

Molar Mass Determination by Freezing Point Depression

If a nonvolatile solute is added to a liquid, a number of physical properties of the pure substance change, including vapor pressure depression, freezing point depression, and boiling point elevation. These alterations are collectively known as **colligative properties** of solutions. The colligative properties of a solution change in proportion to the concentration of solute dissolved in solvent. These properties depend only on the number of solute particles present in a given amount of solvent and not on the type of particles dissolved. Therefore, the concentration of the solute is most conveniently expressed in terms of molality (m)

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

The change in the freezing point (ΔT_f) in $^{\circ}\text{C}$ for a nonvolatile organic solvent can be determined using the following equation, where k_f is characteristic for the solvent used:

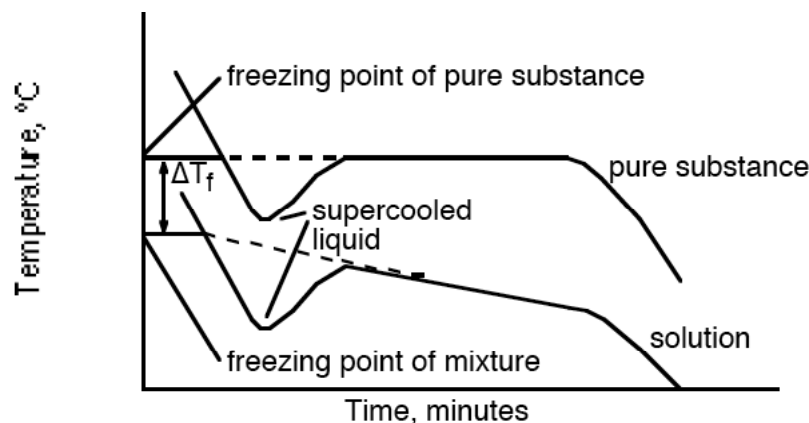
$$\Delta T_f = k_f m$$

We can determine the molar mass of the solute using this equation by measuring the change in the freezing point of the solution and solving the equation for molality. The calculated molality can be used to determine the moles of solute that in turn can be used to calculate the molar mass (grams / mole) of the solute.

When a pure substance is heated to a liquid state and allowed to cool, initially the temperature will fall quite rapidly. As the substance approaches its **freezing point**, solid will begin to form and the temperature will begin to level. The freezing point of the pure liquid is the constant temperature observed while the liquid is solidifying.

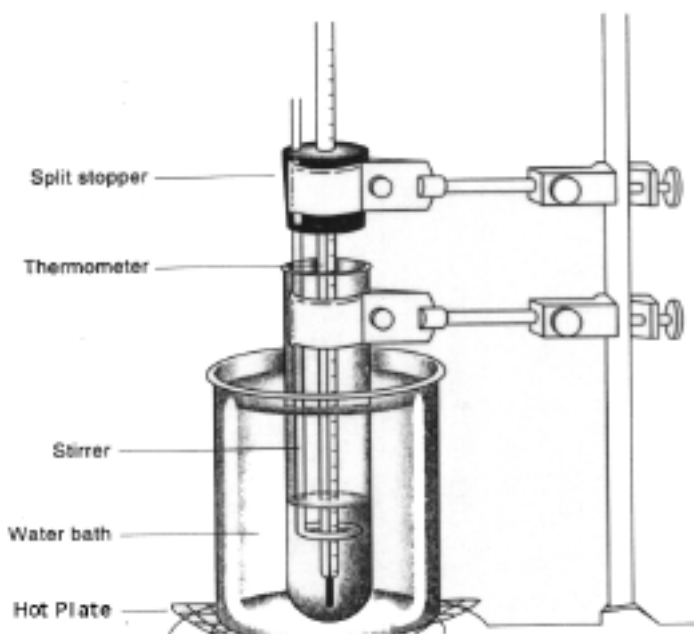
The cooling behavior of a solution is somewhat different from that of a pure liquid. The temperature at which the solution begins to freeze is **lower** (i.e. *depressed*) than for the pure solvent. Additionally, there is a slow gradual fall in temperature as freezing proceeds. The **change in temperature, ΔT** , between the freezing point of the pure substance and the freezing point of the mixture is used to calculate the molality of the solution.

In both the pure liquid and the solution, a **supercooling** effect may be seen. As the solid begins to form, the temperature may drop *below* the actual freezing point initially and then come back up to the freezing point temperature as the solid forms. Supercooling is usually not observed if adequate churning of the sample is provided. When determining the freezing point, the super-cooling effect should be ignored if present; see the figure below.



Graph showing the freezing points of the pure substance, the freezing point of the mixture, the change in temperature (ΔT), and the supercooling effect

In this experiment, you will first determine the freezing point of a pure solvent, namely cyclohexane, using a salt water ice bath. Next, you will use a known solute, naphthalene ($C_{10}H_8$), to determine the k_f freezing point constant for cyclohexane. Finally, you will use the known freezing point of cyclohexane and the value of k_f to calculate the molar mass of an unknown organic solute.



PROCEDURE: We will use apparatus similar to that as shown above. A salt water ice bath will be used to cool the samples. Please be very careful with the thermometers and stirrers. If the sample becomes solid, please warm the sample gently before attempting to stir.

Part A: Determining the Freezing Point for Cyclohexane

1. Using a 25 mL buret, accurately dispense 20 mL of cyclohexane into a dry large test tube. Record the volume of cyclohexane dispensed to 0.02 mL. (Density of cyclohexane: 0.77855 g/mL)
2. Prepare the ice/water bath in a 400 mL beaker. Add rock salt to the ice. Wrap a two-hole rubber stopper around a thermometer and insert a stirrer with a loop end through the second hole. Place the rubber stopper on your test tube so that the thermometer is in the cyclohexane but not touching the test tube. Record the initial temperature of the cyclohexane.
3. During this next part of the experiment, one lab partner will be recording the temperature of the solution every 30 seconds and the other lab partner will be giving "30 seconds" notices. Record the time and temperature values in your lab notebook, and be sure to record the temperatures to 0.1 °C. Clamp the test tube to the ring stand and immerse only the bottom 1" of the tube in the ice water. It is important to **continue to gently stir the mixture** (as if churning butter) until the sample has just begun to solidify and the temperature has leveled off. Continual mixing ensures a more even freezing point and lowers the chance of supercooling. Once the temperature has leveled off and the cyclohexane has frozen, you may discontinue the recording of temperature and time values.

4. Hold the test tube just above the ice water and allow the sample to warm up until all of the solid has melted, recording the temperature to 0.1 °C every 30 seconds as in part 3. Stir continuously while this is happening. At some stage the temperature should stay reasonably constant before all of the solid has completely melted. Record the temperature at the instant when the solid has melted.
5. Ideally the temperatures observed in steps 3 and 4 should be the same. Repeat steps 3 and 4 at least one more time to determine a consistent value for T_f that you consider reliable. (Note: This cycling between steps 3 and 4 should proceed quite rapidly if cooling is stopped the instant some solid appears and warming is stopped as soon as the solid disappears.)

Part B: Determining the Freezing Point Constant (k_f) for Cyclohexane using Naphthalene ($C_{10}H_8$)

6. Using a balance, weigh out 0.2 to 0.3 grams of naphthalene ($C_{10}H_8$) and dissolve in the cyclohexane used in part A. Make sure it all dissolves! Record the mass of the naphthalene to 0.001 grams. Record the starting temperature of the naphthalene solution to 0.1 °C.
7. As in Part A, record the temperature every 30 seconds with the assistance of your lab partner. Determine the T_f of the solution by conducting at least two cooling-warming cycles as in Part A. Here you should rely more on the temperature at which solid first appears. Also note where most of the solid disappears. Is there a plateau where the temperature remains constant for a minute or more?
8. Dispose of the solution into the labeled waste container in the hood. Rinse the test tube with acetone and dispose of in the waste bottle. Be sure the test tube is completely dry before continuing.

Part C: Determining the Molar Mass of an Unknown Organic Compound

9. Using a 25 mL buret, dispense 20 mL of cyclohexane into a dry large test tube and record the volume.
 10. Measure 0.2 to 0.3 grams of an unknown sample to 0.001 g. Record the mass and the unknown number. Dissolve the unknown completely in the cyclohexane. You will not need to record the time and temperature values as you did in Part A and Part B, but you will need to determine the freezing point of the solution.
 11. Remember to gently stir the solution as it freezes. Determine a reliable value for the freezing point of the solution.
 12. Dispose of the solution into the labeled waste container in the hood. Rinse the test tube with acetone and dispose of in the waste bottle. Be sure the test tube is completely dry before returning it to the stockroom.
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CALCULATIONS: Determining the Molar Mass of the Unknown Solute

Once you have completed your experiment, you will need to create a **graph in Excel or a similar program; no hand drawn graphs will be accepted**. Use **time** as the x-axis and **temperature** as the y-axis. Plot the data from your pure cyclohexane experiment (Part A) and also the data from the naphthalene solution (Part B) using the same graph; use different colors and/or marking symbols to distinguish the two trials. Determine the freezing point for each trial graphically; draw a circle on your graph representing the freezing point in each trial.

Using the data from Part A and Part B, determine the freezing point depression and calculate the observed k_f for cyclohexane. Be careful with units and significant figures! Calculate your **percent error** given that the accepted (literature) value of k_f for cyclohexane is $20.4\text{ }^\circ\text{C/m}$.

Using the literature value of k_f , the freezing point of the cyclohexane, the freezing point of the solution, and the mass of unknown placed in the cyclohexane solution in part C, calculate the molar mass of the unknown solute.

POSTLAB QUESTIONS:

- Determine the effect of the following on the final molar mass calculation. Give your reasoning. Tell if the molar mass will be higher, lower or not change.
 - The thermometer you were using read temperatures consistently $1.2\text{ }^\circ\text{C}$ higher than the real temperature.
 - You added 3 g of unknown solute during your freezing point determination.
 - In adding your unknown solute to your cyclohexane, you spilled some into your water bath.
- A student performs a freezing point analysis. She determines that the freezing point of 21.00 g of stearic acid (where $k_f = 4.89^\circ\text{C/m}$) is $68.20\text{ }^\circ\text{C}$. She adds 2.07 grams of an unknown compound to her sample and determines the freezing point to be $65.53\text{ }^\circ\text{C}$. She adds an additional 1.97 g of the unknown compound and determines the new freezing point to be $63.03\text{ }^\circ\text{C}$.
 - Determine the molar mass of the unknown compound using the 2.07 g of sample.
 - Determine the molar mass of the unknown compound using the *combined* samples (*hint*: $2.07 + 1.97 = 4.04\text{ g}$ total solute)
 - Determine the average molar mass of the compound and the parts per thousand for the two trials.