

## Experiment 12: Freezing point depression

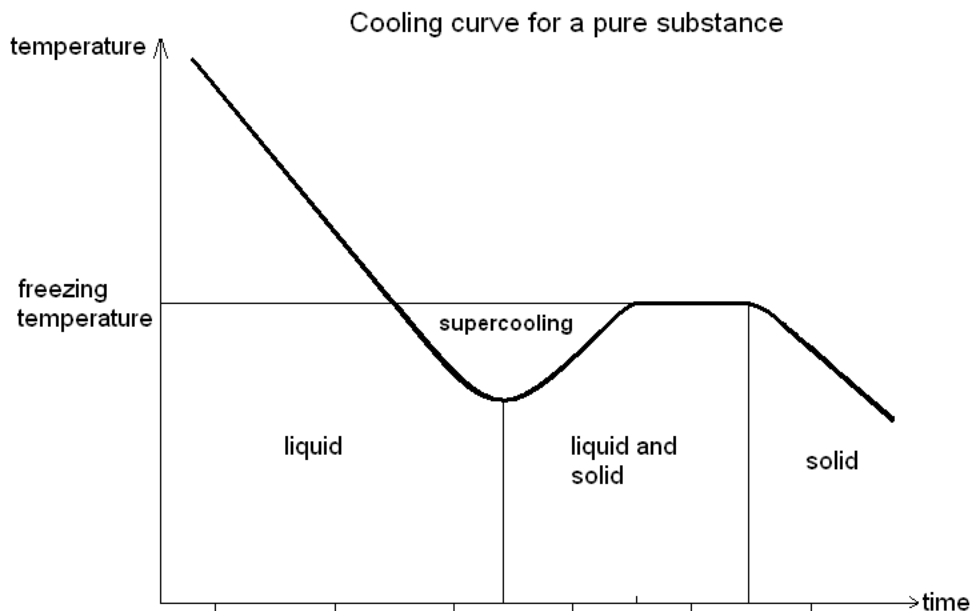
Some properties of solutions do not depend on the nature of the solute: they only depend on the number of solute particles (ions or molecules) relative to the number of solvent particles. We call these properties colligative properties. In these experiments we will focus on one particular colligative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

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

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

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

The plot below represents a typical cooling curve of a pure solvent. It illustrates a very common phenomenon, supercooling, where the temperature of the solvent gets lower than its freezing point. This can be avoided by careful stirring of the liquid.

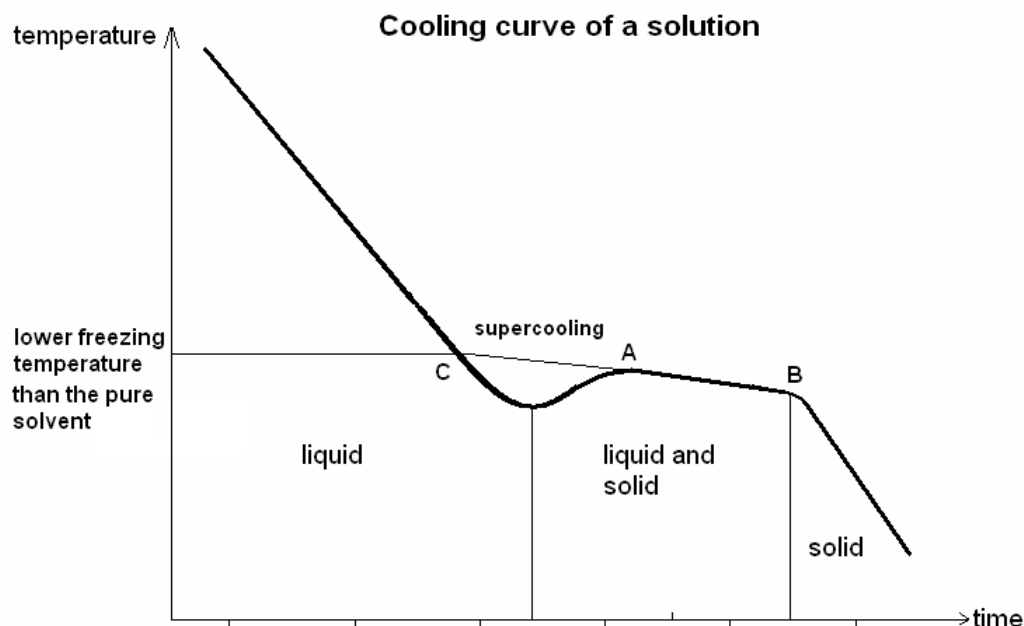


## Background

## Cooling curve (pure substance)

The next plot 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, which lowers the freezing point even further. In general the freezing point is calculated by interpolation of the line AB to obtain the point C (this is the temperature at which the first crystals of solvent would appear, if there was not any supercooling).

## Cooling curve (solution)



In the following experiments we will obtain the cooling curve of a pure solvent, acetic acid (HAc) and the equivalent curves after an unknown solute has been added to the solvent. From the measurements of  $\Delta T_f$  we will be able to determine the molecular mass of the unknown. In a couple of similar experiments with sucrose solutions we will measure the value of  $K_f$  for water. Finally we will calculate the van't Hoff  $i$  factor for the electrolyte  $\text{CaCl}_2$ .

### Safety hazards

Acetic acid is strongly corrosive to skin and clothing. Avoid contact. It is also a lachrymator. Wash hands before leaving the laboratory.

## Safety Hazards

## 1. Freezing point depression of acetic acid

Prepare the computer for data collection by opening the experiment 15 folder from 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 from 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.
3. Insert the temperature probe through the large hole of the stopper.
4. Insert the metal stirrer through the thin hole of the stopper.
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 with an up and down motion to avoid supercooling.
7. You can stop stirring once the sample starts freezing (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.
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.

1. Add to the previous sample 1.5 mL of the unknown provided by the instructor and 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 and do not remove the stopper.
7. Add 1.5 more mL of the unknown to the sample. 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 and dispose of it as indicated by your instructor.

## Experimental Procedure

### Part 1: Freezing Point Depression of Acetic Acid

## Calculations for Part 1

The density of acetic acid is 1.049 g/mL and  $K_f$  (acetic acid) =  $3.90\text{ }^\circ\text{C}\cdot\text{kg/mol}$

The density of the unknown is 0.791 g/mL.

1. Freezing point of HAc = $T_f =$
2. Mass of acetic acid in kg =
3. Volume of unknown in solution #1 =
4. Mass of unknown in solution #1 =
5. Freezing point of solution #1 = $T_{f1} =$
6. $\Delta T_f = T_f - T_{f1} =$
7. Molality of solution #1 =
8. Number of mole of unknown in solution #1 = $n_1 =$
9. Molecular mass of the unknown =
10. Volume of unknown in solution #2 =
11. Mass of unknown in solution #2 =
12. Freezing point of solution #2 = $T_{f2} =$
13. $\Delta T_f = T_f - T_{f2} =$
14. Molality of solution #2 =
15. Number of mole of unknown in solution #2 = $n_2 =$
16. Molecular mass of the unknown =
17. Average mass of the unknown =

## **2. Determination of the freezing point depression constant of water.**

In this part of the experiment you will determine the freezing point of two sucrose solutions of known molalities: 0.5 and 1.0 m. From the freezing point depression you will be able to calculate  $K_f$  for water.

Because the freezing point of water is  $0^\circ\text{C}$ , you will need to prepare a rock salt-ice bath so that temperatures lower than  $0^\circ\text{C}$  can be achieved. To do this take a 400 mL beaker and fill it with alternating layers of ice and rock salt until it is  $2/3$  full. Mix the contents of the beaker and use a thermometer to verify that the temperature is around  $-15^\circ\text{C}$ . You are now ready to start the experiment. You will first determine the freezing point of pure water, then the freezing point of a 0.5 m sucrose solution and finally the freezing point of a 1 m sucrose solution

### **A. Freezing point of pure water.**

1. Using a 10 mL pipet, add 30 mL of water to a large test tube and stopper with a 2-hole stopper.
2. Insert the temperature probe through the large hole of the stopper.
3. Insert the metal stirrer through the thin hole of the stopper.
4. Place the tube in the rock-salt ice bath and start collecting the data.
5. While the data is being collected stir the sample with an up and down motion to avoid supercooling.
6. You can stop stirring once the sample starts freezing.
7. Collect data for 8-10 minutes.
8. Determine the freezing point of the solution using the computer graph. Enlarge the y-axis (cursor on y-axis; click on  $\sim$  symbol and drag) to better determine the freezing temperature.
9. Remove the temperature probe.
10. Melt the sample under the tap's warm water and dispose of it in the sink.

### **B. Freezing point of the sucrose solutions**

1. Using a 10 mL pipet, add 30 mL of 0.5 m sucrose solution to a large test tube and stopper with a 2-hole stopper.
2. Repeat steps 2-7
8. Determine the freezing point of the solution using the computer graph. Enlarge the y-axis (cursor on y-axis; click on  $\sim$  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.
9. Remove the temperature probe.
10. Melt the sample under the tap's warm water and dispose of it in the sink.
11. Repeat steps 1-10 with the 1 m solution.

## **Experimental Procedure**

### **Part 2: Determining $K_f$ of Water**

**Calculations for Part 2:**

a. Data from the 0.5 m solution	b. Data from the 1.0 m solution
$T_f =$	$T_f =$
$\Delta T_f = T_f - T_f(\text{water})$	$\Delta T_f = T_f - T_f(\text{water})$
$\Delta T_f = K_f \times m$	$\Delta T_f = K_f \times m$
$K_f =$	$K_f =$
<b>Average value of <math>K_f =</math></b>	

Knowing that  $K_f$  for water is  $1.86 \text{ }^\circ\text{C}\cdot\text{kg}/\text{mol}$  calculate the relative error of your experimental  $K_f$  value.

relative error = $(   \text{average } K_f - 1.86   / 1.86 ) \times 100\% =$
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### 3. Determination of the van't Hoff factor, $i$ , for $\text{CaCl}_2$

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

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

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 this experiment you will use two different solutions of  $\text{CaCl}_2$  to determine the van't Hoff factor,  $i$ , using the known  $K_f$  value for water,  $1.86 \text{ }^\circ\text{C} \cdot \text{kg/mol}$ .

- Using a 10mL pipet, add 30 mL of 0.5 m  $\text{CaCl}_2$  solution to a large test tube and stopper with a 2 hole stopper.
- Insert the temperature probe through the large hole of the stopper.
- Insert the metal stirrer through the thin hole of the stopper.
- Place the tube in the rock-salt ice bath and start collecting the data.
- While the data is being collected stir the sample with an up and down motion to avoid supercooling.
- You can stop stirring once the sample starts freezing.
- Collect data for 8-10 minutes.
- Determine the freezing point of the solution using the computer graph. Enlarge the y-axis (cursor on y-axis; click on  $\sim$  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.
- Remove the temperature probe.
- Melt the sample under the tap's warm water and dispose of it as indicated by your instructor,
- Repeat steps a-j with the 1 m solution.

## Experimental Procedure

### Part 3: Determining the van't Hoff factor, $i$

#### Calculations for Part 3

a. Data from the 0.5 m solution	b. Data from the 1.0 m solution
$T_f =$	$T_f =$
$\Delta T_f = T_f - T_f(\text{water})$	$\Delta T_f = T_f - T_f(\text{water})$
$\Delta T_f = K_f \times m \times i$	$\Delta T_f = K_f \times m \times i$
$i =$	$i =$

***Follow-up questions***

1. 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 molecular weight of the unknown.

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 molecular weight of the unknown. What can you conclude about the importance of determining the temperature accurately in this experiment?

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

3. Explain at the molecular level why does the mixing of rock salt with ice produce temperatures well below 0°C.

3. The literature value of  $K_f$  for water is  $1.86\text{ }^\circ\text{C}\cdot\text{kg mol}^{-1}$ . Are your results in agreement with this value? Suggest how you could improve the experiment.

***Pre-lab assignment—To be completed BEFORE lab!***

1. Define molality of a solution.
2. Why do we use molality instead of molarity in the context of colligative properties?
3. Calculate the molality of a solution prepared by dissolving 125.0 g of glucose ( $C_6H_{12}O_6$ ) in 500 g of water.
4. 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.
5. You dissolve 93.24 g of an unknown in 1000 g of water and obtain  $\Delta T_f = 2.34^\circ C$ . What is the molecular weight of the unknown if  $K_f = 1.86^\circ C \cdot kg/mol$ ?