

## Introduction

Freezing point depression is a colligative property. Colligative properties are those properties that depend on the amount of solute added to a solution. They are independent of the identity of the solute in an ideal solution where the interactions between solute and solvent molecules are similar to the intermolecular interactions of either pure solute or pure solvent. In addition to freezing point depression, other colligative properties include boiling point elevation, vapor pressure lowering, and osmotic pressure.

Freezing point depression is based on a constant specific for the particular solvent and is proportional to the concentration of solute dissolved in the solvent. In this experiment, the solvent is naphthalene and the solute will initially be biphenyl, and then will be an unknown. Mothballs contain naphthalene, so you might recognize the odor.

## Theory

In dilute solutions, the freezing point depression ( $\Delta T_f$ ) is calculated using Equation 1:

$$\Delta T_f = T_f(\text{solvent}) - T_f(\text{solution}) = K_f \times m \quad (\text{Equation 1})$$

In this experiment,  $T_f(\text{solvent})$  is the point at which crystals first appear in pure naphthalene as determined graphically (see Figure 4.1). The literature value for  $T_f(\text{naphthalene})$  is 80.2 °C. Any slight variations in your experimental results will be due to minor impurities present in the experimental grade naphthalene or to the thermometer.

Next,  $T_f(\text{solution})$  will be determined experimentally by freezing a mixture of naphthalene with a dissolved solute. It is the point at which crystals first appear in either the naphthalene/biphenyl or naphthalene/unknown mixtures (see Figure 4.2).

$K_f$  is the molal freezing point depression constant. This is a property of the solvent. Molality,  $m$ , is defined as moles solute (either biphenyl or an unknown) per kilograms of solvent (naphthalene), and is calculated by Equation 2:

$$\text{Molality} = m = \frac{\text{moles of solute}}{\text{kilograms of solvent}} \quad (\text{Equation 2})$$

The molecular formula for biphenyl is  $\text{C}_{12}\text{H}_{10}$ . In the first part of this experiment, Equation 1 will be arranged to determine the molal freezing point depression constant for naphthalene. In the second part of the experiment, Equation 1 will be rearranged to determine the molality of the naphthalene/unknown solution. Subsequently, the molar mass of the unknown will be determined.

See Figure 4.1 for a cooling curve of pure naphthalene. You will note that the temperature decreases steadily until the freezing point. At this point, solid and liquid naphthalene are in equilibrium and the temperature is constant. When all of the naphthalene is frozen, the temperature drops. The line labeled  $T_f$  indicates the experimental freezing point of naphthalene (80.3 °C).

In a solute/solvent mixture, the solvent (naphthalene) generally freezes out of solution. The freezing is not constant as it was for pure naphthalene. Instead, the cooling curve of the mixture will show a gradual drop in the temperature during the time when freezing takes place. An additional feature of this graph may be the appearance of a region of supercooling where the mixture cools below the freezing point without the appearance of any crystals. The first crystal appears and the temperature begins to rise. The maximum temperature after the appearance of the first crystal is the freezing point of the mixture. This occurs at a lower temperature than that of the pure substance.

See Figure 4.2 for a cooling curve of a naphthalene/biphenyl mixture. The line labeled  $T_f$  indicates an experimental freezing point of 72.5 °C.

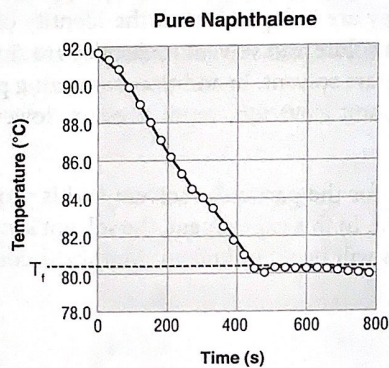


Figure 4.1. Cooling Curve

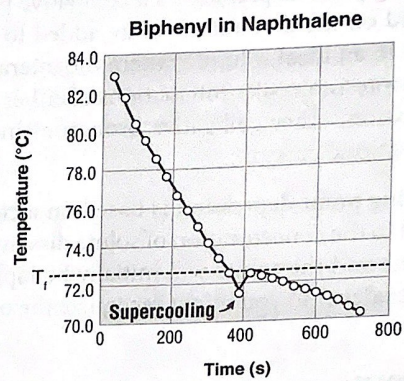


Figure 4.2. Cooling Curve

## Data and Results

\_\_\_\_/15 points

| Data Table 1: Pure Naphthalene                                                          |         |
|-----------------------------------------------------------------------------------------|---------|
| MeasureNet Station No.                                                                  |         |
| Mass of Test Tube + Naphthalene (g)                                                     | 33.6423 |
| Mass of Test Tube (g)                                                                   | 24.056  |
| Mass of Naphthalene (g)                                                                 |         |
| Time at Which Crystals First Appeared (s)                                               | 116     |
| Temperature at Which Crystals First Appeared (°C)                                       | 80.09   |
| Maximum Temperature Attained After Crystals Appeared (°C)<br>(from graph)               |         |
| Freezing Point of Pure Naphthalene (°C)<br>( $T_f$ (naphthalene), from graph)           |         |
| Data Table 2: Biphenyl and Naphthalene                                                  |         |
| Mass of Biphenyl (g)                                                                    | 1.4909  |
| Mass of Naphthalene (g)<br>(from Data Table 1)                                          |         |
| Time at Which Crystals First Appeared (s)                                               | 75      |
| Temperature at Which Crystals First Appeared (°C)                                       | 72.08   |
| Maximum Temperature Attained After Crystals Appeared (°C)<br>(from graph)               |         |
| Freezing Point of Naphthalene/Biphenyl Solution (°C)<br>( $T_f$ (solution), from graph) |         |
| Freezing Point Depression (°C)<br>( $\Delta T_f$ )                                      |         |
| Molality of Naphthalene/Biphenyl Solution (mol/kg or m)                                 |         |
| Freezing Point Depression Constant of Naphthalene (°C m <sup>-1</sup> )<br>( $K_f$ )    |         |

| Data Table 3: Unknown and Naphthalene                                                  |         |
|----------------------------------------------------------------------------------------|---------|
| Unknown No.                                                                            | N/A     |
| Mass of Test Tube (g)                                                                  | 24.1808 |
| Mass of Test Tube + Naphthalene (g)                                                    | 33.4506 |
| Mass of Test Tube + Naphthalene + Unknown (g)                                          | 34.6750 |
| Mass of Naphthalene (g)                                                                |         |
| Mass of Unknown (g)                                                                    |         |
| Time at Which Crystals First Appeared (s)                                              | 23      |
| Temperature at Which Crystals First Appeared (°C)                                      | 76.08   |
| Maximum Temperature Attained After Crystals Appeared (°C)<br>(from graph)              |         |
| Freezing Point of Naphthalene/Unknown Solution (°C)<br>( $T_f$ (solution), from graph) |         |
| Freezing Point Depression (°C)<br>( $\Delta T_f$ )                                     |         |
| Molality of Naphthalene/Unknown Solution (mol/kg or m)<br>(m)                          |         |
| Experimental Molar Mass of Unknown (g/mol)                                             |         |
| Identity of Unknown                                                                    |         |
| Percent Error for Molar Mass of Unknown (%)                                            |         |

**Post-Lab Data Analysis**

\_\_\_\_/15 points

Create a cooling curve in Excel for each part of the experiment (pure naphthalene, naphthalene/biphenyl, and naphthalene/unknown). Plot temperature versus time. **Do not have Excel plot a trend line through the data.** Indicate the appearance of the first crystal and  $T_f$  on each cooling curve, and record the values in the appropriate data tables. Turn in a printed copy of each cooling curve with your lab report. Do not print raw data from MeasureNet.

**Sample Calculations**

(For credit, show your work for each of the following sample calculations, including units. Additional calculations must be performed to complete all data tables, but you do not have to show a sample of each of these. Record all calculated results in the appropriate data table.)

**Data Table 2**

Freezing Point Depression of Naphthalene/Biphenyl Solution

\_\_\_\_/5 points

Molality of Naphthalene/Biphenyl Solution

\_\_\_\_/5 points

Freezing Point Depression Constant of Naphthalene

\_\_\_\_/5 points

## Data Table 3

Molality of Naphthalene/Unknown Solution

\_\_\_\_/5 points

## Experimental Molar Mass of Unknown

\_\_\_\_/5 points

Calculate the molar mass of your unknown in the space below. Use the chart to determine the identity of the unknown based on the calculated experimental molar mass and record the name of the compound in Data Table 3.

| Compound           | Molar Mass (g/mol) |
|--------------------|--------------------|
| p-Dimethoxybenzene | 138.2              |
| Biphenyl           | 154.2              |
| Diphenylamine      | 169.2              |
| Benzil             | 210.2              |