

Molar Mass of an Unknown Organic Solid by Freezing Point Depression

Goal and Overview

The decreases in the freezing points of a series of solutions of known molalities will be used to determine the freezing depression constant, K_f , of cyclohexane. The molar mass of an unknown organic solid will be found via the freezing point change observed for a cyclohexane solution containing a known mass of the unknown solid.

Objectives and Science Skills

Understand and explain colligative properties of solutions, including freezing point depression.

Measure the freezing point of a pure solvent and of a solution in that solvent containing an unknown solute.

Calculate the molar mass of the unknown solute and determine its probable identity from a set of choices.

Quantify the expected freezing point change in a solution of known molality.

Quantitatively and qualitatively compare experimental results with theoretical values.

Identify and discuss factors or effects that may contribute to the uncertainties in values determined from experimental data.

Suggested Review and External Reading

Reference material and textbook sections on molality, phase changes, thermodynamics, and colligative properties

Introduction

Under constant pressure conditions, if a pure liquid (the system) is at a higher temperature than its surroundings, the liquid's temperature will decrease until it reaches its freezing point, T_f . As the phase change from liquid to solid occurs, the temperature will remain constant as the potential energy of the system decreases. The temperature will only begin to fall again once the entire volume of liquid has frozen.

The quantity of heat released during the freezing process is equal in magnitude but opposite in sign to the heat of fusion, ΔH_{fus} . ΔH_{fus} is defined as the heat absorbed by the solid during the melting process, so $\Delta H_{\text{fus}} = -\Delta H_{\text{freezing}}$. The freezing point of a liquid and the melting point of a solute occur at the same temperature, and at this temperature the solid and liquid phases coexist in equilibrium.

If a solute is dissolved into the liquid, it is generally assumed that the solute does not enter the solid phase because the incorporation of solute particles into the solid is generally energetically unfavorable. The solute remains in the solution (liquid phase).

On a macroscopic level, the freezing point decrease associated with adding a solute to a pure liquid has probably been observed (*e.g.*, salt added to snow and ice on frozen roadways; using salt-ice-water baths to make ice cream; etc.). On a molecular level, the phenomenon can be explained by thermodynamics – both enthalpy and entropy are important. In a simplified view, one can think of the solute as increasing the entropy of the solution relative to that of the pure solvent, so the temperature must be lower in order for the solution to freeze; the freezing point is depressed. In the ideal case, the change in the freezing point is proportional to the amount of solute added to the solvent.

Freezing point depression is one of four important colligative properties of ideal solutions (freezing point depression, boiling point elevation, vapor pressure reduction, and osmotic pressure increase). The changes in the solvent's properties are assumed independent of the solute's identity and solely dependent on concentration.

Molality is generally the preferred concentration unit when quantifying freezing point depression because volume changes can be significant at phase changes.

$$\text{Molality, } m = \frac{\text{amount of solute in mol}}{\text{mass of solute in kg}} = \frac{n_{\text{solute}}}{\text{kg}_{\text{solvent}}}$$

In an ideal solution, the magnitude of the freezing point change is proportional to the molality of the solution, with a proportionality constant called the freezing point depression constant, K_f , with units of $^{\circ}\text{C} \cdot \text{kg}/\text{mol}$; this course uses the convention of positive K_f values. Each solvent has a unique K_f . The equation works best with low solute concentrations and when solute-solvent/solvent-solute intermolecular forces are similar.

$$\Delta T_f = T'_{f_{\text{solution}}} - T_{f_{\text{solvent}}} = -K_f \cdot m = -K_f \cdot \frac{n_{\text{solute}}}{\text{kg}_{\text{solvent}}}$$

The equation can be rearranged to solve for moles of solute.

$$n_{\text{solute}} = -\frac{\Delta T_f \cdot \text{kg}_{\text{solvent}}}{K_f}$$

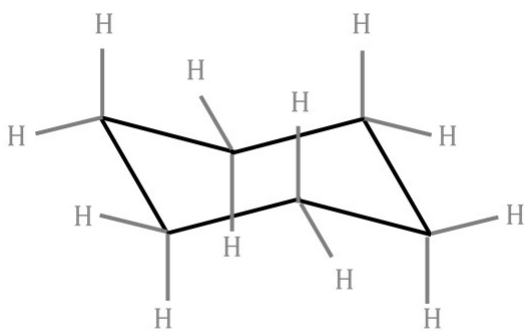
If known masses of solute and solvent are used, the solute's molar mass can be determined.

$$MM_{\text{solute}} = \frac{\text{mass}_{\text{solute}} \text{ in grams}}{\text{amount}_{\text{solute}} \text{ in moles}} = \text{mass}_{\text{solute}} \times \left(-\frac{K_f}{\Delta T_f \cdot \text{kg}_{\text{solvent}}} \right)$$

This lab uses cyclohexane as the solvent. Cyclohexane molecules primarily experience London dispersion forces, and low molality solutions produce significant freezing point changes because K_f is fairly large at $20.2 \text{ }^\circ\text{C} \cdot \text{kg}/\text{mol}$.

Cyclohexane, C_6H_{12}

Molar mass, MM	84.160 g/mol
Density, $\rho^{20^\circ\text{C}}$	0.779 g/mL
Normal freezing point, T_f	6.5°C
Freezing point depression constant, K_f	$20.2 \text{ }^\circ\text{C} \cdot \text{kg}/\text{mol}$



C_6H_{12} (C atoms are not labeled)

Equipment List

250- or 400-mL labeled beaker for ice-water bath, ice, deionized water
 test tube, clamp, stand
 stir plate, magnetic stir bar
 thermometer*, split stopper
 analytical balance
 cyclohexane, p-dichlorobenzene, unknown organic solid
pipet, pipetter

*It is likely that you will use an alcohol thermometer ($\pm 0.1^\circ\text{C}$). If you use a mercury thermometer (usually $\pm 0.01^\circ\text{C}$), be very careful.

Procedure

Caution

Cyclohexane is **flammable**. Any sources of flames or sparks are not permitted.

Cyclohexane has a **distinctive odor**. Prolonged inhalation can cause dizziness and drowsiness, but the procedure is designed to minimize risk. Please carefully follow the procedure and your TA's instructions. Keep a stopper in the test tube containing the cyclohexane or solution as much as possible.

Both the p-dichlorobenzene and the solid organic unknown are **mild skin irritants**. You can use gloves, but please also wash your hands thoroughly.

If you pipet the cyclohexane volumes, use the dedicated pipets from the reagent counter. Please be careful with the pipet and pipetter. Do not push the pipet into the pipetter with force; only a seal is required to draw the liquid into the pipet. Give any pipetter contaminated with liquid to your TA. Do not wash the pipet with water; return it to the reagent counter.

Never try to push a thermometer through a rubber stopper. Always make sure you are using a **split stopper**, and always **pull the stopper open** before trying to insert or adjust the thermometer. If you do not pull the stopper open, the thermometer might break and significantly injure your hand.

When you are finished with a solution, carefully remove the split stopper/thermometer and gently insert the solid stopper. Ask your TA if you are to remove the stir bar. Label the test tube with your name(s), date, and contents. Place the test tube in the rack in the waste fume hood. Do not pour anything down the sink.

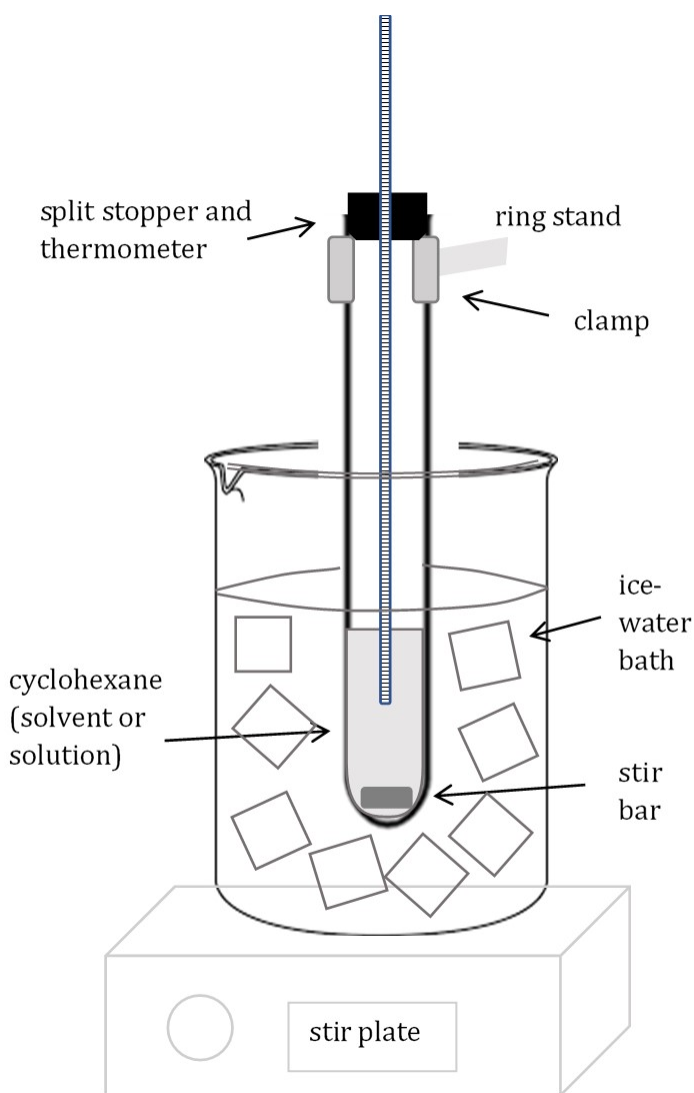
General procedure to determine freezing point (pure solvent or solution)

1. Ask your TA if you are to pipet the cyclohexane volumes you will use or if the solvent has been pre-measured and dispensed for you.
 - If the cyclohexane has been dispensed for you, obtain one test tube containing 20.00 mL cyclohexane from the fume hood. Please leave the solid stopper in until you are ready to determine the freezing point. Calculate the mass of cyclohexane in kilograms.

$$\text{mass cyclohexane} = 20.00 \text{ mL} \times \frac{0.779 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ kg}}{1000 \text{ g}}$$

- If you are to pipet your own cyclohexane volume into the test tube, place the test tube with solid stopper into a small beaker and record the mass on the pan balance (± 0.01 g). Working in the fume hood, use one of the dedicated volumetric pipets to pipet 20.00 mL cyclohexane out of a small labeled beaker into the test tube. Gently insert the solid stopper. Do not pipet out of the reagent bottle. Please be careful with the pipet and pipetter. Mass the beaker, test tube, stopper, and cyclohexane. Gently slide the magnetic stir bar into the liquid, quickly removing and replacing the solid stopper. Leave the solid stopper in place until you are ready to determine its freezing point. Calculate the mass of cyclohexane in grams by difference and convert to kilograms.

2. Set a large beaker (250- or 400-mL) on the stir plate. Hold the test tube containing the cyclohexane (or solution) so that it is inside the beaker but so that its base is a short distance from the bottom of the beaker (and top of the stir plate). Carefully fasten the test tube at this level with the clamp on the ring stand.



3. Carefully pour ice into the beaker around the test tube so that the level of the ice is slightly above the level of the cyclohexane (or solution) in the test tube. Add some deionized water to the ice to create an ice-water slurry.

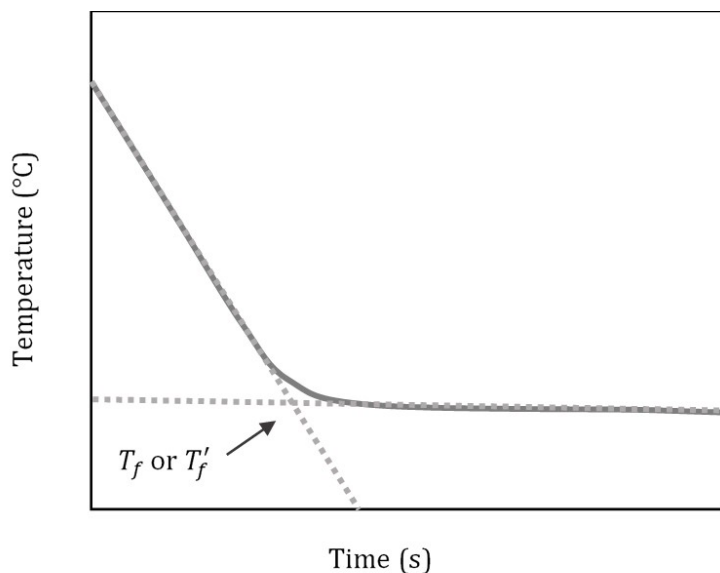
4. Carefully pull a split stopper open and insert the thermometer. Holding the thermometer to the side of the test tube and beaker, adjust the height of the thermometer so that the bulb will be in the cyclohexane (or solution) but above the stir bar. Please pull the split stopper open before trying to move the thermometer; do not try to push the thermometer up or down. Make sure you can see the thermometer gradations (lines).

5. Quickly remove the solid stopper from the test tube and gently insert the split stopper/thermometer. Turn on the stir plate to a low setting so that the stir bar is slowly rotating.

6. To determine the freezing point, you will follow one of two methods, and you may be asked to perform repeated trials. Ask your TA which method to use and how many trials are required.

- Method 1: Watch the temperature fall until it levels off at a temperature above 0.0°C . You should see the cyclohexane (or solution) in the test tube turning to a slush of liquid and solid. As precisely as possible, record this temperature to one decimal place ($\pm 0.1^{\circ}\text{C}$) and take it as the freezing point.
- Method 2: When the temperature of the cyclohexane (or solution) reaches approximately 13.0°C , start recording temperature to one decimal place every 5 seconds, transitioning to 10 second intervals when the rate at which the temperature changes has slowed down. When the cyclohexane (or solution) starts to freeze, the temperature changes will be very small. Take several data points after this happens (when the temperature is relatively constant).

To determine the freezing point, plot temperature vs. time for each trial. Use a straight edge to draw a line tracing the decrease in temperature. Draw a second straight line that traces the roughly constant temperature; this line should be roughly horizontal. Determine the temperature where the lines intersect and take this as the freezing point.



Part 1. Freezing point of pure cyclohexane and determination of K_f

Follow your TA's instructions regarding which method to use (method 1 or method 2).

7. Determine T_f of pure cyclohexane to one decimal place ($\pm 0.1^\circ\text{C}$). Perform repeat trials as instructed.

Check with your TA if you are to find K_f experimentally or if you are to use the literature K_f value of $20.2^\circ\text{C} \cdot \text{kg}/\text{mol}$. If the latter is the case, go to part 2.

If you are determine K_f experimentally, you will prepare cyclohexane solutions of known molalities using p-dichlorobenzene (p- $\text{C}_6\text{H}_4\text{Cl}_2$, 147.0 g/mol) as the solute, measure their freezing points, and extract K_f by graphical analysis of the solutions' changes in freezing point.

Caution

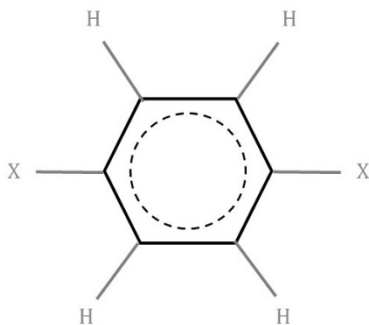
p-Dichlorobenzene is an **irritant with a strong odor**. Wear gloves while handling it and work in a fume hood as much as possible. Use a weigh boat when massing the p- $\text{C}_6\text{H}_4\text{Cl}_2$ and keep the analytical balance area clean. Do not leave the bottle of p- $\text{C}_6\text{H}_4\text{Cl}_2$ in the balance room (return it to the reagent hood). The procedure lists the ideal masses of p- $\text{C}_6\text{H}_4\text{Cl}_2$ to use; use the masses you actually measured on the analytical balance (four decimal places, ± 0.0001 g) in your molality calculations.

8. Determine T_f of a 0.050 m solution prepared by dissolving 0.1145 g p-C₆H₄Cl₂ in 20.00 mL cyclohexane.
9. Determine T_f of a 0.10 m solution prepared by adding 0.1145 g p-C₆H₄Cl₂ to the 0.050 m solution that you have already made.
10. Determine T_f of a 0.15 m solution prepared by adding another 0.1145 g p-C₆H₄Cl₂ to the 0.10 m solution that you have already made.
11. When you are finished with a solution, follow the handling instructions. An appropriate waste label for your test tube includes your name(s), date, and contents (*e.g.*, cyclohexane containing p-dichlorohexane, $\sim 0.15 m$).

Part 2. Molar mass of an unknown organic solid from ΔT_f

Caution

The solid unknown will likely be a p-dihalobenzene, p-C₆H₄X₂, where X = F, Cl, Br, or I.



Some p-dihalobenzenes can be **irritants with strong odors**. Wear gloves while handling it and work in a fume hood as much as possible. Use a weigh boat when massing it and keep the balance area clean. Do not leave the bottle of unknown in the balance room; please return it to the reagent hood.

12. Mass out approximately 0.3700 g of the solid unknown p-C₆H₄X₂ on the analytical balance. Record the actual mass to four decimal places (± 0.0001 g). Add the massed unknown to the test tube containing 20.00 mL cyclohexane. Determine T_f' . Perform repeat trials as instructed.
13. When you are finished with a solution, follow the handling instructions. An appropriate waste label for your test tube includes your name(s), date, and contents (*e.g.*, cyclohexane

containing solid organic unknown p-C₆H₄X₂). Wash your hands and wipe down your lab bench.

Calculations

14. Calculate ΔT_f for each solution that you prepared.

15. If you performed part 2, calculate the molality of each p-dichlorobenzene solution.

$$m = \frac{n_{\text{solute}}}{\text{kg}_{\text{solvent}}} = \frac{\# \text{ grams}_{\text{p-C}_6\text{H}_4\text{Cl}_2}}{\# \text{ kg}_{\text{C}_6\text{H}_{12}}} \times \frac{1 \text{ mol}}{147.0 \text{ g}}$$

Create a plot that graphs $-\Delta T_f$ vs. molality. You should have four data points for $\sim 0 m$, $\sim 0.050 m$, $\sim 0.10 m$, and $\sim 0.15 m$ (use your experimental molalities). Determine the slope of the best-fit line that has a y-intercept forced through (0,0). The slope is your experimental K_f . Calculate the % error relative to the literature value of $20.2 \text{ }^\circ\text{C} \cdot \text{kg}/\text{mol}$.

If you did not perform part 2, use the literature value for $K_f = 20.2 \text{ }^\circ\text{C} \cdot \text{kg}/\text{mol}$.

16. Calculate the molar mass of your unknown.

$$MM_{\text{solute}} = \frac{\text{mass}_{\text{solute}} \text{ in grams}}{\text{amount}_{\text{solute}} \text{ in moles}} = \text{mass}_{\text{solute}} \times \left(-\frac{K_f}{\Delta T_f \cdot \text{kg}_{\text{solvent}}} \right)$$

17. You may be asked to identify the solid organic unknown based on its molar mass. Typical unknowns include the p-dihalobenzenes, p-C₆H₄X₂, where where X = F, Cl, Br, or I.

Formula	Name	Molar mass
p-C ₆ H ₄ F ₂	p-difluorobenzene	114 g/mol
p-C ₆ H ₄ Cl ₂	p-dichlorobenzene	147 g/mol
p-C ₆ H ₄ Br ₂	p-dibromobenzene	236 g/mol
p-C ₆ H ₄ I ₂	p-diiodobenzene	330. g/mol

Results / Sample Calculations

T_f of cyclohexane; T'_f of the cyclohexane solutions prepared; and, ΔT_f for each solution
If K_f was determined experimentally: temperature-time graphs for the p-dichlorobenzene solutions and the experimental K_f (and % error)
Molar mass and identity of the solid organic unknown

Complete the online inlab or write a lab report as directed by your TA.

Discussion Questions and Review Topics

What did you find and how did you do it?

How close were your experimental values to those expected/in literature? What are possible reasons for the observed differences?

What changes to the procedure might improve the accuracy and precision of the results?

Water is a polar solvent with $K_f = 1.86 \text{ } ^\circ\text{C} \cdot \text{kg}/\text{mol}$. How large would be freezing point change be for a $0.05 \text{ } m$ aqueous solution? How easy would it be to measure that change experimentally? In order to observe a 2.5°C drop in the freezing point, what molality would be required? Would you expect the solution to behave ideally, particularly at higher molalities?