Experiment

Molar Mass by Freezing Point Depression

OBJECTIVES:

In this experiment, you will determine the freezing point of cyclohexane and the freezing point of a solution containing a weighed amount of unknown solute and cyclohexane. You will determine the molar mass of the unknown solute based on the decrease in the freezing point.

INTRODUCTION:

Several important properties of solutions depend on the number of solute particles in the solution and not on the nature of the solute particles. These properties are called COLLIGATIVE PROPERTIES, because they all depend on the number of solute particles present, whether these particles are atoms, molecules, or ions. The colligative properties are: vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure.

FREEZING POINT DEPRESSION:

The addition of a solute to a solvent will decrease the freezing point (temperature) of the solvent. The decrease in freezing point, ΔT_f, when a nonvolatile, nonionizing (nondissociating) solute is dissolved in a solvent is proportional to the molal concentration, m, of the solute present in the solution.

$$\Delta T_f \quad \alpha \quad m$$

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

K_f is a constant for a given solvent. K_f is called the molal freezing point depression constant and represents how many degrees the freezing point of the solvent will change when 1.00 mole of a nonvolatile nonionizing (nondissociating) solute dissolves in one kilogram of solvent. The table below gives values of K_f for various solvents. The molal freezing point depression constant for H_2O, K_f , is given as 1.86 °C.kg/mole. Thus a1.00 m aqueous solution freezes at -1.86 °C instead of 0.00°C which is the normal freezing point for water.

Table: Molal freezing point depression constants of several solvents

Solvent	**Freezing point, °C**	**K_f , °C.kg/mole**
acetone	-95.4	2.4 0
benzene	5.5	5.12
cyclohexane	6.5	20.1
water	0.0	1.86

Notice that the freezing point of a substance or a mixture is the temperature at which the solid and liquid phases are in equilibrium at one atm of pressure. The next exercise illustrates how to use the experimentally measured decrease of freezing point, ΔT_f, to calculate the molar mass of an unknown nonvolatile nondissociating solute.

Exercise: The freezing point of cyclohexane is 6.50 °C. A solution is prepared by dissolving 0.5580g of an unknown solute in 33.50 g cyclohexane. The freezing point of the solution is 4.32 °C. Calculate the molar mass of the unknown solute. K_f for cyclohexane is 20.0 °C.kg/mole.

Setup:

a) Find the molality of the solution **:**

$\Delta T_f = K_f\ m$

$$\text{molality} = \frac{\Delta T_f}{K_f} = \frac{2.18\ °C}{20.0\ °C.kg/mole} = 0.109 \text{ mole solute/kg}$$

b) Find the number of moles of solute dissolved in 52.4 g H_2O:

molality = number of moles of solute / kgs of solvent

$$\text{Number of moles of solute} = \text{molality} \times \text{kgs of solvent} = 0.109\ \frac{\text{mole solute}}{\text{kg}} \times 0.03350 \text{ kg}$$

$$= 0.00365 \text{ mole solute}$$

c) Find molar mass of solute:

$$\text{Molar mass of solute} = \frac{0.5580 \text{ g solute}}{0.00365 \text{ mole solute}} = 153 \text{ g/mole}$$

PROCEDURE:

1. Obtain from the stockroom a nickel spatula, a timer, and a 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. Obtain from your lab instructor a sample of unknown molar mass. Record the sample number on your report sheet.

SAFETY:
1) CAUTION: The unknown sample is toxic. Make sure to handle it carefully without spilling. Wash your hands before leaving the lab.
2) Cyclohexane is very flammable, so the liquid and its vapors should not be exposed to any flames. You should also avoid smelling its vapors.
3) When the experiment has been completed, dispose of the cyclohexane in the red waste container The waste container is found under the fume hood.
4) Return the vial containing the unused unknown to your instructor.

3. 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 data sheet (page 7).

4. Use the graduate cylinder found in the fume hood to transfer approximately 15 ml of cyclohexane into the test tube. Recork the test tube and reweigh it in the tared beaker to within 0.01 g. Record the mass on the data sheet (page 7).

PART A: THE FREEZING POINT OF CYCLOHEXANE:

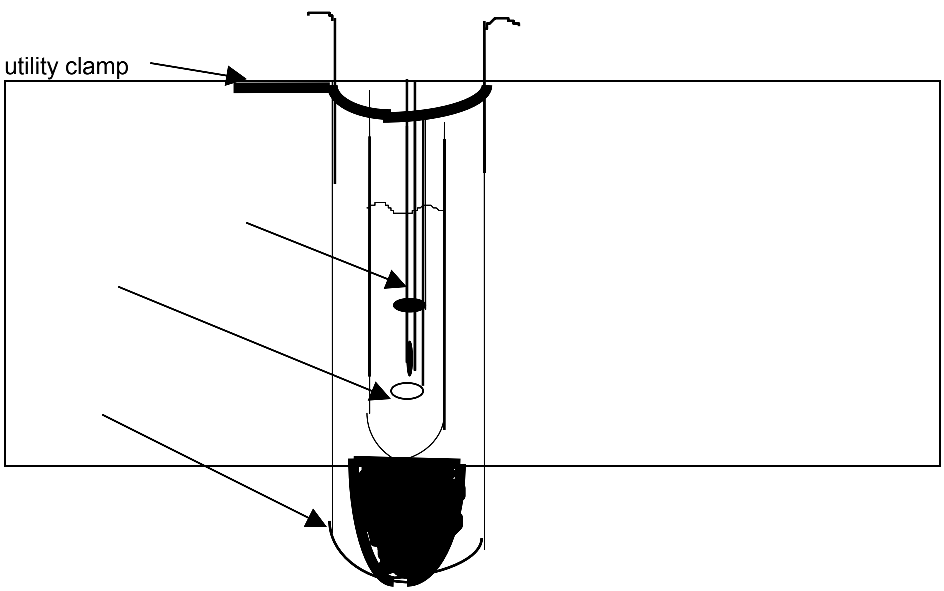
1. Fill a 600 ml beaker with ice. Add 15 g of rock salt. Add enough water to almost cover the ice. Stir. This beaker will be used as an ice bath. Check the ice bath temperature using the thermometer from your drawer. Do not use the thermometer for stirring (it can break easily). If the bath is not at 0 °C or lower add more rock salt to lower the temperature.

2. 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.

3. 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 given below. The cork helps adsorbing the shock during stirring. The outer test tube serves as an air- jacket to prevent the solvent from cooling too quickly.

4. Immerse the assembled test tubes into the ice bath and secure the outer test tube by using a utility clamp attached to a ring stand as shown in the figure. Make sure that the entire cyclohexane sample is immersed in the ice bath.

5. 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 from 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.



6. 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 warming up to about room temperature.

7. While the cyclohexane is melting, on the graph paper provided by the instructor plot a cooling cove for cyclohexane. Graph the temperature of the cyclohexane as it cools versus the 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 point depending on the **purity** of your cyclohexane and the **accuracy** of your thermometer reading.

PART B: THE FREEZING POINT OF THE SOLUTION

CAUTION: 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) Weigh accurately between 0.2000 - 0.2500 grams of unknown as follows:

a) Tare a piece of **weighing paper** on the analytical balance.

b) Pour out carefully between 0.2000 - 0.2500 grams of unknown onto the piece of weighing paper. Note: It helps in pouring to put a crease in the weighing paper before you pour out the sample onto it! **DO NOT LOSE ANY UNKNOWN!**

c) Record the mass of your unknown on the report sheet page 7.

NOTE: RETURN ALL UNUSED UNKNOWN TO YOUR INSTRUCTOR IN ITS ORIGINAL VIAL.

2) **Quantitatively**, 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 labeled, "Freezing Point Unknown/Weighing Paper Waste" , found under the Hood.

3) **COMPLETELY** dissolve the unknown by stirring.

4) Drain some of the excess water from the ice bath. Add approximately ten grams of rock salt and 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.

5) Again reinsert the freezing point test tube into the larger tube which is attached to a ring stand.

6) Immerse the large tube containing the freezing point apparatus into the rock -ice bath.

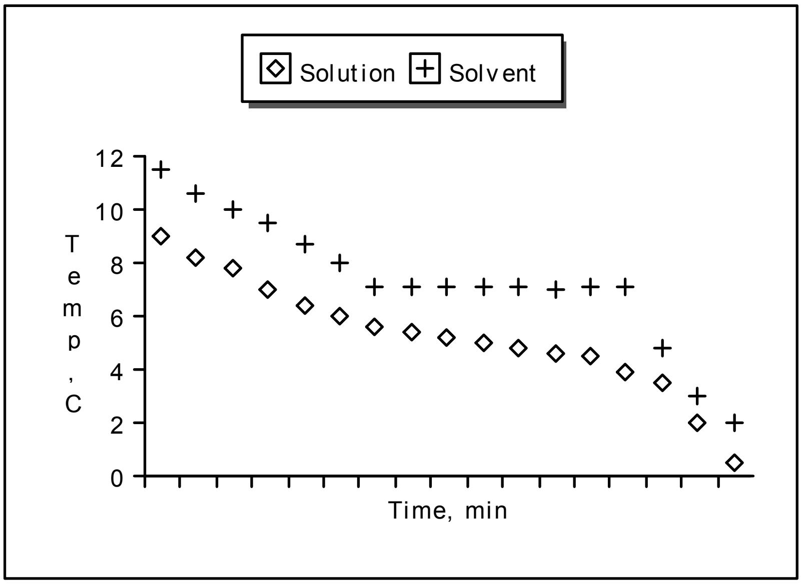
7) Stir the cyclohexane solution gently and start taking readings and record your data on the report sheet page 9 as before. Do not take the tube out of the ice -bath while taking readings to see if it is frozen yet!

8) 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 no visible crystals, you may have not reached the freezing point of the mixture. You will need to **repeat the entire freezing** 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 IS IMMISCIBLE.

CALCULATIONS:

1) On the graph paper plot temperature versus time for the cooling curve for the cyclohexane alone and then plot temperature versus time for the cooling curve for the unknown -cyclohexane solution. Label your axis and each curve. The freezing points of cyclohexane and cyclohexane solution are obtained from the cooling curves as follows:



a) The freezing points of cyclohexane alone reaches a **plateau** at its freezing point. Extrapolation of the plateau to the temperature axis determines its freezing point.

b) 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.

2) Find the difference in freezing points , ΔT_f, of cyclohexane and that of cyclohexane solution. On the graph mark the freezing points that you chose to calculate ΔT_f.

3) Calculate the molar mass of your unknown as illustrated in the exercise given on page 2.

EXPERIMENT

Name ______________________
Last First

Molar Mass by Freezing Point Depression

Instructor's initial____________

REPORT SHEET

Part A: Cyclohexane data

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

Mass of cyclohexane = ______________ g

Data approval _________________
(instructor's approval)

Time-temperature data for **cyclohexane**:

Time, min	Temp,° C	Time	Temp,° C	Time	Temp,° C	Time	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**			

Data approval _____________

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

Time, min	Temp,° C	Time	Temp,° C	Time	Temp,° C	Time	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**			

Part B: Unknown solution data
Unknown number ____________

Mass of unknown = __________ g

Time-temperature data for **cyclohexane unknown solution**

Time, min	Temp,° C	Time	Temp,° C	Time	Temp,° C	Time	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**			

Data approval ________________

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

Time, min	Temp,° C	Time	Temp,° C	Time	Temp,° C	Time	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**			

Calculations:

1. Freezing point of cyclohexane from your graph. ____________________° C

2. Freezing point of unknown-cyclohexane solution. ____________________° C

3. Freezing point depression, ΔT_f.
   Show calculation:
   ____________________° C

4. Molality of the solution.
   (K_f for cyclohexane= 20.0 °C.kg/mol.)
   Show calculation:
   _______________mole/kg

5. Mass of solvent (cyclohexane) in units of kg. ____________________kg

6. Moles of the unknown.
   Show calculation:
   ________________mol

7. Molar mass of the unknown.
   Show calculation:
   _______________g/mole

8. Unknown number _______________

PROBLEMS:

1) 5.00 kg glycol, $C_2H_4(OH)_2$, [this is antifreeze!] is added to your radiator. If your radiator contains 12.0 kg of water, what would be the freezing point of the water-antifreeze mixture? The molal freezing point depression constant for water is 1.86 ˚C.kg/mole.
Setup:

Answer_________________

2) How many grams of ethanol, $C_2H_5OH(l)$, must be added to 500.0 g of water to make a solution that freezes at 0.00 ºF? The molal freezing point depression constant for water is 1.86 ˚C.kg/mole.
Setup:

Answer_____________

3) 3.92 g of a nondissociating compound are dissolved in 400. g of liquid benzene. The freezing point of the solution is 5.19 ˚C. Calculate the molar mass of the compound. (The freezing point of pure benzene is 5.50 ˚C and its molal freezing point depression is 5.12 ˚C.kg/mole).
Setup:

Answer______________

4) a) If a thermometer is miscalibrated to read 1.0 ºC higher than the actual temperature over its entire scale, will the reported molar mass of the solute be: a) too high, b) too low, or c) the same.
(Hint: Follow a complete set-up for the calculation to see the effect of the error.
Explain:

b) If the cyclohexane is initially contaminated with a soluble non-reactive, nonvolatile substance, will the change in freezing point, ΔT_f, be a) higher b) lower, or c) the same as the uncontaminated cyclohexane?
Explain:

5) Explain why the freezing point of a pure solvent is constant, whereas the freezing point of a solution decreases with steady cooling.