

Experiment 5

Colligative Properties - Freezing Point Depression

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Name:

Date:

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Key Objectives

1. Define colligative properties
2. Explain why the freezing point decreases for an impure substance
3. Measure the freezing point depression constant for a solvent
4. Measure the molecular weight of an unknown compound

Discussion

Colligative Properties

The properties of a solution (solute + solvent) (impure substance) are different than those of the pure solvent (pure substance). Depending on the nature of the solute it may effect both the chemical properties (by a chemical reaction) and the physical properties of the solution (density or viscosity). Some physical properties are only effected by the amount (moles, atoms or molecules) of solute and **NOT** on the chemical identity of the solute. These properties are collectively called **Colligative Properties** and include the vapor pressure, boiling point, freezing point and osmotic pressure.

Everyday examples of all four properties abound from the use of fractional distillation to separate crude oil into different fuels, the use of ethylene glycol (anti-freeze) in engines to both raise the boiling point and lower the freezing point of water in car radiators, salting of roads to melt ice and importance of osmotic pressure in reverse osmosis purification of water.

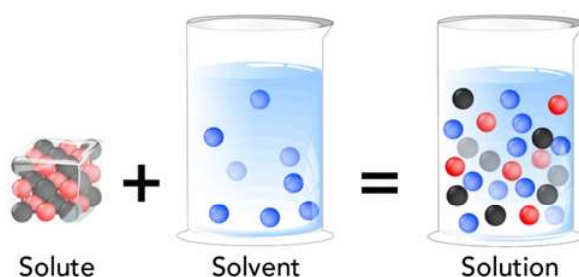


Figure 5.1: A solute (smaller quantity) is added to a solvent (larger quantity) to create a solution. credit: unknown

The first three colligative properties can be explained by examining the graph in Figure 5.2 showing the relationship between the vapor pressure, boiling point and freezing point of a pure substance (blue line) and the corresponding solution after addition of as solute or impure substance (red line). The vapor pressure of in impure substance is lowered by addition of a solute which effects the vapor pressure equilibrium by reducing the rate of evaporation of pure solvent molecules, but does not effect the rate

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of condensation. This simple explanation captures the basics, but a more detailed explanation would involve the entropy of the systems, which is beyond the scope of this experiment.

The lowering of the vapor pressure affects both the boiling point and freezing point of a substance. Boiling occurs when the vapor pressure of the solution is equal to the vapor pressure of the atmosphere, thus, an impure solution having a lower vapor pressure will require more energy to reach atmospheric pressure resulting in a higher boiling point. A similar argument can be made for the freezing point lowering as more energy must be removed from the liquid in order to freeze. As with vapor pressure lowering a more detailed explanation involving the entropy of the system is beyond the scope of the experiment.

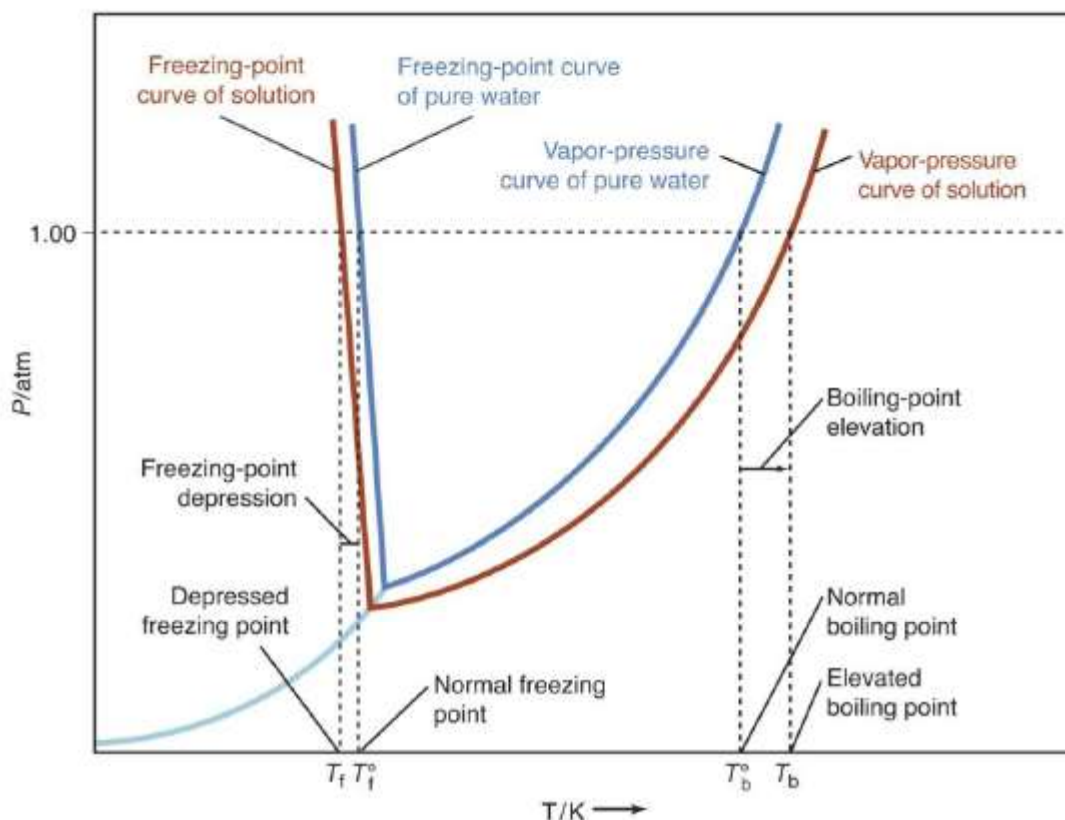


Figure 5.2: Phase diagram for a pure and impure substance showing the relationship between vapor pressure, boiling point and freezing point. credit: "Determination of the Molar Mass by Freezing Point Depression (Experiment)" by Santa Monica College, LibreTexts is licensed under CC BY-NC.

Mathematically colligative properties can be described using the equations in Figure 5.3. Notice that all of the equations depend in some way on the moles of solute dissolved in the solvent and do not depend on the chemical identity of the solute.

One use of colligative properties is the determination of molecular weight for unknown compounds. While osmotic pressure is the most sensitive to molecular weight, experimentally for us, the determination of freezing point depression is easier. A variety of different systems can be studied, Figure 5.6 gives the freezing point of a pure solution and the freezing point depression constant for a variety of solvents. Note that in general the change in the freezing point of a substance is larger than the corresponding change in the boiling point.

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<p>Vapor Pressure Lowering:</p> $\Delta P_{\text{soln}} = P_{\text{soln}} \cdot X_{\text{solute}}$ <p>ΔP = change in pressure (atm) X = mol fraction</p>	<p>Boiling Point Elevation:</p> $\Delta T_b = mK_b$ <p>ΔT = change in temperature ($^{\circ}\text{C}$) m = molality = $\frac{\text{mols solute}}{\text{kg of solvent}}$ K_b = molal boiling point elevation constant $\left(\frac{^{\circ}\text{C} \cdot \text{kg solvent}}{\text{mol solute}}\right)$</p>
<p>Osmotic Pressure:</p> $\Pi = MRT$ <p>M = molarity = $\frac{\text{mols solute}}{\text{L of solution}}$ $R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$ T = temperature (K)</p>	<p>Freezing Point Depression:</p> $\Delta T_f = mK_f$ <p>ΔT = change in temperature ($^{\circ}\text{C}$) m = molality = $\frac{\text{mols solute}}{\text{kg of solvent}}$ K_f = molal freezing point depression constant $\left(\frac{^{\circ}\text{C} \cdot \text{kg solvent}}{\text{mol solute}}\right)$</p>

Figure 5.3: Mathematical equations describing the dependence of the 4 colligative properties on the number of moles of solute (impurity) added. credit: author

Solvent	Freezing Point ($^{\circ}\text{C}$)	K_f $\frac{^{\circ}\text{C} \cdot \text{kg solvent}}{\text{mol solute}}$	Boiling Point $^{\circ}\text{C}$	K_b $\frac{^{\circ}\text{C} \cdot \text{kg solvent}}{\text{mol solute}}$
Water	0.0	1.86	100.	0.512
Acetic Acid	16.6	3.90	118.5	3.07
Benzene	5.5	5.1	80.1	2.53
Camphor	178	40.	208.2	5.95
Cyclohexane	6.5	20.2	80.75	2.79
Ethylene Glycol	197.3	2.26	-12.9	3.11

Figure 5.4: Freezing point, freezing point depression constant, boiling point and boiling point elevation constant for several compounds. credit: https://en.wikipedia.org/wiki/List_of_boiling_and_freezing_information_of_solvents

Determining the Freezing Point and Freezing Point Depression

Depending on the solvent chosen, the experiment can be performed using a hot-water bath (for solvents with freezing point $>$ room temperature) or with an ice-water bath (for solvents with freezing point $<$ room temperature). In either case the solvent is heated past its freezing point and allowed to cool while measuring the temperature as a function of time. Figure 5.5 shows the cooling data for a pure solvent and for a solution (impure).

As a pure solvent cools, it will freeze at a consistent temperature as shown in Figure 5.5(a). For an impure solution, once freezing starts, the temperature slowly decreases over time, to determine the freezing point draw a line as shown in Figure 5.5(b) and where it intersects the cooling data is the freezing point. Both curves may show a phenomenon called **super-cooling** which is a non-equilibrium state where a liquid is still liquid below the freezing point, but rises to the freezing point as it begins to solidify. When drawing the straight line in the solid-liquid region of the graph, ignore points where super-cooling is observed.

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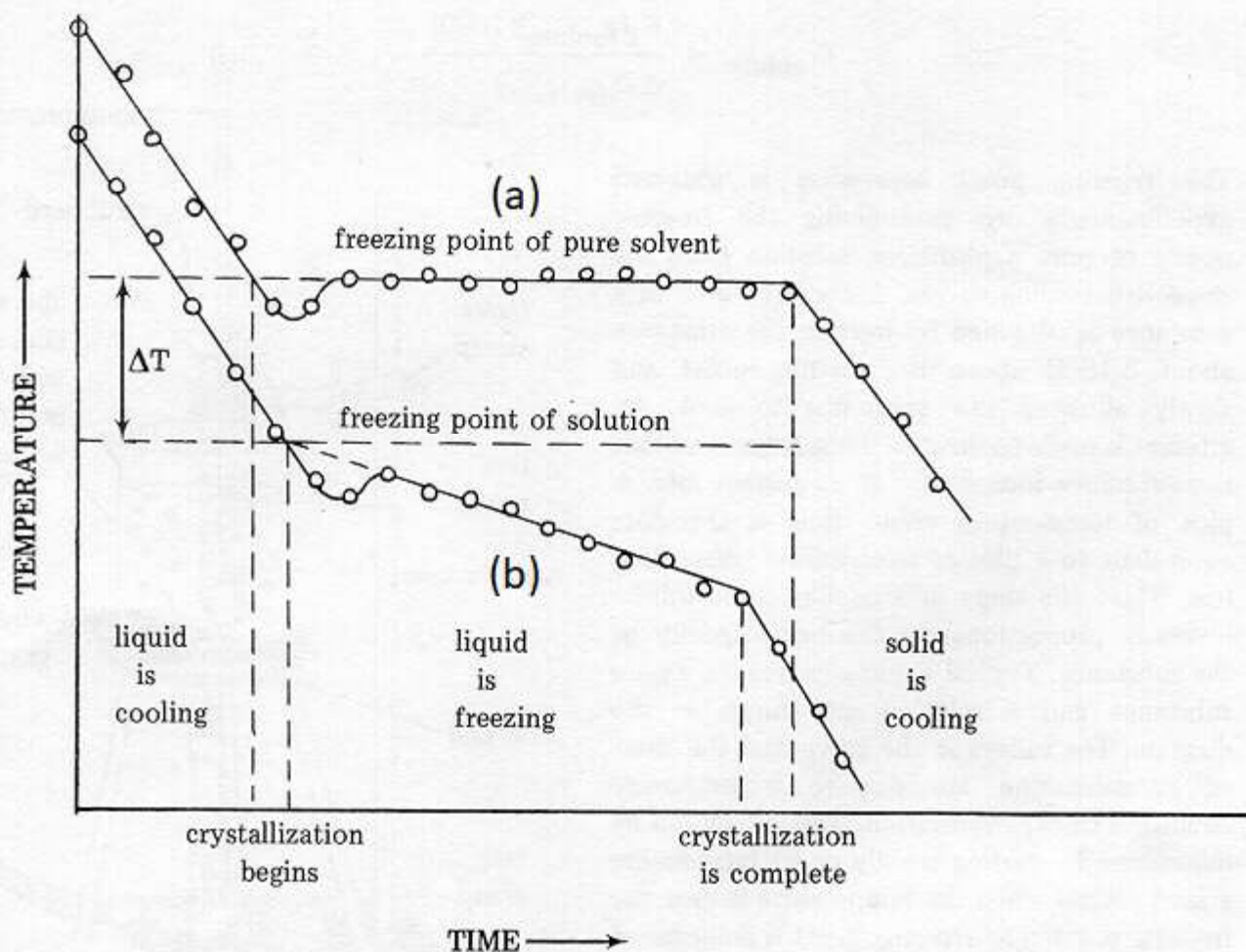


Figure 5.5: Freezing curves for (a) pure solvent and (b) impure solution. credit: <http://www.chem.latech.edu/~daddy/chem104/104Freeze.htm>

Given the freezing point depression equation in Figure 5.3 you will measure the mass of the solute, mass of the solvent and the change in temperature which will allow calculation of the mols of solute and thus the molecular weight of an unknown solute.

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Procedure

This experiment will be broken into three parts. In part 1 you will measure the freezing point of a solvent to determine the accuracy and precision of your measurements. In part 2 you will measure the freezing point depression constant of the solvent by adding a known quantity of solute. In part 3 you will determine the molecular weight of an unknown solute by adding a known mass to your solvent and measuring the freezing point depression.

Your instructor will assign a solvent/solute/unknown system to you. Possible options are:

Part 1				Part 2		Part 3
Solvent	Freezing Point (°C)	K_f	Amount Solvent	Solute (Known)	Amount Solute	Amount (Unknown)
Water	0.0	1.86	25 mL	Sucrose	11 g	10-11 g
BHT			8.0 g	Cetyl Alcohol	1.0 g	1.0-2.0 g
Cyclohexane	6.5	20.2	12.0 mL	Heptane	1.0 ml	0.1-0.2 g
Lauric Acid	45	3.9	8.0 g	Benzoic Acid	1.0 g	1.0 g
Tert-butyl alcohol	25.5	8.37	12 mL	Acetic Acid	1.0 mL	0.1-0.2 g

Figure 5.6: Potential freezing point depression systems to study. credit: author

A. Determine the Freezing Point of Solvent

- Assemble the apparatus as shown in Figure 5.7. The water bath will either be a hot-water bath (using a bunsen burner or hot-plate) or a cold-water bath (using ice) depending on the solvent chosen.
- Be sure to clamp the thermometer securely in place.
- Make a stirrer out of wire with a bent circle at the bottom that goes around the thermometer.
- You may or may not use a cork/rubber stopper to support the thermometer, in either case do not seal the system.
- Make sure that when the solvent (solid or liquid) is added to the test tube it will be below the surface of the water **AND** that it will cover the entire tip of the thermometer.
- Measure out (by mass or volume) enough solvent to cover the thermometer bulb. Record the mass or volume).
- If your solvent has a melting point above room temperature heat the hot water bath to approximately 5°C above the theoretical freezing point. Lower the test tube containing the solvent into the water, once it is melted insert the thermometer and stirring wire.
- If your solvent has a melting point below room temperature, simply lower it in the cold water bath.
- Be sure to clamp the test tube and thermometer securely in place.
- Record the temperature every 30 seconds. You can manually note the temperature if using a thermometer or set up the electronic thermometer to record the data every 30 seconds.

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11. continue recording data until the freezing occurs, continue recording until a crystallization is complete (or about 10 minutes).
12. Plot your data, if it looks good repeat the experiment a second time using a new solvent sample. If your data does not look right consult your instructor. Print your graph to turn in.
13. Dispose of all solvents in the appropriately labeled waste container.

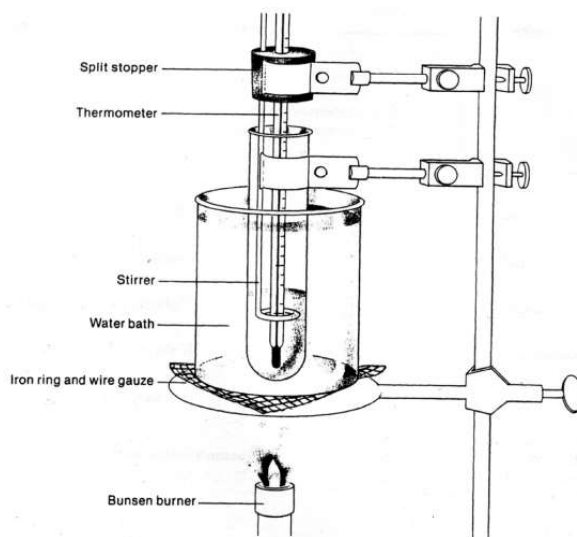


Figure 5.7: Experimental apparatus for determining freezing point of a solution. A hot-water or cold water bath may be used. credit: "Determination of the Molar Mass by Freezing Point Depression (Experiment)" by Santa Monica College, LibreTexts is licensed under CC BY-NC .

B. Determining a Freezing Point Depression Constant

1. Follow the instructions in the previous example but add the specified amount of **known** solute to the solvent. Record all masses.
2. Plot your data, if it looks good repeat the experiment a second time using a new solvent/solute sample. If your data does not look right consult your instructor. Print your graph to turn in.
3. Dispose of all solvents in the appropriately labeled waste container.

C. Determining an Unknown Compound's Molecular Weight

1. Follow the instructions in the previous example but add the specified amount of **UNKNOWN** solute to the solvent. Record all masses.
2. Plot your data, if it looks good repeat the experiment a second time using a new solvent/solute sample. If your data does not look right consult your instructor. Print your graph to turn in.
3. Calculate the Molecular weight of your unknown.
4. Dispose of all solvents in the appropriately labeled waste container.

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Results

Sample Data						
Amount Solvent						
Amount Solute						

Freezing Point Data							
Time (min:sec)	Elapsed time (s)	Trial 1: Pure Solvent	Trial 2 Pure Solvent	Trial 3 Solvent + Known	Trial 4 Solvent + Known	Trial 5 Solvent + Unknown	Trial 6 Solvent + Unknown
0	0						
0:30	30						
1:00	60						
1:30	90						
2:00	120						
2:30	150						
3:00	180						
3:30	210						
4:00	240						
4:30	270						
5:00	300						
5:30	330						
6:00	360						
6:30	390						
7:00	420						
7:30	450						
8:00	480						
8:30	510						
9:00	540						
9:30	570						
10:00	600						

A. Determining the Freezing Point of a Solvent

Complete the following table. Include a graph of Trial 1. Show calculations in the space provided.

	Trial 1	Trial 2
Experimental Freezing Point ($^{\circ}\text{C}$)		
Average Freezing Point ($^{\circ}\text{C}$)		
Theoretical Freezing Point ($^{\circ}\text{C}$)		
Percent Error		

B. Determining a Freezing Point Depression Constant

Rearrange the freezing point depression equation in Figure 5.3 to solve for K_f and write it next to the table. Using your experimental data from Trials 3 and 4 and the equation determine the K_f for the solvent. Finally compare your answer to the theoretical value. Complete the following table. Include a graph of Trial 3. Show calculations in the space provided.

	Trial 3	Trial 4
Experimental Freezing Point ($^{\circ}\text{C}$)		
ΔT_f ($^{\circ}\text{C}$)		
Calculated K_f		
Average K_f		
Theoretical K_f		
Percent Error		

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C. Determining an Unknown Compound's Molecular Weight

Rearrange the freezing point depression equation in Figure 5.3 to solve for MW (Molecular Weight) and write it next to the table. Use the Theoretical K_f for all calculations. Using your experimental data from Trials 5 and 6 and the equation determine the molecular weight of the unknown solute. After determining the experimental molecular weight, obtain the theoretical molecular weight from your instructor and determine your percent error. Show calculations in the space provided. Include a graph of Trial 5.

	Trial 5	Trial 6
Amount of Unknown Solute		
Experimental Freezing Point ($^{\circ}\text{C}$)		
ΔT_f ($^{\circ}\text{C}$)		
Calculated Molecular Weight (g/mol)		
Average Molecular Weight (g/mol)		
Theoretical Molecular Weight (g/mol)		
Percent Error		

Post Lab Questions

1. In lab you measured the freezing point of the pure solvent and compared it to the theoretical value. Why didn't we just skip the measurement and use the theoretical value given in lab to calculate the K_f value of the solvent?

2. When choosing a solvent to determine the molecular weight of an unknown compound, why would it be a good idea to choose one that has a large value for the freezing point depression constant (K_f)?

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3. For each of the following experimental errors occurred, how would each affect the calculated molecular weight of the solute (high, low, no effect)? Explain.

(a) The thermometer used always reads 1.5°C to high. 3(a) _____

(b) You spilled some of the solvent before the solute was added. 3(b) _____

(c) Instead of spilling the solvent you spilled some of the solute. 3(c) _____

(d) After mixing the solute/solvent together you spill some of the solution before measuring the freezing point. 3(d) _____

4. Explain why the pure solvent shows a level horizontal curve as solidification occurs while the curve for the impure solution slopes downwards.

5. What would happen if the unknown solute was an ionic compound instead of a molecular compound? How would this affect the measured molecular weight (higher, lower, no effect)? Explain.

6. In lab we measured the freezing point depression, what advantage does this have over measuring the boiling point elevation to determine molecular weight? Give two reasons. Explain.

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Prelab Questions

1. Define the term "Colligative Property". What property(s) is it independent of, and what property(s) is it dependent on?

2. Why is possible to determine the molecular weight of an unknown substance by simply dissolving it in water and measuring the freezing point?

3. The following data was collected in lab to determine the freezing point of an unknown solute. In lab 2.00 grams of the unknown substance was dissolved in 25.0 grams of Lauric Acid. The freezing point of the impure solution was 37.5°C Finish the table. Explain.

Solvent:	
Solute:	
Freezing Point Depression Constant:	
Freezing Point of Pure Solvent:	
Mass of Solvent:	
Mass of Solute:	
Freezing Point of Pure Solvent:	
Freezing Point of Solution:	
ΔT_f :	
Molecular Weight of Unknown:	

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