
Freezing Point Depression

INTRODUCTION

A liquid with something dissolved in it has different physical properties than the pure liquid alone. We call the liquid a *solvent*, the substance dissolved in it a *solute*, and the resulting mixture a *solution*. Compared to the values for the pure solvent, the vapor pressure of the solvent in the solution drops, the boiling point goes up, and the freezing point goes down. If a sample of the solution is placed side-by-side to the pure solvent with a porous barrier of the proper pore size separating them, osmosis will occur. Osmosis is an unequal flow rate through the porous barrier for the two liquids. All of these changes take place because some of the solvent molecules have been replaced by solute molecules (or ions). Because of this replacement, there are fewer solvent molecules per unit of volume in the solution than there are in the pure solvent. Hence, in the solution, not as many solvent molecules are available to leave the liquid and enter the gas phase or the solid phase as there are in the pure solvent. Similarly, there are not as many solvent molecules on the solution side as there are on the pure solvent side to pass through a porous barrier.

These physical properties of solvents that change as solutes are dissolved in solvents are called *colligative properties*. The amount of change depends on the number, not the kind, of solute molecules added per unit of solvent molecules. When NaCl is dissolved in H₂O, two particles (Na⁺ and Cl⁻) are produced for every one formula unit added. If CH₃OH is dissolved in water, no dissociation occurs, and the number of molecules added is the same as the number of formula units added. To take account of this, an *i* factor is used in calculating concentrations of solutes in solvents. NaCl has *i* = 2. CH₃OH has *i* = 1. For freezing point depression and boiling point elevation, colligative molality is the concentration unit. If a solution of NaCl in water had a molality of 1, then its colligative molality, m_c , would be 2. That is, $m_c = i \cdot m$. Ionic compounds usually have an *i* > 1. Covalently bonded substances often have *i* = 1.

In this experiment, you will observe the freezing point depression (ΔT_f) that takes place when a solute is dissolved in a solvent.

In **Part 1**, you will measure the freezing point of pure cyclohexane (C₆H₁₂).

In **Part 2**, you will add a measured quantity of paradichlorobenzene (C₆H₄Cl₂) to the cyclohexane and measure the freezing point of the solution. You will use

this data to calculate the freezing point constant (K_f) for cyclohexane. The relationship is

$$\Delta T_f = K_f \cdot m_c \quad (\text{equation 1})$$

In **Part 3**, you will add a measured amount of an unknown substance to cyclohexane, and use the freezing point depression to calculate the molecular mass of the unknown. To do this, insert the units of molality in equation 1:

$$m_c = \frac{\text{mol}_{\text{solute}}}{\text{kg}_{\text{solvent}}}$$

Moles of solute can be calculated by dividing the grams of solute by the molecular mass of the solute:

$$\text{mol}_{\text{solute}} = \frac{\text{g}_{\text{solute}}}{\text{MM}_{\text{solute}}}$$

If these substitutions are made, equation 1 becomes

$$\Delta T_f = \frac{K_f \cdot \text{g}_{\text{solute}}}{\text{kg}_{\text{solvent}} \cdot \text{MM}_{\text{solute}}}$$

This is rearranged to give

$$\text{MM}_{\text{solute}} = \frac{K_f \cdot \text{g}_{\text{solute}}}{\text{kg}_{\text{solvent}} \cdot \Delta T_f} \quad (\text{equation 2})$$

All of the substances used in this experiment are covalently bonded, and they do not dissociate in cyclohexane, so that *i* is equal to 1.

A major problem in this experiment is measuring the freezing point. Visually reading a thermometer gives marginal accuracy. The better way to get the data would be to use a temperature dependent diode connected to a recording device. We are not equipped to do this in our lab.

EQUIPMENT

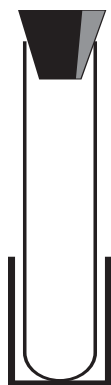
Work in pairs

- A kit from the storeroom containing:
 - 1 heavy gauge copper stirring rod
 - 20 x 150 disposable test tube
 - 1-hole stopper with a slit
 - 1 small vial
- 1 thermometer
- 1-400 ml beaker
- 1-250 ml flask
- 1 stirring rod
- Rock salt (to fill a 50 ml beaker)
- Ice (to fill the 400 ml beaker)
- Hardware for the setup diagrammed on the next page

EXPERIMENT

Part 1: Freezing point of pure cyclohexane

Use a 10 ml graduated cylinder to measure 10 ml of cyclohexane. Do not use a transfer pipet from your locker, but directly pour from the reagent bottle. Bring the graduated cylinder with the cyclohexane to the balance, along with the



vial, test tube, and stopper. If using an electronic balance, first place the vial on the balance and zero it out. Then place the test tube and stopper in the vial as shown at left, and record the weight to the nearest 0.001 g in Data Table item 1. Pick the test tube up and hold it away from the balance while you add the cyclohexane to the test tube. Weigh the assembly again, and record the weight to the nearest 0.001 g in Data Table item 2. **At your work area, set the test tube assembly in the flask when you are not holding it.** Put the apparatus together as shown in the diagram at right. Make sure you can read from 10° on down through zero and below

on the thermometer. You will be reading the temperatures through the wall of the test tube. The stopper should not be inserted very tightly into the test tube. Hold the test tube at the stopper with one hand, while your other hand is on the stirrer. Fill the beaker with ice, then add water to an inch of the top of the beaker. **Once you immerse the test tube into the ice bath, stir the cyclohexane constantly.** Lift the test tube out of the ice occasionally to see if crystals of solid are forming in the liquid or if solid cyclohexane is forming on the walls of the test tube. Note the temperature at that point. There should only be small amounts of solid formed. Pull the test tube out of the ice bath until all the solid melts, then repeat the measurement of the freezing point. If the second temperature varies from the first by more than 0.1°C, repeat until you get identical readings. Record the temperature to the nearest 0.1°C in Data Table item 4.

Part 2: Obtaining a value of K_f

Pour the water off of the ice in the beaker. Add more ice to bring the level to within an inch of the top. Pour the rock salt from the 50 ml beaker onto the ice. Stir the ice/salt mix well with a stirring rod. Add enough water to bring the liquid level to just under the ice level. Weigh out between 0.5 and 0.6 grams of paradichlorobenzene on a weighing paper. Make sure you zero out the weight of the paper. Record the weight to the nearest 0.001 g in Data Table item 5. Add this to the cyclohexane in the test tube from Part 1. Stir until all of the p-dichlorobenzene dissolves. Warm the tube in your hand if necessary. Place the test tube in the ice/salt mix, and stir the contents of the test tube constantly as in Part 1. Look at the contents of the test tube often. Try to catch the temperature when the first solid or crystals appear. Record that temperature to the nearest 0.1°C in Data Table Part 2 item 6. Warm the tube to melt the crystals, and repeat the freezing point observation. Record the second value. It is more difficult to get good consistent data with solutions than it is with pure solutes, so use the average value of your data in Part 2 (rather than trying to get identical readings).

POUR THE CONTENTS OF THE TEST TUBE INTO THE WASTE CONTAINER.

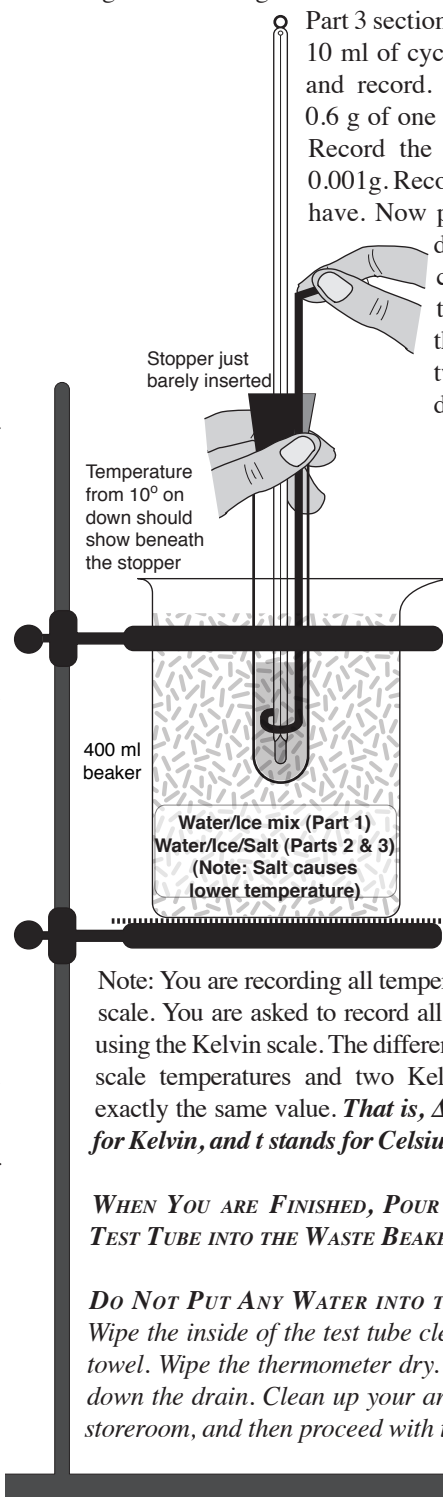
Use a folded paper towel to get the last of the liquid out of the test tube. Dry the thermometer with a paper towel.

DO NOT USE WATER FOR CLEANUP OF THE TEST TUBE ASSEMBLY.

Part 3: Molecular mass of an unknown substance

Reweigh the empty test tube and the stopper in the vial, zeroing the vial weight as before. Record the weight in the

Part 3 section of the Data Table. Add 10 ml of cyclohexane. Weigh again and record. Add between 0.5 and 0.6 g of one of the unknown solids. Record the weight to the nearest 0.001g. Record which unknown you have. Now proceed as in Part 2 to dissolve the solid in the cyclohexane. Determine the freezing point of the solution, taking two measurements as directed in Part 2.



Note: You are recording all temperatures using the Celsius scale. You are asked to record all changes in temperature using the Kelvin scale. The difference between two Celsius scale temperatures and two Kelvin temperatures gives exactly the same value. **That is, $\Delta T = \Delta t$, where T stands for Kelvin, and t stands for Celsius.**

WHEN YOU ARE FINISHED, POUR THE CONTENTS OF THE TEST TUBE INTO THE WASTE BEAKER.

DO NOT PUT ANY WATER INTO THE WASTE BEAKER.

Wipe the inside of the test tube clean with a folded paper towel. Wipe the thermometer dry. Pour the icy salt water down the drain. Clean up your area, return the kit to the storeroom, and then proceed with the calculations.

Data Table		Parts 1 & 2		Part 3	
		Part 2: Solute is p-dichlorobenzene		Solute is Unknown Substance	
1.	Mass of empty test tube, stopper	g		g	
2.	Mass after adding cyclohexane	g		g	
3.	Mass of cyclohexane	g		g	
4.	Freezing point of pure cyclohexane	°C			
5.	Mass of added solid	dichlorobenzene	g	Unknown#_	g
		Trial 1	Trial 2	Trial 1	Trial 2
6.	Freezing point of the solution	°C	°C	°C	°C
7.	ΔT_f (4-6) Note that $\Delta t \text{ } ^\circ\text{C} = \Delta T \text{ Kelvin}$	K	K	K	K
8.	Average ΔT_f	K		K	
Calculations	Show calculations below.	You will usually have 2 or 3 significant digits.			
9.	kg of cyclohexane (from Parts 1&2, #3)	kg			
10.	Moles of p-dichlorobenzene (from Parts 1&2, #5: $\text{C}_6\text{H}_4\text{Cl}_2$, $147.0 \text{ g}\cdot\text{mol}^{-1}$)	mol			
11.	Molality of solution, Parts 1&2 $m = \frac{\text{mol}_{\text{solute}}}{\text{kg}_{\text{solvent}}}$	<i>m</i>			
12.	ΔT_f for p-dichlorobenzene (value in Parts 1&2, #8)	K			
13.	K_f value for cyclohexane $\Delta T_f = K_f m$; solve for K_f	$\text{K}\cdot\text{m}^{-1}$			
14.	ΔT_f for unknown (value in Part 3, #8)	K			
15.	Molecular mass of unknown $\text{MM} = \frac{K_f \cdot \text{g}_{\text{unknown}}}{\Delta T_f \cdot \text{kg}_{\text{solvent}}}$; use Part 3 data	$\text{g}\cdot\text{mol}^{-1}$			

QUESTIONS

1. Show a step by step transition from equation 1 on page 1 to equation 2 on page 1 substituting the expressions given.
2. In part 2 of the experiment, as crystals of solid form, pure cyclohexane is the substance in the crystals. (This is the general process that takes place when a solution freezes. When salt water freezes, the solid that forms is pure water, not salt water.) What happens to the concentration of the p-dichlorobenzene in the liquid cyclohexane as pure cyclohexane freezes out of the solution? What does that do to the freezing point of the solution if the freezing process is carried out for some time? (That is, does the freezing point stay constant, or does it change. If it changes, in what direction does it change?)
3. The addition of salt to the ice in part 2 is an application of the freezing point depression property. In equation 1, K_f for water is $1.86\text{K} \cdot \text{m}_c^{-1}$. For salt, m_c is two times the molality. How many grams of salt must dissolve in 400 grams of water to lower the ice bath temperature to -10°C ?
4. If all of the solid does not dissolve in part 2, would the K_f you calculate be high or low? (Look at items 13 and 11 on page 3. If all the p-dichlorobenzene does not dissolve, is the value of m you use high or low? What does this do to the K_f you calculate?)
5. If all of the unknown does not dissolve in part 3, would the calculated molecular mass be high or low? Do an analysis for item 15 on page 3 similar to the analysis you did in question 4.