Page Intentionally Left Blank

Lab #7
Determining Molar Mass of Benzoic Acid by Freezing Point Depression in Lauric Acid

Goals

Part A: **Freezing Point Depression and Colligative Properties –** To become familiar with freezing point depression and colligative properties.

Part B: **In-Lab Portion –** To measure the freezing point of pure lauric acid and a mixture of lauric and benzoic acids to determine the freezing point depression of the solution and the molar mass of benzoic acid.

Part A: Freezing Point Depression and Colligative Properties

Chemical substances undergo reversible phase transitions between the solid state, liquid state, and gas state. **Figure 1** shows these phase transitions. This lab will study the process of freezing.

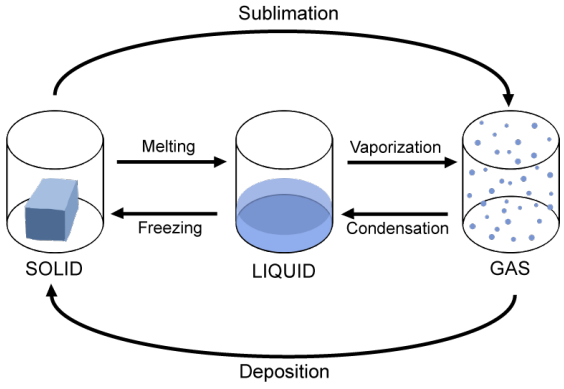


Figure 1. Phase transitions for chemical states of matter. Each transition occurs at a predictable temperature when pressure is constant.

Recall that particles in the solid phase are in a fixed position in the solid. Individual particles may vibrate but do not have enough kinetic energy to move out of position. Liquid particles have more kinetic energy and continuously move between other particles, though they always maintain some sort of weak intermolecular interaction with other particles. Gas particles have the highest amount of kinetic energy, and interact with other gas particles hardly at all. For a gas to condense to liquid, or a liquid to freeze into a solid, energy must be released from the chemical system into the environment.

Causes of Freezing Point Depression

At constant pressure, the freezing point of a pure liquid is constant. At 1 atm of pressure, the temperature at which pure water freezes, also known as its freezing point, is exactly 0 °C (32 °F). If a contaminant (solute) is added to the pure liquid (solvent), the freezing point of the solution is lowered (depressed) to less than the freezing point of the pure liquid. [**Note:** for a solution, the substance with

the greater mole amount is defined to be the **solvent**, and the substance with the lesser mole amount (usually the substance "being added" to make the solution) is defined to be the **solute**.

This phenomenon is known as Freezing Point Depression. This property explains the use of salt on icy roads during the winter. Adding a soluble salt (the solute) to the water (the solvent) on a cold day will decrease the temperature at which water will freeze. The presence of salt in the water causes the freezing point of the water to decrease; the ice will not form unless the temperature decreases significantly. Instead of the roads being covered with ice at a temperature of 32 ºF, ice may not form until the temperature decreases to about 19 ºF. Driving to school and work becomes a safer endeavor!

But why does the freezing point decrease when a solute is added to a pure substance? Consider the effect of entropy on a chemical system. In a pure substance, the distribution of particles has an intrinsic degree of order (or disorder, also called entropy). When other particles are added to the chemical system, the degree of disorder in the system usually increases, resulting in an increase in entropy. This is shown in **Figure 2**. In the system we are studying, entropy does increase.

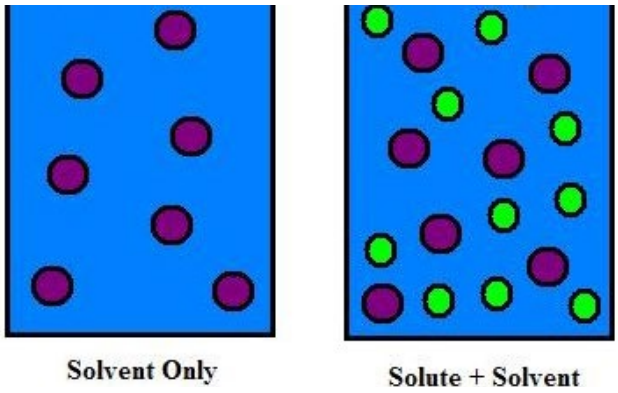


Figure 2. The addition of solute particles to a pure solvent typically increases the entropy of a solution.

In the system we are studying today, the solute is non-volatile, meaning it has negligible vapor pressure. A good example of this is the addition of salt to water; the water can turn into a vapor, but the salt cannot. Consequently, the vapor pressure of the solution is proportional to the purity of the solvent; as its purity decreases—more solute is added to the solution—the total vapor P decreases. (See discussion of Raoult's Law in text.)

Fundamentally, the reduction in vapor P is caused by the increased entropy of the solution. Why? Vaporization involves a large gain in entropy as molecules move from the liquid to the gas phase. The entropy of the solvent molecules is higher in the solution, thus fewer solvent molecules need to enter the gas phase for the solution to achieve the same absolute entropy, compared to the pure solvent. The vapor pressure of the solution is diminished, by an amount proportional to the amount of solute molecules present in the solution.

What does vapor pressure have to do with freezing? When solvent freezes from a solution, it is pure; solute molecules are left behind. When ice forms on the surface of the ocean, it is pure water; salts are excluded. The freezing point of a solution is the temperature at which its vapor pressure equals that of the pure solvent; that is when solid solvent and liquid solution are in equilibrium. Freezing point depression (ΔT_f) occurs because the vapor pressure of the solution is always lower than that of the solvent. Hence the solution freezes at a lower temperature. This effect is illustrated in **Figure 3**. The liquid-solid line of the solution is to the left of the liquid-solid line for the pure solvent. These lines represent the point when liquid and solid are in equilibrium. Solid and liquid have the same vapor pressure and the rate of molecules entering the solid phase equals the rate of molecules entering the liquid phase.

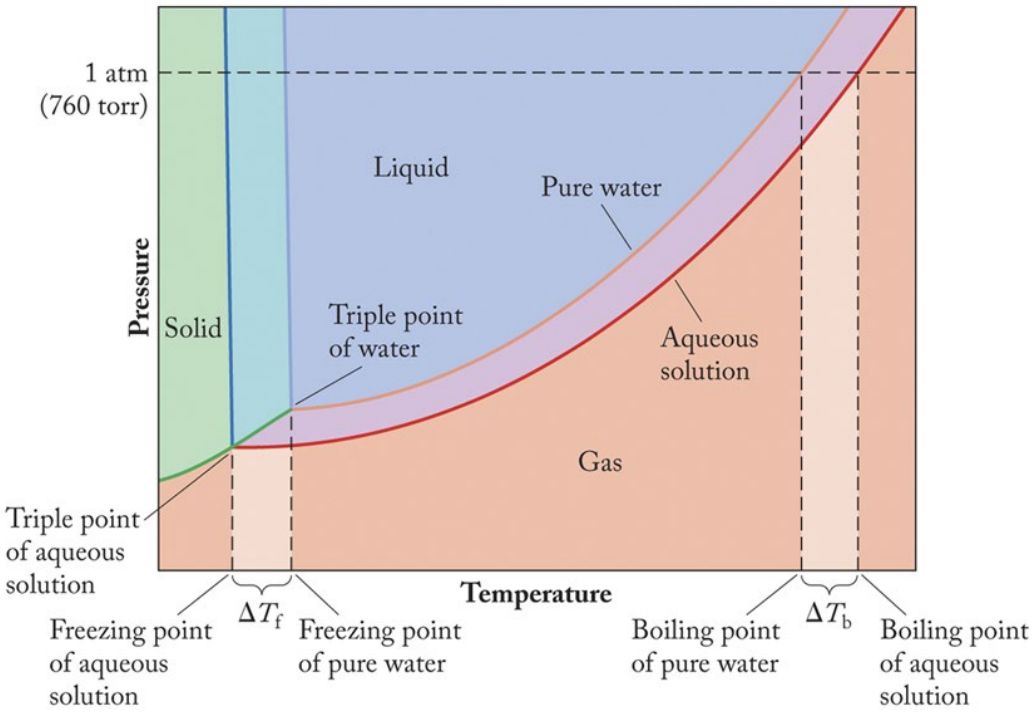


Figure 3. Phase diagrams of pure water and an aqueous solution, compared. The reduction in vapor pressure of the solution leads to depression of the freezing point, and elevation of the boiling point. A color version of this diagram is available in the textbook: *Silberberg and Amateis (2018) Chemistry: The Molecular Nature of Matter and Change, 8th edition.*

Cooling Curves

During the process of cooling a pure liquid, the temperature of the liquid actually falls slightly below its freezing point before crystallization (freezing) begins. This is shown in **Figure 4**. Often crystallization is initiated only when the system is cooled beyond the normal freezing point. This is termed "sub-cooling." As the first few liquid molecules freeze into a solid, they release energy to the surrounding liquid, and the temperature rebounds. The temperature of the solid/liquid mixture remains constant throughout the remainder of the freezing process. As energy from the system is continually drawn away from an outside cooling source, such as colder room air, more and more liquid particles will lose enough kinetic energy to freeze. When all of the particles are in the solid phase, the temperature of the solid will begin to decrease.

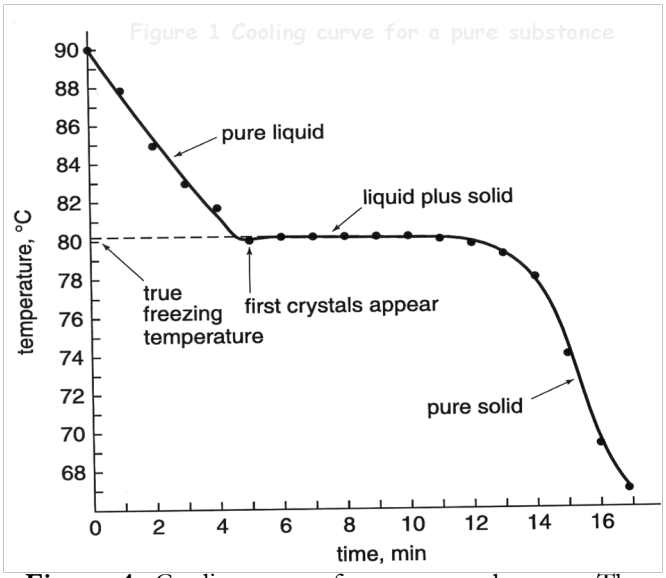


Figure 4. Cooling curve for a pure substance. The temperature of the liquid/solid mixture remains constant as long as any liquid exists. The temperature begins to decrease once all of the chemical substance is solidified.

In contrast, a solution does not freeze at a constant temperature. Why is this? As noted above, the solid that forms is pure solvent; solute molecules are largely excluded from the solid. As the freezing progresses, more solvent is removed from the liquid, so the concentration of the solute increases. Thus, the freezing point is depressed further and further. One also observes that the subcooling required to initiate crystallization is greater for the solution, most likely due to the presence of solute particles which interfere with the formation of pure solvent crystals. As in the first cooling curve, the temperature of the system rebounds. We take the **freezing point of a solution** to be the **highest temperature attained after crystals first appear**. This is shown in **Figure 5**.

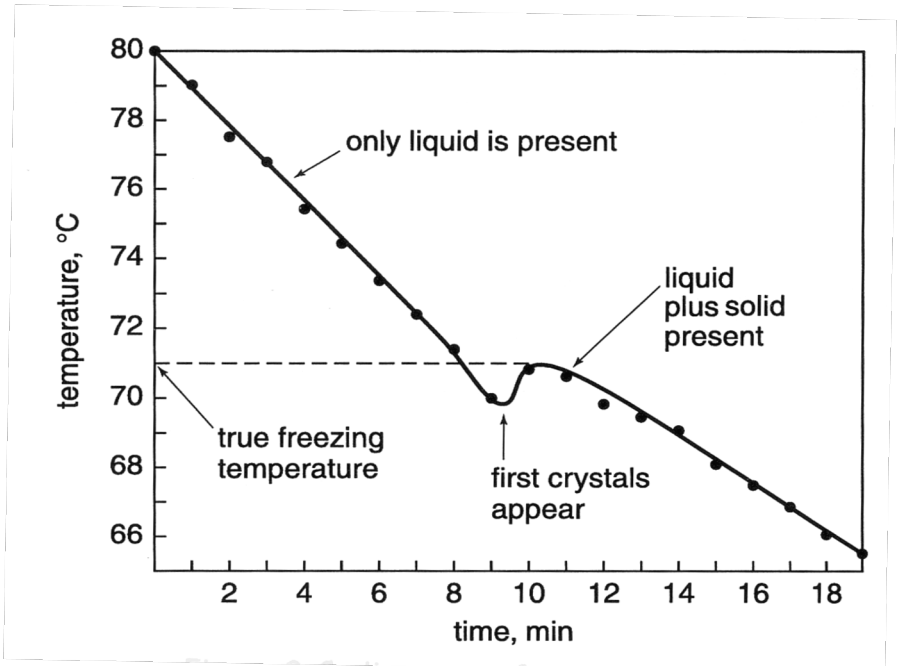


Figure 5. Cooling curve for a solution. The temperature of the solution does not remain constant once the first crystals of solvent have appeared.

Colligative Properties

Freezing point depression is an example of a colligative property of a solution. Like other colligative properties, depression of the freezing point of a solution is dependent upon the concentration of solute particles in the solution. For example, two moles of solute particles in a given mass of solvent will depress the freezing point of the solution twice as much as one mole of solute particles. The chemical identity of the solute is not relevant to the freezing point depression, since any solute will increase the entropy of a solution[1]. Other examples of colligative properties are boiling point elevation, vapor pressure lowering, and osmotic pressure. See your textbook for further discussion of these properties.

[1] Well, this is not ALWAYS the case. As you learned in the Solubility Lab, some solutes can lead to reduced entropy of the solvent. These substances tend to be **insoluble**, so are not very effective at creating a solution!

Calculations

Freezing point depression, ΔT_f, is defined as the amount, in °C, that a substance's freezing point is lowered. Symbolically it is:

$$\Delta T_f = T_{f,\text{ pure solvent}} - T_{f,\text{ solution}} \ (^oC) \qquad \textbf{(Equation 1)}$$

So ΔT_f is not the freezing point of either the pure solvent or the solution. Rather, it is the difference between the two freezing points. It is always a ***positive number.***

The unit of concentration used in freezing point depression is molality, m. It is defined as shown in **Equation 2**:

$$\text{molality (m)} = \frac{\text{moles of solute}}{\text{kg of solvent}} \qquad \textbf{(Equation 2)}$$

Note the difference between **molality** (small m) and **molarity** (big M). Molality is based on the mass of the solvent, while molarity is based on the volume of the solution.

The relationship between freezing point depression, ΔT_f, and molality is shown in **Equation 3**.

$$\Delta T_f = K_f \times m \times n \qquad \textbf{(Equation 3)}$$

where

K_f = molal freezing point depression constant, $°C \cdot kg \cdot mol^{-1}$

m = molality (see Eqn. 2)

n = # of particles the solute dissociates into when dissolved in solution

The molal freezing point depression constant (K_f) is specific to the **solvent** and is independent of the solute. The number of particles for solute dissociation (n) is equal to 1 for an organic solute (e.g., benzoic acid), and greater than 1 for an ionic solute. For example, n = 3 for $CaCl_2$ since it dissociates into three ions:

$$CaCl_2\ (aq) = Ca^{2+} + 2Cl^-$$

In this experiment we are interested in determining the molar mass of an unknown solute. We can do so by dissolving the unknown solute in a solvent with a known K_f. We can then experimentally determine ΔT_f. The calculations for doing so are given below. **Equation 3** can be rearranged to calculate the molality of the unknown solution (**Equation 4)**.

$$m = \frac{\Delta T_f}{n \cdot K_f} \qquad \textbf{(Equation 4)}$$

We are measuring an organic solute, benzoic acid, so n = 1. Equation 4 simplifies to:

$$m_{(\text{organic solute})} = \frac{\Delta T_f}{K_f} \qquad \textbf{(Equation 5)}$$

Thus, we can experimentally determine molality by measuring the freezing point depression, ΔT_f. Using definition of molality from **Equation 2**, and the masses of unknown solute and the known solvent, one may relate the experimentally-determined molality of the solution to the molar mass (MM) of the solute. This is shown in **Equation 6.**

$$\text{m(organic solute)} = \frac{\text{moles solute}}{\text{kg solvent}} = \frac{(\text{g solute}) \div (\text{MM solute})}{\text{kg solvent}} \qquad \textbf{(Equation 6)}$$

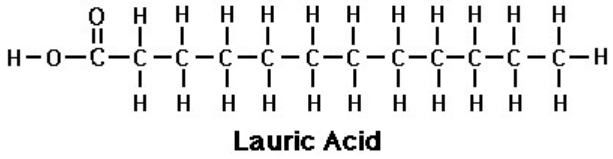
Equation 6 can be rearranged to solve for MM:

$$\text{MM} = \frac{\text{g organic solute}}{(\text{kg solvent}) \cdot \text{m}} \qquad \textbf{(Equation 7)}$$

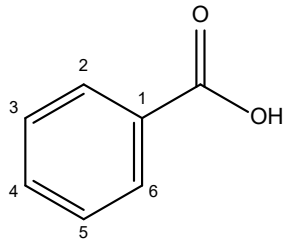
In this experiment, we will employ lauric acid[2], shown in **Figure 6**, as the solvent. You will first determine the freezing point (FP) of pure solvent experimentally. Second, a measured amount of benzoic acid (**Figure 6**) will be added to the known mass of lauric acid. The freezing point of the resulting solution will be experimentally determined. The freezing point depression of the solution, ΔT_f , is simply the difference between these two temperatures.

Using this measured ΔT_f, the known K_f of lauric acid (**3.9ºC·kg/mol**), we can calculate molality using **Equation 5. Finally,** given the masses of solute and solvent, the molar mass of the benzoic acid may be calculated using **Equation 7**.

==========



Lauric Acid



benzoic acid

Figure 6. Structures of lauric acid, $CH_3(CH_2)_{10}COOH$, and benzoic acid, C_6H_5COOH. All the H atoms are shown in the lauric acid. H atoms are present but not shown at positions 2 – 6 of the benzoic acid. (This simplified, less-cluttered depiction of structure is often used in organic chemistry.)

[2] Lauric acid (dodecanoic acid) is a compound commonly used to make shampoos. It is derived from coconut and other palm trees, often planted in place of native tropical forest species. ☹

Notes

Page Intentionally Left Blank

Name _____ Partner _____
Today's Date _____ Section _____ Instructor _____
CHM 152 Lab; Determining Molar Mass of Benzoic Acid, rev. January 12, 2021

Pre-Laboratory Assignment

Complete prelab questions prior to lab. Prelab questions will be collected before the prelab lecture. All answers must be handwritten neatly.

1. Explain, in your own words, what a colligative property is.

2. What are the units used for the freezing point depression constant, K_f? _____

3. In a handbook or database, look up the melting point of lauric acid. Write the melting point and a full citation for the source here. Also, enter this melting point on **Data Table 1**.

4. Define **molality**, m, of a solution. _____

5. For any solution, explain how you define which substance is the solute and which is the solvent.

6. The freezing point depression, ΔT_f, of a solution can be calculated from the molality of the solution and the freezing point depression constant (**Equation 1**). Which K_f is needed: the K_f of the solute or the K_f of the solvent? _____

7. Pure benzophenone freezes at 48.1ºC, $K_f = 98\ ^oC \cdot kg \cdot mol^{-1}$. A mixture of 1.03 g of unknown plus 23.94 g of benzophenone had the following behavior:

Time, min	Temperature, °C		Time, min	Temperature, °C
0.0	24.1		10.0	13.5
1.0	23.0		10.9	1st crystals appear
2.0	21.8		11.0	12.7
3.0	20.8		11.5	13.3
4.0	19.8		12.0	13.6
5.0	18.8		12.5	13.4
6.0	17.7		13.0	13.2
7.0	16.7		14.0	12.7
8.0	15.6			
9.0	14.6			

   a. Plot these data by hand, using the graph paper following the prelab, OR use graphing software (e.g. Excel, Calc). Show **temperature** on the **ordinate** and **time** on the **abscissa**. Label the point at which crystals first appeared, and identify the freezing temperature of the solution. Connect the data points by hand-drawing a smooth curve (as in **Figure 5**). Remember to include a title, axis titles and units, and axis values.

b. Calculate the **molality** of the solution. Show all calculations.

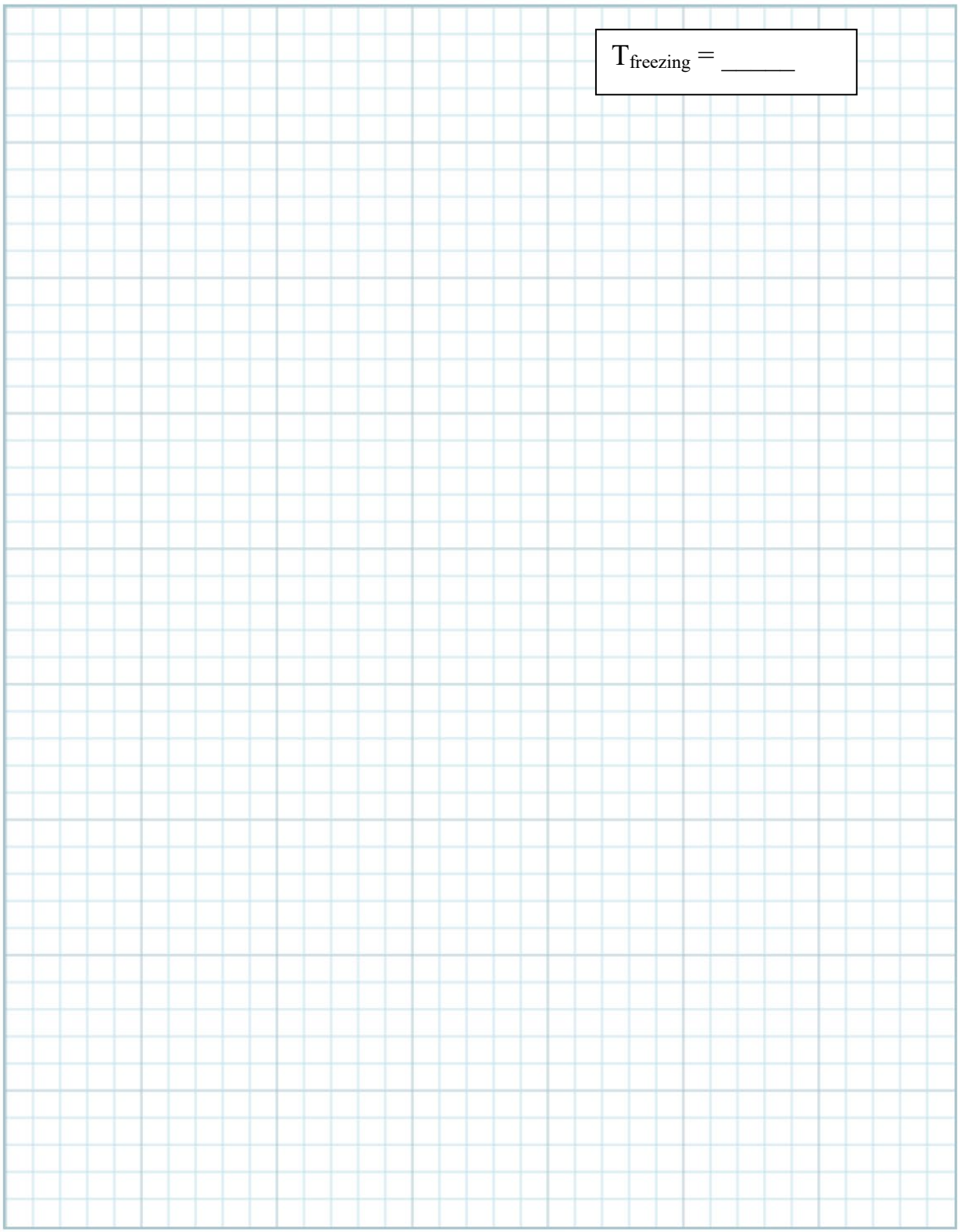
c. Calculate the **molar mass** of the unknown. Show all calculations.

Name _____ Partner _____

Today's Date _____ Section _____ Instructor _____

CHM 152 Lab; Determining Molar Mass of Benzoic Acid, rev. January 12, 2021

Prelab graph



Page Intentionally Left Blank

Part B: In-Lab Portion

Chemical Alert

Lauric acid, $CH_3(CH_2)_{10}COOH$ **None**

Benzoic acid, C_6H_5COOH **Skin irritant, eye damage**

Caution: Wear safety goggles while doing this experiment. Do not ingest or inhale chemicals. Wash hands at the end of lab.

Laboratory Materials

Reagents	**Apparatus**
lauric acid	hot plate
benzoic acid	1,000-mL and 800-mL beakers
isopropyl alcohol	600-mL beaker
Apparatus	glass thermometer
medium test tube	timer
utility clamp & ring stand	temperature probe/meter
	watch glass

Procedure

This is a partnered lab. Partner 1 will conduct Part A, and then leave the lab so that Partner 2 can do Parts B and C. Both partners will add data to the data tables and the time-temperature graph (Part D). You will need to get together after the lab to complete this graph and do the calculations.

A. Determining the Freezing Point of Pure Lauric Acid (Partner 1)

1. Hot-water bath for melting the solid acid. You will share this with other students at your bench. Fill a 1000-mL beaker about half full with tap water, and place on a large hot plate. Set the hot plate to approximately 130 °C. Place a glass thermometer in the water so you can monitor its temperature. Your goal is a constant water temperature between 60 and 65 °C.

2. Hot-water supply beaker. Fill an 800-mL beaker about ¾-full with tap water, and place on a the same hot plate. You will use this water for warming up the "cooling bath."

3. Thoroughly clean and dry the test tube. The test tube must be completely dry. Use a paper towel and/or alcohol rinse to ensure it is dry and free of any residues. Compressed air can be used to completely evaporate the alcohol.

4. Crease a piece of weighing paper in half. Weigh out approx. 4 g of lauric acid onto a piece of weighing paper. Record the exact mass (± 0.01 g) on **Data Table 2**.

5. Carefully transfer the lauric acid to the test tube. Be careful not to lose any of the lauric acid during the transfer.

6. Once the hot water bath has achieved a temperature of at least 60°C, place the test tube into the water. Leave it there until the lauric acid is completely melted.

7. As this is heating, set up a "cooling bath" in a 600-mL beaker. This water bath is for gradual cooling of the melted lauric acid, or lauric acid-benzoic acid mixture. Do so by filling the beaker approximately half-full with **hot water** from the tap. Check the temperature of the water with the electronic temperature meter at the bench. It should be about 40 °C. Now add hot water from the Hot-water supply beaker to bring the temperature up to about 55°C. Cover with a **watch glass** to help maintain its temperature.

8. Set up a stopwatch (or other timing device), and be prepared to start recording time-temperature data in the data table. You will need to look for the appearance of crystals as well.

9. Place the cooling bath near a ring-stand and set up a utility clamp as shown in **Figure 6**. When the lauric acid is completely melted, take the test tube out of the hot-water bath and place it in the cooling bath. (Put the watch glass on the bench.) Insert the temperature probe into the test tube, and stir the contents.

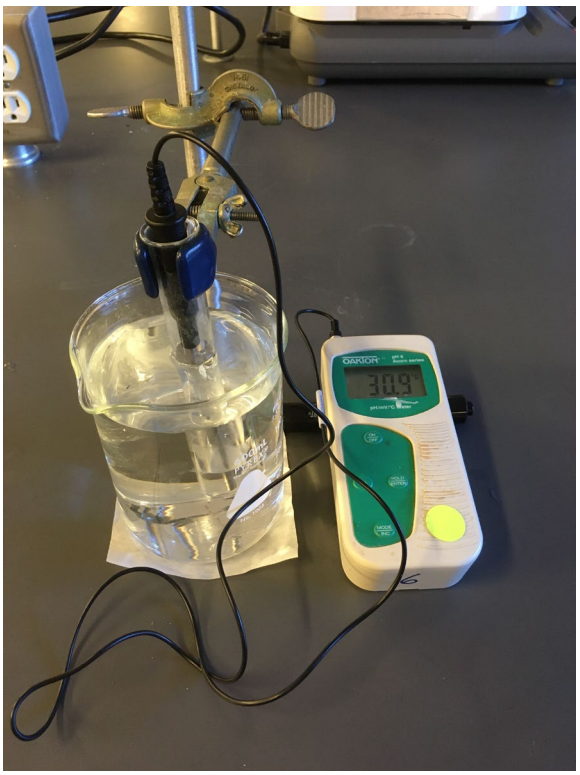


Figure 6. Experimental set-up for gradual cooling of the lauric and lauric-benzoic acids

10. When the temperature of the lauric acid gets below 50°C, start the timer and begin recording temperatures to 0.1°C precision at 1-minute intervals. Let the system **slowly cool** as you gently and periodically stir the liquid in the test tube with the temperature probe. Take temperature readings while stirring. Watch the temperature readings carefully.

11. Record these time-temperature readings for the pure lauric acid on **Data Table 1**. (Record time-temperature readings for the mixture on **Data Table 2**). Keep the probe centered in the test tube. You are not interested in the temperature of the glass; it may skew your results.

12. In the meantime, watch closely for the appearance of crystals in the liquid. Note the time and temperature at which crystals **first appear**. Once crystals start to form, record the temperature every 15-30 seconds.

a. If the temperature immediately rises after the first crystals appear, carefully note the maximum temperature before it begins to decrease again. This maximum temperature is the **freezing point**.

b. If the temperature continues to decrease after the first crystals appear, monitor the temperature until it shows a slight increase before again starting to decrease. Record this slight temperature increase as the **freezing point**.
c. If the temperature maintains a constant value for several minutes, that is the freezing point.

13. Once you have noted the freezing point, record the temperature at one-minute intervals until the lauric acid has completely solidified, or until 8 minutes have elapsed.

B. Determining the Freezing Point of a Lauric Acid/Benzoic Acid Mixture (Partner 2)

1. Weigh out ~0.5 g of benzoic acid, and record to the nearest 0.01 g. Record this mass on **Data Table 2**.

2. Carefully add the benzoic acid to the test tube that contains the now solidified lauric acid and temperature probe. (You may temporarily remove the probe so that it is easier to add the benzoic acid. Do not lose any of the lauric acid that adheres to the probe.) Place the test tube in the hot water bath (60-65°C) to melt the mixture. Use the probe to stir the acid mixture.

3. Adjust the temperature of the cooling bath to 40-42°C. You will probably need to replace some of the water with hotter water from the hot water supply beaker. Cover with a watch glass to help maintain its temperature.

4. Perform Steps 8 – 13 in Part A to gather data for determining the freezing point of the acid mixture. In Step 10, begin recording temperatures when the temperature of the lauric acid/benzoic acid mixture reaches about 46°C.

C. Removing the Temperature Probe from the Frozen Mixture and Cleanup (Partner 2)

1. Place the test tube with the solidified acids back into the hot water bath to melt the mixture.

2. Remove the probe from the melted mixture, and wipe the lauric acid mixture with a paper towel or KimWipe.

3. Pour the liquid contents of the test tube out onto a folded paper towel. Once solidified, dispose of this into the trash. You may then remove residual acid from the test tube by scraping it out with a metal spatula and/or test-tube brush. Do this over the trash container.

4. Use a small amount of isopropyl alcohol to perform a final cleaning of the test tubes, as needed. Do this in the hood, and collect the solvent in a designated waste container.

D. Creating Graphs for both Data Sets (both partners)

Note: The graph can be set up before the experiment is completed.

1. Plot both sets of data into cooling curves of **Temperature vs Time** on the same graph paper (provided in lab). Label the axes and title the graph. Graphing guidelines:

    - Orient the paper vertically, so that temperature is on the tall edge, and time is on the short edge. Take care to scale the graph to accommodate ***both*** sets of data.
    - The graph needs to show the transition from the cooling liquid to the solid phase for each data set. The early part of the liquid cooling may be omitted, if needed, to fit the graph. One way to accommodate the two sets of data is to create two x-axes at the bottom of the graph. For example, one axis covers 0-15 min for pure lauric acid, and while the other covers 5-20 min for the mixture. See your instructor for guidance.
    - Use a different symbol for each data set.
    - Recall that each cooling curve should be a smooth curve for that data set.

2. Label the **freezing point of the pure lauric acid** and the **freezing point of the mixture** on the graph.

Name _____ Partner _____
Today's Date _____ Section _____ Instructor _____
CHM 152 Lab; Determining Molar Mass of Benzoic Acid, rev. January 12, 2021

Data Table 1. Pure Lauric Acid

Temperature _____ (ºC) and time _____(min) at which crystals first appeared.

Maximum temperature attained after crystals appeared, ºC _____

Freezing point of pure lauric acid, ºC (literature value) _____

Freezing point of pure lauric acid, ºC (from data and hand-drawn graph) _____

Time, min	Temp, ºC		Time, min	Temp, ºC		Time, min	Temp, ºC		Time, min	Temp, ºC

Data Table 2. Mixture of Lauric Acid and Benzoic Acid

Mass of lauric acid, g _____ Mass of lauric acid, kg _____

Mass of benzoic acid, g _____

Time, min	Temp, ºC		Time, min	Temp, ºC		Time, min	Temp, ºC		Time, min	Temp, ºC

Temperature _____ (ºC) and time _____(min) at which crystals first appeared.

Maximum temperature attained after crystals appeared, ºC _____

Freezing point of solution, ºC (from data and graph) _____

Calculations

Show all calculations. Handwrite your answer neatly. Enclose your final answer for each question in a box.

1. Calculate the freezing point depression, $\Delta T_f = T_{\text{pure solvent}} - T_{\text{solution}}$.

2. Calculate the molality of the solution using **Equation 4**. ($K_f = 3.9\ ^\circ C \cdot kg \cdot mol^{-1}$)

3. Calculate the experimental molar mass of benzoic acid using **Equation 6**.

4. Determine the accepted molar mass of benzoic acid from its formula, C_6H_5COOH.

5. Calculate the percent error between your experimental molar mass and the accepted molar mass.

Name _____ Partner _____
Today's Date _____ Section _____ Instructor _____
CHM 152 Lab; Determining Molar Mass of Benzoic Acid, rev. January 12, 2021

Post Laboratory Questions

Answer the following questions using complete sentences unless otherwise indicated. Show all calculations. Handwrite your answer neatly.

1. Let's suppose that, after you weighed the benzoic acid, you inadvertently spilled some as you added it to the lauric acid How would that affect your experimental results? Specifically, how does it affect your determination of molar mass?

2. Give one other potential experimental error, and explain how and why it would affect your molar mass result. Be specific.

3. The freezing point of camphor is 178.4ºC and its molal freezing point depression constant (K_f) is 37.7 $ºC \cdot kg \cdot mol^{-1}$. How many grams of naphthalene ($C_{10}H_8$; molar mass = 128.17 g/mol) should be added to 12.0 g of camphor to lower the freezing point to 170.0ºC?