Determination of Molar Mass by Freezing Point Depression

Experimental Notes:
Students work in pairs.

Safety:
Goggles and closed shoes must be worn. Dispose of all chemical in the plastic waste container under the hood. If skin comes in contact with chemicals, the affected area should be flushed with water.

Pre-Lab Notebook Content:
Your notebook should include the title, date, purpose, procedure; data tables.

Pre-Lab Questions:

1. A sample of 4.6434 g of benzoic acid, C₇H₆O₂, is dissolved in 50.0033 g of camphor. What is the freezing point of the resulting solution? For camphor, \( T_f = 179.5 \, ^\circ C \), \( K_f = 40 \, ^\circ C/m \).

2. A 12.5855 g sample of an unknown compound (X) is dissolved in 32.0000 g of water. The resulting solution has a freezing point of \(-4.3^\circ C\). What is the molar mass of X? \( K_f = 1.858 \, ^\circ C/m \)

3. What are some practical applications of freezing point depression?

4. (Complete after lab) Discuss sources of error for the freezing point depression experiment. What effect should these sources of error have on the experimental results?
Introduction
Homogeneous mixtures, or solutions, have properties that are dependent on the concentration of the solute; such properties are known as colligative properties. Freezing point depression, $\Delta T_f$, is an example of a colligative property. In order to understand this concept, consider the following. Even though sucrose and ethylene glycol are two completely different compounds with different physical properties, a solution of 1.5 molal sucrose has the same freezing point depression as a solution of 1.5 molal ethylene glycol because $\Delta T_f$ is a concentration dependent property.

Freezing point depression can be defined as the difference between the freezing point ($T_f$) of the solution and the $T_f$ of the pure solvent.

\begin{equation}
\Delta T_f = |T_f \text{ soln} - T_f \text{ solvent}|
\end{equation}

When a non-volatile solute is dissolved in a solvent, the vapor pressure of the solvent is lowered; this results in depression of the solvent freezing point. Thus, the freezing point of the solution is always lower than the freezing point of the pure solvent. The amount by which the solvent freezing point is lowered depends on the concentration of the solute, as shown below.

\begin{equation}
\Delta T_f = K_f \cdot m
\end{equation}

where

- $m = \text{molal concentration}$
- $K_f = \text{freezing point depression constant}$

The freezing point depression constant is a value associated with the solvent; it is a numerical constant that can be found in a reference text. Note that the greater the molal concentration of the solute, the greater the freezing point depression will be. It follows that a solution that is 5.0 molal sucrose will have a lower freezing point than a solution that is 1.0 molal sucrose.

Determination of Molar Mass using $\Delta T_f$

Colligative properties can be used to determine the molar mass of a compound. Freezing point depression is particularly useful for molar mass determination because the freezing point of a solution is comparatively easy to find experimentally. The experiment involves measuring the freezing point of the pure solvent and the freezing point of a solution of the compound in the solvent. The freezing point depression is the difference between the two temperatures. The molar mass is found through a series of calculations. Consider a general example in which 5.00 grams of compound X are mixed with 25.00 grams of solvent, and the freezing temperatures of the pure solvent and the solution are measured. The calculations for finding molar mass are as follows:
Step one: find the freezing point depression.

\[ \Delta T_f = \left| T_f \text{soln} - T_f \text{solvent} \right| \]

Step two: use freezing point depression to determine the molal concentration of the solution.

\[ m = \frac{\Delta T_f}{K_f} \]

Step three: find the moles of compound X using solution molality and mass of solvent.

\[ \text{mol X} = (\text{molal concentration of solution}) \cdot (\text{kg of solvent}) \]

Step four: calculate the molar mass of X from calculated moles and measured mass.

\[ \text{Molar mass} = \frac{\text{grams X}}{\text{mol X}} \]

Procedure

The objective of this experiment is to determine the molar mass of an unknown alcohol, Z.

Preparation of Ice-Salt Bath

Into a large Styrofoam cup (set upright in a large beaker or other stabilizing container) place a stir bar, about 10 mL of water, and approximately 100 mL of crushed ice combined with 30 g of rock salt. Place an alcohol thermometer mounted with a clamp attached to a ring stand in the cup. Mix the contents and monitor the temperature of the ice-salt mixture. Within a few minutes the temperature of the mixture should approach -7°C to -10°C.

Add an additional 100 mL of crushed ice or enough to fill the Styrofoam cup to an inch of the rim and additional small amounts of rock salt with mixing to achieve a temperature that remains stable near -10°C ± ca. 1°C. Depending on the size Styrofoam cup, the ratio of ice and salt can be adjusted to maintain the -10°C target temperature. Begin stirring the bar at a moderate speed to agitate solid rock salt settling to the bottom.

NOTE1: During the experiment a large amount of ice may melt. When this happens, the salt mixture may become difficult to keep cold due to the amount of liquid. Use a bottle adapted with rubber tubing to siphon off melted ice and mix in fresh ice with a spatula. There should still be enough solid ice at the bottom of the bath to restore the -10°C temperature.
Measuring the Freezing Point of Pure Water (two trials)

Into a clean dry large test tube add 25.00 mL of distilled water dispensed from either a pipet or buret. Set the test tube into the ice-salt bath so that the test tube is about ½ inch above the stir bar. Place a clean wire mixing loop and a clean digital thermometer in the test tube. Immediately, while the 25.00 mL sample of water is still near room temperature begin taking an initial temperature and time measurements at time zero (t₀) and repeat this each 30 seconds until about 5 consecutive steady readings are reached at or around 0ºC when ice crystals begin forming within the test tube. It will take about 5 consecutive constant temperature readings at or near 0ºC for the water in the test tube to solidify completely. The run is complete at this point and you should prepare for a duplicate trial by cleaning and drying the test tube, then adding a new 25.00 mL aliquot of distilled water and repeating the steps.

NOTE 2:  It is possible for the test tube temperature to reach a few steady readings at or near 0ºC and then progressively decline to the temperature of the ice-salt bath itself. This is unusable data because it merely represents the additional cooling of solidified water in the test tube below its freezing point.

NOTE 3: When time and temperature readings begin do not remove the wire mixer or the thermometer, because dripping can change the sample size. It is especially important that you not use the same thermometer for the test tube and water-salt bath, since this would introduce salt into the test tube and alter the results.

Measuring the Freezing Point of the Water/Alcohol Z solution (two trials)

Measure 25.00 mL of water and 5.00 mL of alcohol Z into a large test tube, and stir the sample. Place a temperature probe with a clean digital readout into the solution. Record the solution temperature. Place the test tube into the ice – rock salt bath and record the temperature every 30 seconds. Use the temperature probe to stir the sample. Continue to record the temperature until one of the following conditions is met: 1) there are five consecutive temperature readings that are the same; 2) the sample freezes; or 3) the temperature reaches –10ºC. Repeat the procedure for a second trial.

Waste Disposal at the End of Lab

- Pour the water and unknown down the drain.
- Return unused salt to the instructor.
- Pour the ice/ water/salt slurry into the salt water collection tub.
- Turn the digital thermometer off.
- Rinse and dry both thermometers and the other lab ware.
- Return the cups, burets, clamps, stands and stir motors to their storage areas.
Analysis

Pure water
Prepare a graph of temperature versus time for each trial. The graphs should clearly indicate the freezing temperature of the water. Each graph should look similar to the following example:

![Pure water graph](image)

Alcohol solution
Prepare a graph of temperature versus time for each trial. Each graph should look similar to the following example:

![Solution graph](image)

This graph clearly indicates the freezing temperature of the solution. However, in the case of the solution, it is possible to obtain results that deviate from the expected graph shown above.
Occasionally, the digital thermometer reads the temperature of the bath rather than the sample, and the temperature readings decrease to \(-10^\circ\text{C}\), as shown below.

In this case, lines can be drawn from the graph as indicated below. The \(y\) value that corresponds to the intersection of these lines is taken as the freezing point of the solution.
It is also possible to observe supercooling, a condition where the temperature dips below the freezing point of the sample while the sample remains in liquid form. This occurs when the sample is cooled too quickly for crystals to form the ordered structure of the crystal lattice. Consider the following graph:

![Solution Graph](image)

In this case, the freezing point is taken to be the temperature after stabilization.

**Calculations**

Take the average freezing point from the two water trials and the average freezing point from the two solution trials to find $\Delta T_f$. \{Recall, $Z$ is the unknown alcohol.\}

$$\Delta T_f = |T_f \text{ soln} - T_f \text{ water}|$$

Determine molar mass via the following calculations:

$$\text{mass } Z = (\text{mL } Z) \cdot (0.785 \text{ g/mL})$$

$$\text{molality } _{\text{soln}} = \frac{\Delta T_f}{1.858 \circ C/m}$$

$$\text{mol } Z = (\text{molality } _{\text{soln}}) \cdot (\text{kg water})$$

$$\text{Molar mass } = \frac{\text{mass } Z}{\text{mol } Z}$$
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1. **Average** Freezing point (pure water):________

2. **Average** Freezing point (solution):________

3. Freezing point depression:

4. Molal concentration of the solution.

5. Mass of the unknown. (Note the density of the unknown is 0.785 g/ml)

6. Moles of unknown

7. Molar mass of the unknown.

Each student must prepare his/her own graphs and calculations.

end