JoVE: Science Education

Using Freezing-Point Depression to Determine the Identity of an Unknown Compound
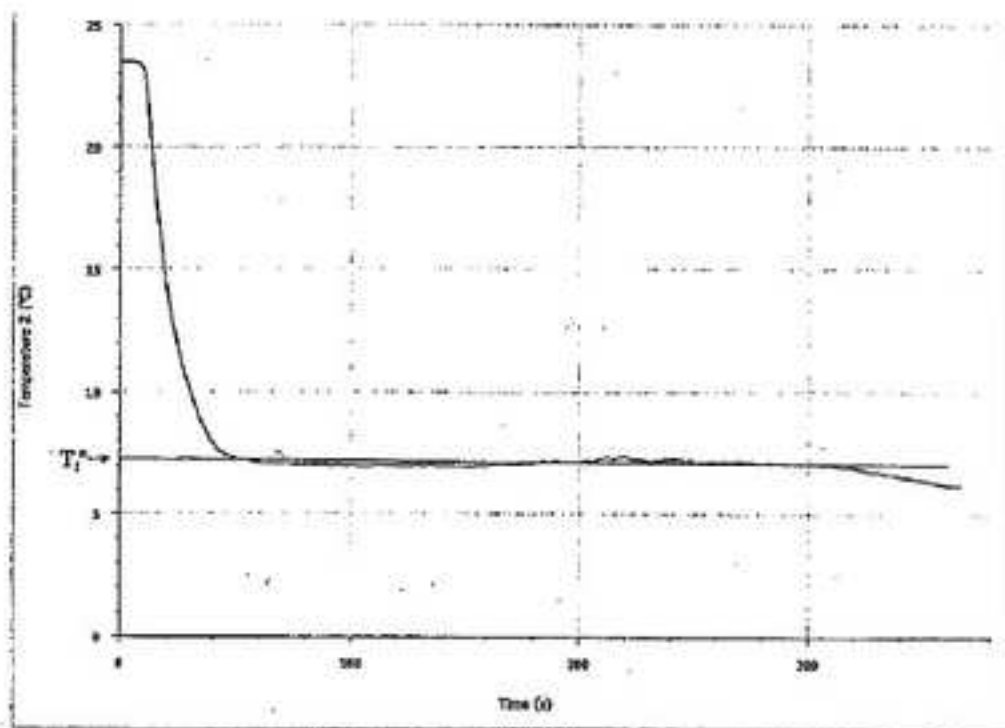### --Manuscript Draft--

Figure 1a. Plot of temperature as a function of time for the determination of T_f° for the *pure solvent.*
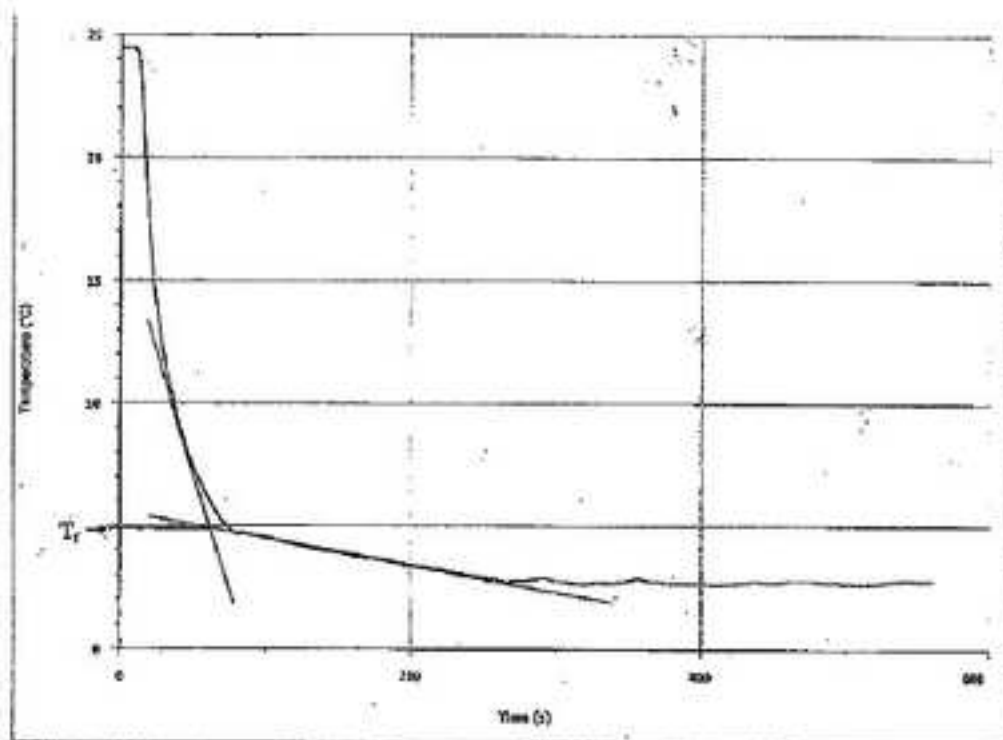
Figure 1b. Plot of temperature as a function of time for the determination of T_f for the *solution.*

Photo or Graphic File

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Chemistry Science Education Title: Using Freezing-Point Depression to Determine the Identity of an Unknown Compound

Overview:

When a solid compound is dissolved in a solvent, the freezing point of the resulting solution is~~will be~~ lower than that of the pure solvent. ~~-~~This phenomenon is known as freezing-~~-~~point depression, and the change in temperature is directly related to the molecular weight of the solute. ~~-~~This experiment is designed to find the identity of an unknown compound by using the phenomenon of freezing-~~-~~point depression to determine its molecular weight. The compound will be dissolved in cyclohexane, and the freezing point of this solution, as well as that of pure cyclohexane, will be measured. The difference between these two temperatures ~~will~~ allows~~-us to~~ for the calculati~~on of~~e the molecular weight of the unknown substance.

~~This experiment is designed to find the identity of an unknown compound by determining its molecular weight. The compound is dissolved in cyclohexane, and then the freezing point of this solution is measured. The freezing point of the solution is lower than that of pure cyclohexane, and this temperature difference is used to calculate the molecular weight of the unknown compound.~~

> **Commented [AW1]:** The Overview should include the background and significance of the topic. In this case, include a brief introduction to freeze-point depression, and the fact that it can be used for a few key uses. You might be able to move some of the content from the Principles to here.

Principles:

Certain properties of a solution differ from those of a pure solvent due to interactions that take place between the solute and solvent molecules. The properties that exhibit such changes are called the colligative properties~~, which~~ and include vapor-pressure lowering, boiling-point elevation, freezing-point depression, and changes in osmotic pressure. These properties are dependent only upon the number of particles dissolved in the solvent, not on the identity of the particles. A particle, in this instance, is defined as an ion or a molecule. This experiment focuses on the ~~phenomenon~~ property of freezing-point depression.

When a particular solute is dissolved in a solvent, the following expression holds true:

$$\Delta T = T_f^\circ - T_f = K_f m$$

The terms T_f° and T_f refer to the freezing-point temperatures of the pure solvent and the solution, respectively. The term "m" indicates the molality of the solution, which is defined as the number of moles of solute per 1,000 g of solvent. This quantity is used, rather than molarity, because it is not temperature dependent. The constant, K_f, is referred to as the freezing-point-depression constant and is dependent only upon the solvent. The change in temperature is also dependent upon the number of solute particles in solution — the more particles present, the larger the change in temperature.

For this reason, the previous equation is sometimes written as:

$$T_f^\circ - T_f = K_f i m$$

where i = the number of solute particles produced per formula unit that dissolves. In a solution containing an electrolyte, each ion is considered to be a particle.

This experiment uses cyclohexane, an organic compound that is a liquid at room temperature, as the solvent. The unknown compound is a non-ionic organic molecule;

therefore, i is equal to 1. The molecular weight of this unknown compound can be determined by observing the freezing point of a solution of the compound in cyclohexane and comparing it to the freezing point of pure cyclohexane.

The compound cyclohexane has a melting point (or freezing point) of about 6 °C. A series of temperatures of pure cyclohexane are obtained as it cools down from room temperature through its freezing point in an ice bath. These temperatures are then plotted as a function of time. Similarly, temperatures of a solution of the unknown compound dissolved in cyclohexane are obtained as it cools down to the freezing point, which are also plotted. The plots should look similar to the plots in **Figure 1**. The $T_f°$ and T_f values can be extrapolated, as shown. ~~Notice i~~In **Figure 1b**, ~~that (~~The temperature does not remain entirely constant as the solution freezes. The freezing point of the solution is the point at which it first begins to freeze and is indicated graphically by a change in the slope of the temperature-time curve.

The molality, m, of a solution can be expressed in terms of the molar mass of the solute:

$$m = \frac{\text{moles of solute}}{1 \text{ kg of solvent}}$$

$$= \frac{(\text{g of solute/mol ar mass}_{\text{solute}}, \text{g/mol})}{(\text{g of solvent}) \cdot (\text{kg/1000 g})}$$

$$= \frac{(1000 \text{ g/kg}) \times (\text{g of solute})}{(\text{molar mass}_{\text{solute}}, \text{g/mol}) \times (\text{g of solvent})}$$

Substituting this expression into the equation for freezing-point depression (where $i = 1$), obtains:

$$\Delta T = T_f° - T_f = \frac{(1000 \text{ g/kg}) \cdot (K_f) \cdot (\text{g of solute})}{(\text{molar mass}_{\text{solute}}, \text{g/mol}) \cdot (\text{g of solvent})}$$

Rearranging to solve for molar mass, obtains:

$$\text{molar mass}_{\text{solute}}, \text{g/mol} = \frac{(1000 \text{ g/kg}) \cdot (K_f) \cdot (\text{g of solute})}{(DT) \cdot (\text{g of solvent})}$$

The molecular weight (in amu) of a substance has the same numerical value as its molar mass.

The unknown substance is one of the following compounds:

- Biphenyl ($C_{12}H_{10}$)
- 2-Bromochlorobenzene (C_6H_4BrCl)
- Naphthalene ($C_{10}H_8$)
- Anthracene ($C_{14}H_{10}$)
- 1,4-Dibromobenzene ($C_6H_4Br_2$)

Procedure:

A temperature probe interfaced to a computer is used to acquire the temperature readings in this experiment. The temperature probe has an uncertainty of ±0.1 °C.

1. Setting the ~~P~~parameters in the ~~SLogger Pro~~ software~~.~~

    1.1. ~~Pull down the Experiment menu and choose Data Collection.~~Set the length of the experiment to 800 s~~econds~~.

    1.2. ~~Change the length of the experiment to 800 sec. The~~Set the ~~s~~Sampling ~~r~~Rate ~~should be set~~ to 1 sample per second.~~s/sec. Click on Done.~~

    1.3. ~~Click once on the number at the very top of~~Set the upper limit for the temperature range to 40 °C and the lower limit to 0 °C.~~the y-axis. Type in 40 and press enter.~~

2. Measuring the ~~f~~Freezing ~~P~~point of ~~C~~cyclohexane~~.~~

    2.1. Dispense 12.0 mL of cyclohexane from the dispensing bottle into a 16 x 150 mm test tube that is clean and dry. Caution: ~~C~~cyclohexane is a flammable solvent.

    2.2. Wipe the temperature probe with a ~~paper towel~~Kimwipe to be sure it is dry.

    2.3. Insert the stopper with the temperature probe and wire stirrer into the test tube.

    2.4. Make sure the tip of the temperature probe is in the center of the liquid and not touching the sides or bottom of the test tube.

    2.5. Fill a 600- mL beaker about one-third full of water, and add ice until the beaker is three-fourths full.

    2.6. ~~Click on the green arrow button. This activates the computer's~~Start the data collection. ~~The computer~~ ~~will~~ acquires a ~~of the~~ temperature reading every second.~~s.~~

    2.7. Move the test tube into the ice-water bath and hold it so the level of liquid in the test tube is below the level of water in the bath.

    2.8. Immediately begin stirring the liquid with the wire stirrer, continuously and at a constant rate.

    2.9. Once freezing begins, as long as liquid and solid are both present, the temperature remains constant until the entire mass has solidified. Allow the computer to continue recording the temperature until the plot has leveled off at a constant temperature. Note that once the cyclohexane has frozen solid, the temperature starts to decrease again.

    2.9.

    2.11.   Remove the test tube from the ice-water bath and let it warm up to room temperature.

2.12.　　Save the data.

2.12.2.13.　Adjust the *y*-axis limits so the plot fills the page. -Title the graph, and then print it.

3.　Adjusting and Pprinting the Ggraph.

Commented [AW7]: This step is too close to a laboratory exercise. This could be a single step, 2.12, "Print graph with proper axis limits", or something.

15.1.3.1.　Accurately weigh 0.14 g of the solid unknown material onto a piece of weighing paper.

Commented [AW8]: Is this just an empirically derived value, or is there a specific reason to choose such a value?

15.2.3.2.　Check to be sure the cyclohexane contained in test tube has melted.

Commented [IS9]: I believe this value is empirically derived. This amounts dissolves relatively easily in 12 mL of cyclohexane but is also sufficient to produce a measurable different in the freezing point.

15.3.3.3.　Remove the stopper from the test tube and carefully add the unknown solid to the cyclohexane. while avoiding the loss of any compound adhering to the sides of the test tube or stopper.

Commented [AW10]: Is it imperative to use the same batch of cyclohexane, or could you also use a fresh aliquot?

15.4.3.4.　Replace the stopper and re-weigh the paper to account for any crystals that remain on it.

Commented [IS11]: You could use a new aliquot, but the volume would have to be exactly the same. Also, this would needlessly generate extra hazardous waste.

15.5.3.5.　Stir the solution in order to completely dissolve the solid. It is important that no crystals remain.

15.6.3.6.　Make a new ice-water bath.

16.　Preparing the Ccomputer for the Ssecond Ddata Ccollection.

Commented [AW12]: Similar comment to Step 3.

4.1. Prepare the computer to collect a second set of data.

26.1.4.2.　Click on the green buttonStart the data collection.

26.2.4.3.　Move the test tube that contains the solution into the ice-water bath.

26.3.4.4.　Immediately begin stirring the solution continuously and at a constant rate.

26.4.4.5.　The temperature does not remain entirely constant as the solution freezes. The freezing point of the solution is the point at which it first begins to freeze and is indicated graphically by a change in the slope of the temperature-time curve. Collect the data for 300-500 sec in order to clearly see this clearlythe change in slope that occurs as the solution freezes.

Commented [AW13]: This information would work better in the Principles.

26.5.4.6.　Click on the red button to stopStop the data collection.

26.6.4.7.　Save the data, adjust the limits of the y-axis, title the graph, and print it.

26.7.4.8.　Do not throw any cyclohexane or unknown compound down the sink. Pour the liquid mixture into the "Laboratory Waste" jar. Rinse the test tube and temperature probe with acetone to remove the last traces of any crystals, pouring the rinses in the waste jar.

Results:

The mass of cyclohexane that was dispensed can be calculated. The density of cyclohexane is 0.779 g/mL.

$$\text{mass} = (12.0\text{mL})\left(\frac{0.779\text{g}}{\text{mL}}\right) = 9.35\text{g}$$

The values for T_f^o and T_f can be determined from the plots.

The molar mass, and thus the molecular weight, of the unknown compound can also be calculated. For cyclohexane, $K_f = 20.2$ deg·kg/mole of solute.

$$\text{molar mass}_{\text{solute}}, \text{g/mol} = \frac{(1000 \text{ g/kg})\cdot(K_f)\cdot(\text{g of solute})}{(DT)\cdot(\text{g of solvent})}$$

$$\text{molar mass}_{\text{solute}}, \text{g/mol} = \frac{(1000 \text{ g/kg})\times(20.2 \text{ deg}\times\text{kg/mol})\times(? \text{ g})}{(?)\times(9.35 \text{ g})}$$

$$\text{molar mass} = ? \text{ g/mol}$$
$$\text{molecular weight} = ? \text{ amu}$$

The molecular weights of the possible compounds are:

-   154.21 amu for Biphenyl
-   191.46 amu for 2-Bromochlorobenzene
-   128.17 amu for Naphthalene
-   178.23 amu for Anthracene
-   235.90 amu for 1,4-Dibromobenzene

The value determined experimentally for the molecular weight of the unknown compound is closest to the literature value for naphthalene.

The percent error can be calculated.

$$\% \text{ error} = \frac{|\text{accepted value - experimental value}|}{\text{accepted value}} \cdot 100$$

$$\% \text{ error} = \frac{|128.17 \text{ amu - }?|}{128.17 \text{ amu}} \cdot 100$$

$$\& \text{ error} = ? \%$$

Applications:

Perhaps the most visible application of the phenomenon of freezing-point depression occurs during the winter months, when roads and sidewalks become icy, and salt is used to treat the slippery surfaces (**Figure 2**). When the salt mixes with the ice, the freezing point of the water is depressed so the ice melts at a lower temperature. Because the degree of the freezing point depression is dependent on the number of particles in solution, salts that release three ions per formula unit, such as calcium chloride ($CaCl_2$), are often utilized for this purpose. Ice cream makers also make use of the freezing-point depression that occurs when salt and ice are mixed. The freezing point of cream is well below 0 °C, especially when it is combined with sugar and other ingredients used to make ice cream. For this reason, ice and rock salt are combined in the outer container of an ice cream maker in order to achieve a temperature low enough to freeze the mixture enclosed in the inner container.

Chemists exploit the phenomenon of freezing-point depression in the analysis of solid organic compounds. The purity of a solid product from a chemical synthesis is often determined by measuring the melting point (theoretically, the same as the freezing point) of the material. If an impurity is present in the compound, the observed melting point is lower than expected. This occurs because, as the solid starts to melt, the impurity acts as a solute that is dissolved in the liquid form of the compound; thus, the melting, or freezing, point of the compound is depressed.

The pharmaceutical industry uses large amounts of organic solvents for reactions that lead to the synthesis of therapeutic agents. These solvents create substantial volumes of liquid waste that are hazardous to the environment. Occasionally, it is possible to take advantage of the freezing-point depression phenomenon to eliminate the need for a solvent in a synthesis. When solid reactants involved in a reaction are crushed together, the melting (or freezing) points of the two compounds are lowered. If the two compounds each have a very low melting point, the pair actually become liquids at room temperature when they are ground together, which allows the molecules to interact with each other so the reaction can occur. These solvent-free processes are an example of "green" chemistry, which refers to chemical procedures that reduce or eliminate the use and generation of hazardous substances.

Legend:

Figure 1: **Figure 1a** is a plot of temperature as a function of time for the determination of $T_f°$ for the pure solvent. **Figure 1b** is a plot of temperature as a function of time for the determination of T_f for the solution.

Figure 2: A small vehicle used to snowplow sidewalks. A salt spreader is attached on the back to help melt ice.