Experiment 9: Freezing point depression

Safety hazards
Acetic acid causes severe eye and skin burns. It also causes severe digestive and respiratory tract burns. Keep goggles on at all times. You may want to use gloves as well.

Safety Hazards

Some properties of solutions do not depend on the nature of the solute: they only depend on the number of solute particles (ions or molecules) relative to the number of solvent particles. We call these properties colligative properties. In this experiment we will focus on one particular colligative property, the freezing point depression.

Background

It has been observed that the freezing point of a solution of a non-volatile solute mixed with a solvent is lower than the freezing point of the pure solvent. Quantitatively, for a non-volatile solute that is also not an electrolyte, the lowering of the freezing point is described by the following equation:

$$| \Delta T_f | = K_f \; x \; m$$

where $| \Delta T_f |$ represents the lowering of the freezing point (T_f), m stands for the molality of the solution (moles solute per kg solvent) and K_f is the molal freezing point depression constant that depends only on the identity of the solvent. When the solute is an electrolyte it is necessary to include the van't Hoff factor, i, in the equation (more about this later!).

Figure 1 represents a typical cooling curve of a pure substance (a solvent without a solute added). It illustrates a very common phenomenon called **supercooling** where the temperature of the solvent gets lower than its actual freezing point. This can be avoided by careful stirring of the liquid.
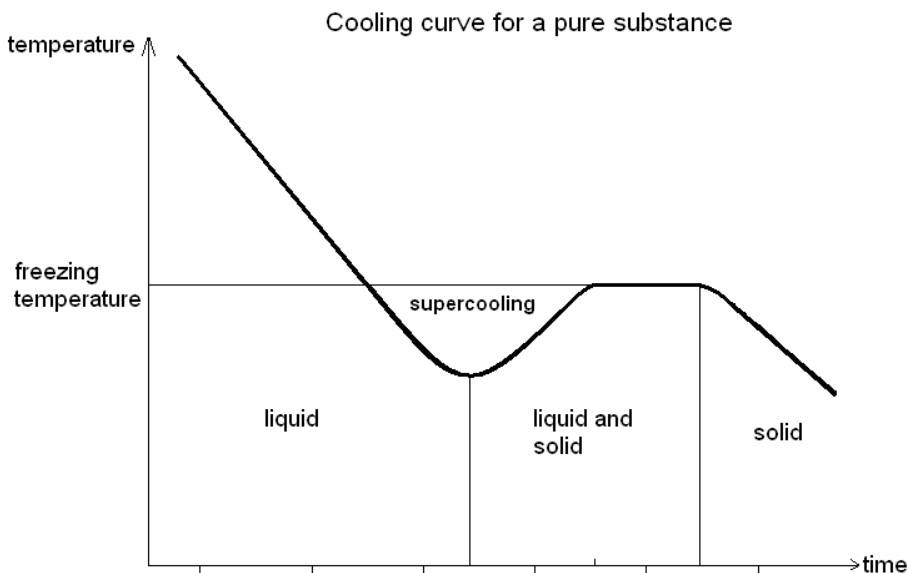
Cooling curve (pure substance)

Figure 1: Cooling curve for a pure substance

Figure 2 illustrates a standard cooling curve for a solution. Besides the phenomenon of supercooling, one notices that the freezing temperature changes with time (see the slope of the line CB). A solution does not have a sharply defined freezing point. This is because as the solvent freezes, solvent molecules are removed from the liquid and deposited on the solid, changing the concentration of solute in the liquid (the molality, m), which lowers the freezing point even further. In general the freezing point is experimentally determined by interpolation of the line AB to obtain the point C prior to supercooling; this is the temperature at which the first crystals of solvent would appear, if there was not any supercooling.

Figure 2: Cooling curve of a solution
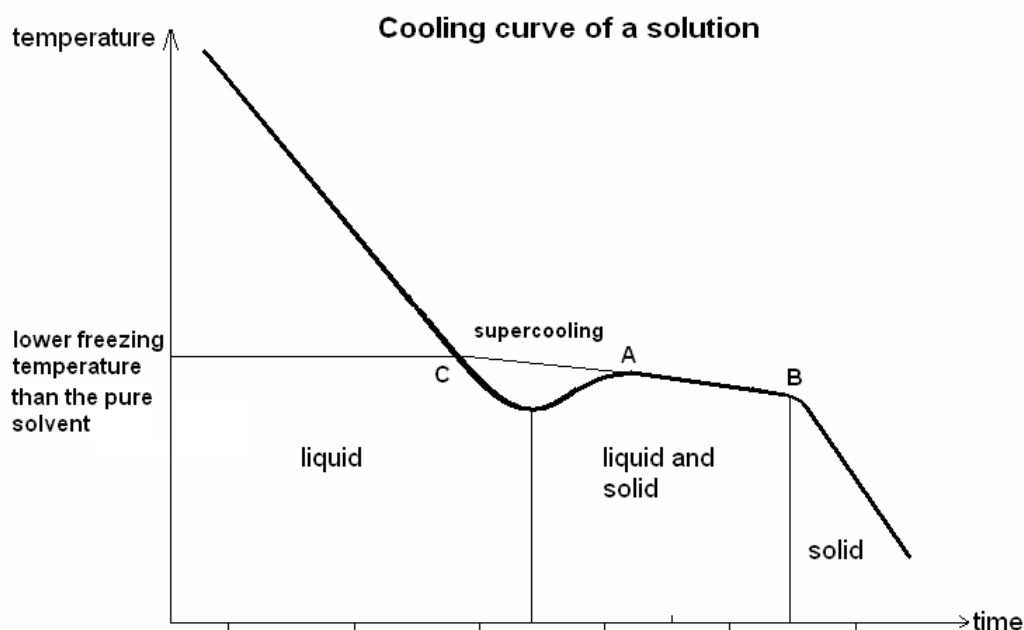
Cooling curve (solution)

For an **electrolyte** solution the change in the freezing temperature can be expressed as

where *i* is the van't Hoff factor and represents the number of ions that would be produced after complete dissociation of the electrolyte in a very dilute solution (ideal conditions).

In the following experiment, we will explore the freezing point depression of solutions. In Part 1, we will obtain the cooling curve of a pure solvent, acetic acid (HAc) and the equivalent curve after an unknown solute has been added to the solvent. From the measurements of $|\Delta T_f|$, we will be able to determine molality of the solution and consequently the molecular mass of the unknown. In Part 2, we will calculate the van't Hoff factor, i, for the electrolyte $CaCl_2$ by measuring $|\Delta T_f|$ for two solutions with different values of molality.

$$|\Delta T_f| = K_f \times m \times i$$

Part 1. Freezing point depression of acetic acid

Procedure
Prepare the computer for data collection by opening experiment 15 in LoggerPro from the folder Chemistry with Computers. The vertical axis of the graph has a temperature scale from 0°C to 100°C. The horizontal axis has time scaled form 0 to 10 minutes.

A. Freezing point determination of pure acetic acid (HAc)
 1. Fill 2/3 of a 400 mL beaker with ice.
 2. In the hood, using a 10 mL pipet, add 30 mL of HAc to a large test tube and stopper it with a 2 hole stopper. ***Keep the stoppered tube in an upright position at all times to avoid spilling any acetic acid.***
 3. Insert the temperature probe through the large hole of the stopper.
 4. Insert the stirrer through the thin hole of the stopper. The paddle-like end of the stirrer goes into the test tube to stir the sample.
 5. Place the tube in the ice bath so that the level of the liquid in the test tube is below the level of the ice and start collecting the data.
 6. While the data is being collected ***stir the sample gently* (you don't want to break the test tube!)** with an up and down motion to avoid supercooling.
 7. You can stop stirring once the sample starts freezing. (Think about it: how would you know when that happens?)
 8. Collect data for 8-10 minutes.
 9. Determine the freezing point of HAc using the computer graph. Enlarge the y-axis (cursor on y-axis; click on ~ symbol and drag) to better determine the freezing temperature.
10. Remove the temperature probe.
11. Melt the HAc under the tap's warm water. ***Do not remove the stopper! You will add the unknown solute to this same HAc sample***.
12. Optional: Repeat the experiment without stirring to observe the supercooling of HAc.

B. Freezing point determination of a solution of HAc and an unknown solute.
1. Add 1.5 mL of the unknown solute to the test tube containing the HAc sample that you used determined the freezing point of pure HAc in experiment A. Stir well. We will call this solution "solution #1".
2. Insert the temperature probe.
3. Repeat steps 4-8.
4. Determine the freezing point of the solution using the computer graph. As explained in the background section you will need to interpolate to accurately determine the freezing temperature.
5. Remove the temperature probe.
6. Melt the frozen solution under the tap's warm water. ***Do not remove the stopper! You will add <u>more</u> unknown solute to this same solution***.
7. Add 1.5 more mL of the unknown to the same test tube. We will call this solution "solution #2".
8. Repeat steps 3-8 from experiment A.

9. Determine the freezing point of the solution using the computer graph. Again, as explained in the background section, you will need to interpolate to accurately determine the freezing temperature.
10. Remove the temperature probe.
11. Melt the frozen solution under the tap's warm water.
12. Dispose of the sample in the provided chemical waste container. Do NOT dispose of this sample anywhere else.

Data for Part 1

Prepare a data table to record the freezing points and composition (measured volumes of solvent and/or solute) of each of three samples for which freezing points were measured (pure acetic acid, solution #1, and solution #2).

Calculations for Part 1

The density of acetic acid is 1.049 g/mL and K_f (acetic acid) = 3.90 °C· kg/mol

The density of the unknown is 0.791 g/mL.

1. Calculate the masses of the solvent and/or solute present in each of the three samples.
2. Calculate the freezing point depression ($|\Delta T_f|$) for the two solutions.
3. Calculate the experimental value of the molality (moles of solute per kg solvent) of the two solutions based on the $|\Delta T_f|$ for the two solutions.
4. Calculate the experimental value for the moles of solute present in each solution.
5. Calculate the molar mass (grams per mole) of the unknown solute.
6. Calculate the average molar mass of the unknown solute based on the values obtained from the two solutions.

Part 2. Determination of the van't Hoff factor, i, for CaCl₂

Procedure
In this experiment you will use two different solutions of $CaCl_2$ to determine the van't Hoff factor, *i*, using the known K_f value for water, 1.86 °C ·kg/mol.

a. Using a 10mL pipet, add 30 mL of 0.5 m $CaCl_2$ solution to a large test tube and stopper with a 2 hole stopper.
b. Insert the temperature probe through the large hole of the stopper.
c. Insert the metal stirrer through the thin hole of the stopper.
d. Place the tube in the rock-salt ice bath and start collecting the data.
e. While the data is being collected stir the sample ***gently*** with an up and down motion to avoid supercooling.
f. You can stop stirring once the sample starts freezing.
g. Collect data for 8-10 minutes.
h. Determine the freezing point of the solution using the computer graph. Enlarge the y-axis (cursor on y-axis; click on ~ symbol and drag) to better determine the freezing temperature. As explained in the background section

you will need to interpolate to accurately determine the freezing
temperature.
i. Remove the temperature probe.
j. Melt the sample under the tap's warm water and dispose of it as indicated
by your instructor,
k. Repeat steps a-j with the 1 m solution.

Data for Part 2
Set up a data table to record the molality of each solution (read the concentration on
the bottle!) and the corresponding measured freezing point.

Calculations for Part 2

The K_f value for water is 1.86 °C ·kg/mol.

1. Calculate the freezing point depression, $|\Delta T_f|$, for each solution.
2. Calculate the value of the van't Hoff factor, i, for each solution.
3. Calculate an average value for i based on the two values for i.

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Report Sheets

Part 1
Record the following information to demonstrate your successful completion of the experimental objectives for Part 1.

Volume of acetic acid	
Volume of unknown solute in solution #1	
Volume of unknown solute in solution #2	
Freezing point of pure acetic acid	
Freezing point of solution #1	
Freezing point of solution #2	
Average molar mass of the unknown solute	

Part 2
Record the following information to demonstrate your successful completion of the experimental objectives for Part 2.

Freezing point of ~0.5 m $CaCl_2$ solution	
Freezing point of ~1 m $CaCl_2$ solution	
Average value of van't Hoff factor	

Follow-up questions
1. Why is molality used instead of molarity in the context of colligative properties?

2.   Assume that in the acetic acid experiment you obtained the following values:
     T_f (acetic acid) = 16.1°C T_f (with 3 mL of unknown) = 11.3°C

a. Calculate the molar mass of the unknown. Show your work.

b. Your instructor shows you that you made a mistake in the interpolation and that the correct value is T_f (with 3 mL of unknown) = 11.0 °C. Calculate the new molar mass of the unknown and compare this value with the molar mass determined based on T_f = 11.3 °C.

2. What do you think are the major sources of error in the determination of the molar mass of the unknown?

3. What is the theoretical value of the van't Hoff factor, i, for $CaCl_2$? How does your experimental value compare to the theoretical value? What does this suggest is happening at the molecular level in the solution?

Pre-lab assignment—To be completed BEFORE lab!

1. Define molality of a solution.

2. Calculate the molality of a solution prepared by dissolving 78.0 grams of butanone (C_4H_8O) in 800 mL of acetic acid. The density of acetic acid is 1.049 g/mL.

3. You dissolve 93.24 g of an unknown solute in 1000 g of water and obtain $|\Delta T_f| = 2.34°C$.
    a. What is the molality of the solution if K_f is 1.86 °C ·kg/mol for water?

    b. How many moles of solute are present in the solution?

    c. What is the molar mass of the unknown solute?