl, are strong electrolytes and dissociate completely upon dissolution in water. Explain clearly the effect upon the freezing point when a 1.00 *m* solution of NaCl in water is made (calculate the freezing point). Hint: What is the van't Hoff *i*-factor for this solute?