

EXPERIMENT 11: Molar Mass by Freezing Point Lowering

OBJECTIVES:

In this experiment, you will determine the freezing point of pure cyclohexane, C_6H_{12} , and the freezing point of a solution containing a weighed amount of unknown solute (a nonvolatile, nonelectrolyte) dissolved in cyclohexane. You will determine the molar mass of the unknown solute based on the difference in the freezing points of pure cyclohexane and the solution containing the unknown in cyclohexane.

INTRODUCTION

Several important physical properties of solutions depend on the number of solute particles in the solution but not on whether these particles are atoms, molecules, or ions. These so-called colligative properties include effects on: vapor pressure, boiling point, freezing point and osmotic pressure of solutions of liquid solvents.

FREEZING POINT LOWERING (ALSO CALLED FREEZING POINT DEPRESSION):

The addition of a solute to a solvent will lower the freezing point of the solvent. The difference between the freezing point of a pure solvent and a solution of a is represented by T_f .

$$T_f = T_f^{\text{solvent}} - T_f^{\text{solution}}$$

T_f is directly proportional to the molal concentration of the solution of a nonvolatile nonelectrolyte in a solvent. (The higher the solute concentration, the greater is T_f).

$$T_f \propto m \quad \text{where} \quad m = \frac{\# \text{ mole solute}}{1 \text{ kg solvent}}$$

The extent of the effect of concentration on freezing point is different for different solvents, so there is a unique proportionality constant for each solvent, which is called its molal freezing point constant, K_f .

$$T_f = K_f \cdot m$$

K_f quantifies the relationship between T_f and m for a particular solvent: $K_f = \frac{T_f}{m}$

This is reflected in the units of K_f :

$$K_f = \frac{^{\circ}\text{C}}{\text{mole/kg}} \quad \text{or} \quad K_f = \frac{^{\circ}\text{C} \cdot \text{kg solvent}}{\text{mole solute}}$$

In the table below are molal freezing point constants for several solvents.

Solvent	Normal Freezing Point ($^{\circ}\text{C}$)	K_f ($^{\circ}\text{C} \cdot \text{kg}/\text{mole}$)
acetone	-95.4	2.40
benzene	5.5	5.12
cyclohexane	6.5	20.1
water	0.0	1.86

The normal freezing point is the temperature at which the solid and liquid phases are in equilibrium at standard pressure (1 atm).

PROCEDURE:

CAUTION

- Your unknown is toxic. Make sure to handle it carefully without spilling. At the end of lab, return the vial containing the unused unknown to your instructor and be sure to wash your hands before leaving.
- Cyclohexane is **FLAMMABLE**. Keep the liquid and its vapors away from flames. Avoid breathing the vapor. At the end of the experiment, dispose of the waste cyclohexane in the red can in the hood.



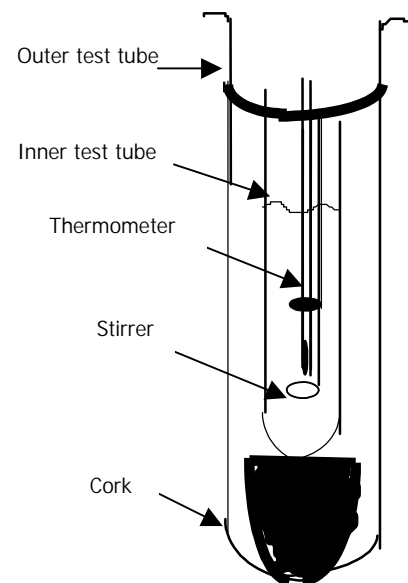
A. Freezing Point of Cyclohexane

1. Sign out the following from the stockroom:

- nickel spatula
- timer
- freezing point apparatus.

The freezing point apparatus consists of a freezing point test tube fitted with a stopper, a digital thermometer and a stirring wire. (The test tube is clean. Do not wash it with water!!).

2. Cork the freezing point test tube and place it into a small tared beaker. Accurately weigh it to the nearest 0.01g using the top-loading balance. Record the mass in the Report Sheet.
3. Use the graduated cylinder found in the fume hood to measure approximately 15 mL of cyclohexane into the test tube. Re-cork the test tube and reweigh it in the tared beaker to within 0.01 g. Record the mass on the Report Sheet.
4. Insert the stirrer and thermometer that you checked out from the stockroom into the small test tube containing cyclohexane. The tip of the thermometer should be immersed in the cyclohexane, and the wire stirrer should move freely around the thermometer.
5. Insert the small freezing point test tube into an 8-inch test tube (from your locker) with a cork (size #7) placed in between the two test tubes as shown in figure at right. Secure the outer test tube by using a utility clamp attached to a ring stand as shown in the figure. (The cork helps to absorb the shock during stirring. The outer test tube serves as an air jacket to prevent the solvent from cooling too quickly.)
6. Fill a 600 mL beaker with ice. Add about 15 g of rock salt. Add enough water to almost cover the ice. Stir. This beaker will be used as an ice bath. Check the ice bath temperature using the thermometer from your drawer. Do not use the thermometer for stirring (it can break easily). If the bath is not at 0 °C or lower add more rock salt to lower the temperature.
7. Immerse the assembled test tubes into the ice bath and Make sure that the entire cyclohexane sample is immersed in the ice bath.
8. Gently and continuously stir the cyclohexane by using the wire stirrer. As soon as the temperature of the cyclohexane drops to about 12°C, start taking readings every 30 seconds. Continue taking readings until the temperature is CONSTANT for about 8 readings (4 minutes). Record your data on the Report Sheet. Do not lift the tube containing the cyclohexane out of the



ice bath through the entire period of recording temperature, otherwise you will introduce bad readings. Notice that the cyclohexane will start to freeze as the temperature is lowered.

9. After you have obtained the freezing point data, remove the assembled test tubes from the ice bath, cork the test tube containing cyclohexane, and allow the liquid to warm up to approximately room temperature.
10. While the cyclohexane is melting, on the graph paper provided by the instructor prepare a cooling curve for cyclohexane. Plot the temperature ($^{\circ}\text{C}$) of the cyclohexane versus time (in minutes). You will notice that the cyclohexane remains at the same temperature for several minutes. This results in a horizontal flat region in the cooling curve. This temperature represents the freezing point of cyclohexane. The freezing point of very PURE cyclohexane measured with a CALIBRATED thermometer is 6.5°C . You may obtain different freezing points depending on the purity of your cyclohexane and the accuracy of your thermometer reading.

B. FREEZING POINT OF THE SOLUTION

NOTE: You must use the same thermometer for both freezing point determinations. If you use two different thermometers for the freezing point determinations, any error inherent in the thermometer will not cancel out.

1. Obtain from your lab instructor a sample of unknown molar mass. Record the sample number on your Report Sheet.
2. Weigh accurately 0.2000—0.2500 grams of unknown onto a piece of weighing paper. Record the mass of your unknown on the Report Sheet.

RETURN ALL UNUSED UNKNOWN TO YOUR INSTRUCTOR IN ITS ORIGINAL VIAL

3. Without spilling, transfer the unknown sample off your weighing paper into your freezing point tube. DO NOT lose any unknown in the transferring process.

Disposal: Discard the used weighing paper or any unknown that may have been accidentally spattered into a special waste container under the hood that is labeled:
Freezing Point Unknown/Weighing Paper Waste

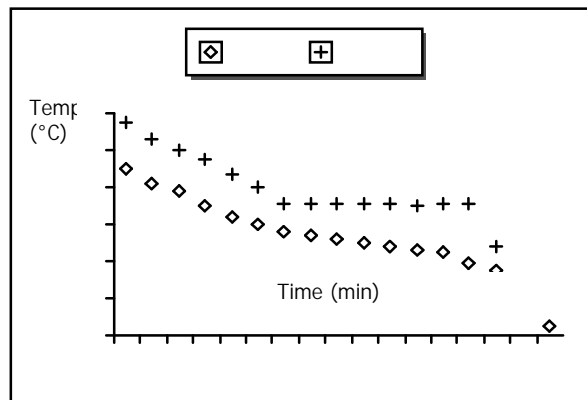
4. COMPLETELY dissolve the unknown by stirring.
5. Drain some of the excess water from the ice bath. Add approximately ten grams of rock salt (or more) ice to the ice bath and stir well with the stirring rod. Bring the temperature of the ice bath to about 0°C or lower.
6. Reinsert the freezing point test tube into the larger tube which is attached to a ring stand.
7. Immerse the large tube containing in the freezing point apparatus into the ice bath.
8. Stir the cyclohexane solution gently and start taking readings and record your data on the Report Sheet as before. Do not take the tube out of the ice bath while taking readings to see if it is frozen yet!
9. After the temperature of the solution has SLIGHTLY leveled off for about 8 readings (4 minutes), look for visible crystals when you remove the tube from the bath. If there are no visible crystals, you may have not reached the freezing point of the mixture and you will need to repeat the entire cooling curve for the mixture.

Disposal: Discard the cyclohexane solution into the red waste container located under the fume hood. Rinse the small test tube with a small amount of acetone and discard into the red waste container. DO NOT RINSE WITH WATER because cyclohexane and water are immiscible.

GRAPHS AND CALCULATIONS:

On the same piece of graph paper plot temperature versus time for the cyclohexane alone and for the unknown/cyclohexane solution. Label your axes and each curve. The freezing points of cyclohexane and cyclohexane solution are obtained from the cooling curves as follows:

1. The freezing point of cyclohexane alone reaches a plateau at its freezing point. Extrapolation of the plateau to the temperature axis determines its freezing point.
2. The cooling curve for the solution does not reach a plateau but continues to decrease slowly as the cyclohexane gradually freezes leaving behind solutions of higher concentrations. The freezing point of the solution is determined from the graph by drawing two straight lines through the data points above and below the freezing point. The temperature corresponding to the intersection of the two lines is the freezing point of the solution.



NOTE: It is not uncommon for a solution to cool below its freezing point, and then show a small rise in temperature (Due to the release of heat when crystallization occurs). This phenomenon is called supercooling.

3. Find the difference in freezing points, $T_{f,i}$, of cyclohexane and that of cyclohexane solution. On the graph mark the freezing points that you chose to calculate T_f .
4. Calculate the molar mass of your unknown.

Calculations

1. Freezing point of cyclohexane (from graph)
2. Freezing point of unknown-cyclohexane solution (from graph).
3. Calculation of freezing point difference, T_f .
4. Calculation of molality of the solution from T_f and K_f .
(K_f for cyclohexane: $20.0\text{ }^\circ\text{C}\cdot\text{kg/mole}$)
5. Convert mass of cyclohexane to kilograms
6. Calculation of moles unknown.
7. Calculation of Molar Mass of Unknown

REPORT SHEET - EXPERIMENT 11

Name _____
last first

Instructor's initials _____

A. Freezing Point of Cyclohexane

Mass of corked test tube	
Mass of corked test tube and cyclohexane	

Calculated mass of cyclohexane _____

Time-temperature data for cyclohexane:

Time (min)	Temp (°C)	Time (min)	Temp (°C)	Time (min)	Temp (°C)	Time (min)	Temp (°C)
0.0		7.5		15.0		22.5	
0.5		8.0		15.5		23.0	
1.0		8.5		16.0		23.5	
1.5		9.0		16.5		24.0	
2.0		9.5		17.0		24.5	
2.5		10.0		17.5		25.0	
3.0		10.5		18.0		25.5	
3.5		11.0		18.5		26.0	
4.0		11.5		19.0		26.5	
4.5		12.0		19.5			
5.0		12.5		20.0			
5.5		13.0		20.5			
6.0		13.5		21.0			
6.5		14.0		21.5			
7.0		14.5		22.0			

Run # 2(if needed): Time-temperature data for cyclohexane:

Time (min)	Temp (°C)	Time (min)	Temp (°C)	Time (min)	Temp (°C)	Time (min)	Temp (°C)
0.0		5.0		10.0		15.0	
0.5		5.5		10.5		15.5	
1.0		6.0		11.0		16.0	
1.5		6.5		11.5		16.5	
2.0		7.0		12.0		17.0	
2.5		7.5		12.5		20.0	
3.0		8.0		13.0		20.5	
3.5		8.5		13.5		21.0	
4.0		9.0		14.0		21.5	
4.5		9.5		14.5		22.0	

B. Freezing Point of Solution

Unknown number _____

Mass of unknown = _____

Time-temperature data for solution of unknown in cyclohexane :

Time (min)	Temp (°C)	Time (min)	Temp (°C)	Time (min)	Temp (°C)	Time (min)	Temp (°C)
0.0		7.5		15.0		22.5	
0.5		8.0		15.5		23.0	
1.0		8.5		16.0		23.5	
1.5		9.0		16.5		24.0	
2.0		9.5		17.0		24.5	
2.5		10.0		17.5		25.0	
3.0		10.5		18.0		25.5	
3.5		11.0		18.5		26.0	
4.0		11.5		19.0		26.5	
4.5		12.0		19.5			
5.0		12.5		20.0			
5.5		13.0		20.5			
6.0		13.5		21.0			
6.5		14.0		21.5			
7.0		14.5		22.0			

Run # 2(if needed): Time-temperature data for solution of unknown in cyclohexane :

Time (min)	Temp (°C)	Time (min)	Temp (°C)	Time (min)	Temp (°C)	Time (min)	Temp (°C)
0.0		5.0		10.0		15.0	
0.5		5.5		10.5		15.5	
1.0		6.0		11.0		16.0	
1.5		6.5		11.5		16.5	
2.0		7.0		12.0		17.0	
2.5		7.5		12.5		20.0	
3.0		8.0		13.0		20.5	
3.5		8.5		13.5		21.0	
4.0		9.0		14.0		21.5	
4.5		9.5		14.5		22.0	

Calculations

1. Freezing point of cyclohexane (from graph) _____

2. Freezing point of unknown-cyclohexane solution (from graph). _____

3. Calculation of freezing point difference, T_f . _____

4. Calculation of molality of the solution from T_f and K_f .
(K_f for cyclohexane: $20.0\text{ }^\circ\text{C}\cdot\text{kg}/\text{mole}$) _____

5. Convert mass of cyclohexane to kilograms _____

6. Calculation of moles unknown. _____

7. Calculation of Molar Mass of Unknown _____

4. If a thermometer is miscalibrated to read 1.0 °C higher than the actual temperature over its entire scale, will the reported molar mass of the solute be higher or lower than it should be, or will the error have no effect. (Hint: Follow a complete set-up for the calculation to see the effect of the error.)

Explanation _____

5. If the cyclohexane is initially contaminated with a soluble non-reactive, nonvolatile nonelectrolyte, will the change in freezing point, T_f , be higher, lower, or the same, as it would be in uncontaminated cyclohexane?

Explanation _____

6. Explain why the freezing point of a pure solvent is constant, whereas the freezing point of a solution decreases steadily with cooling.

Explanation _____
