EXPERIMENT 17

# Molar Mass Determination by Freezing-Point Depression

**Performance Goals**

**17–1** Measure the freezing point of a pure substance.

**17–2** Determine the freezing point of a solution by graphical methods.

**17–3** Knowing the molal freezing-point constant and having determined experimentally the mass of an unknown solute, the mass of a known solvent, and the freezing-point depression, find the molar mass of the solute.

## CHEMICAL OVERVIEW

When a solution is prepared by dissolving a certain amount of solute in a pure solvent, the properties of the solvent are modified by the presence of the solute. Changes in such properties as the melting point, boiling point, and vapor pressure are found to be dependent on the number of solute molecules or ions in a given amount of solvent. The nature of the solute particles (molecules or ions) is not important; the governing factor is the *relative number of particles.* Properties that are dependent only on the concentration of solute particles are referred to as **colligative properties**.

If a pure liquid is cooled, the temperature will decrease until the freezing point is reached. With continued cooling, the liquid gradually freezes. As long as liquid and solid are *both* present, the temperature will remain constant. When all the liquid is converted to solid, the temperature will drop again.

A typical cooling curve for a pure solvent is shown in Figure 17.1. The dip below the freezing point is the result of supercooling, an unstable situation in which the temperature drops below the normal freezing point until crystallization begins. Supercooling may or may not occur in any single freezing process and will probably vary in successive freezings of the same sample of pure substance. As soon as crystal formation begins, the temperature rises to the normal freezing point and remains constant until all of the liquid is frozen.

The freezing point of a solution is always lower than that of the pure solvent. The difference between the freezing points of the solvent and solution is the **freezing-point depression**. This difference is proportional to the molal concentration of solute (see Equation 17.1). During the freezing of a solution, it is the solvent that freezes. Therefore, the solvent is gradually removed from the solution as the freezing progresses, leaving behind an increasingly concentrated solution. Because of this concentration increase, the freezing point drops, producing a solution freezing curve such as that in Figure 17.2. Again, the supercooling effect may or may not be observed in any single freezing experiment.

Colligative properties may be used to find the molar mass of an unknown substance. It is known, for example, that 1 mole of any molecular substance (one that does not produce ions in solution), when dissolved in 1 kg of water, lowers its freezing point by 1.86°C and raises its boiling point by 0.52°C. The freezing-point depression or boiling-point elevation for a 1.0 molal solution of a molecular substance will be the same regardless of the nature of the substance, as long as no ionization takes place. In general, the relationship between freezing-point depression and concentration of solute can be expressed as

$$\Delta T_F = K_F m \tag{17.1}$$

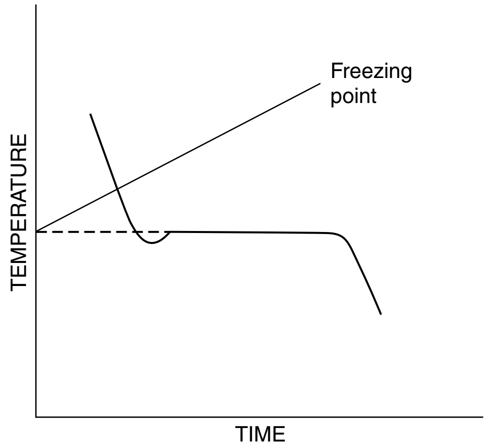



**Figure 17.1**
*Cooling curve of a pure liquid*

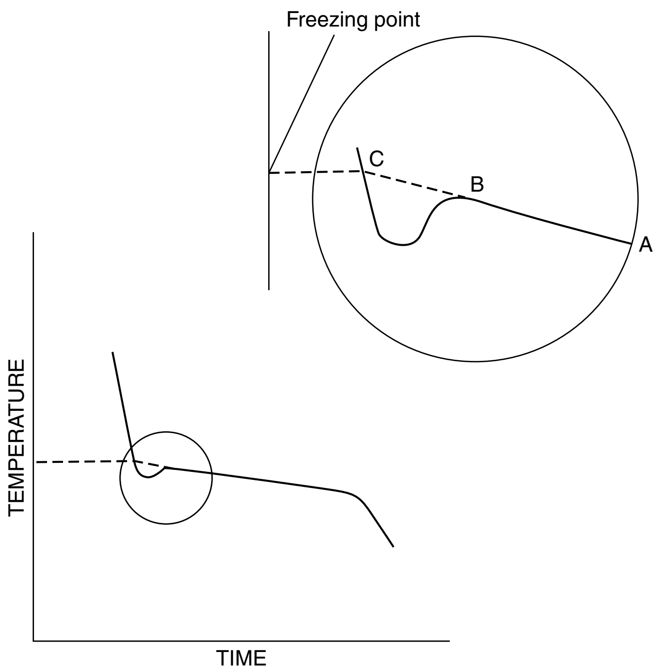



**Figure 17.2**
*Cooling curve of a solution*

where $\Delta T_F$ is the freezing-point depression in °C, $K_F$ is the molal freezing-point constant of the pure solvent, and $m$ is the molality of the solution (moles of solute per kg of solvent).

The solvent in this experiment is naphthalene ($K_F = 6.9°C/m$). You will determine its freezing point experimentally with *your* thermometer. (The literature value of the freezing point is 80.2°C.) You will then prepare a solution from a weighed quantity of naphthalene and a weighed quantity of unknown solute, and determine experimentally its freezing point. When you substitute $\Delta T_F$ into Equation 17.1, the molality of the solution can be calculated.

Molality, by definition, is moles of solute per kilogram of solvent. This may be expressed mathematically as

$$m = \frac{\text{mole solute}}{\text{kg solvent}} = \frac{\text{g solute/MM}}{\text{kg solvent}} \tag{17.2}$$

Knowing the mass of the solute and the mass of the solvent used, the molar mass (MM) can be calculated if the molality ($m$) is determined experimentally.

## SAMPLE CALCULATIONS

**Example 1**

Calculate the molal concentration of a solution of 3.45 g of compound A (MM =120 g/mole) dissolved in 50.0 g of solvent.

Converting the mass of solvent to kg and substituting the given values into Equation 17.2,

$$m = \frac{3.45 \text{ g solute/120 g solute/mole}}{0.050 \text{ kg solvent}}$$
$$= \frac{3.45 \text{ g solute}}{0.050 \text{ kg solvent}} \times \frac{1 \text{ mole solute}}{120 \text{ g solute}} = 0.575 \text{ mole/kg solvent}$$

**Example 2**

Calculate the molar mass of an unknown substance if a solution containing 2.37 g of unknown in 20.0 g of water freezes at −1.52°C. $K_F$ for water = 1.86°C/$m$.

The normal freezing point of water is 0.00°C, and that of the solution is −1.52°C. The freezing-point depression therefore is

$$\Delta T_F = 0.00°\text{C} - (-1.52°\text{C}) = 1.52°\text{C}$$

Solving Equation 17.1 for $m$ and substituting,

$$m = \frac{\Delta T_F}{K_F} = \frac{1.52°\text{C}}{1.86°\text{C}/m} = 0.817 \frac{\text{mole solute}}{\text{kg solvent}}$$

Now you can calculate the molar mass using Equation 17.2:

$$0.817 \frac{\text{mole solute}}{\text{kg solvent}} = \frac{2.37 \text{ g solute/MM}}{0.0200 \text{ kg solvent}}$$

After rearranging to obtain MM,

$$MM = \frac{2.37\,\text{g solute}}{0.0200\,\text{kg solvent} \times 0.817\,\frac{\text{mole solute}}{\text{kg solvent}}} = 145\,\text{g/mole}$$

## SAFETY PRECAUTIONS AND DISPOSAL METHODS

In this experiment you will be handling various organic chemicals. Always use a spatula; do not handle crystals by hand. When using organic liquids, do not breathe their vapors.

Dispose of excess reagents as directed by your instructor. Do not use organic liquids near an open flame.

## PROCEDURE

**NOTE:** Record all mass measurements in grams to the nearest 0.01 g. Record all temperature measurements in degrees Celsius to the nearest 0.1 °C.

### 1. The Freezing Point of Naphthalene

**A.** Assemble the apparatus shown in Figure 17.3 using a thermometer graduated in tenths of degrees Celsius. A circular stirrer may be formed from No. 18 wire. A 600-mL beaker half full of water may be used as the water bath.

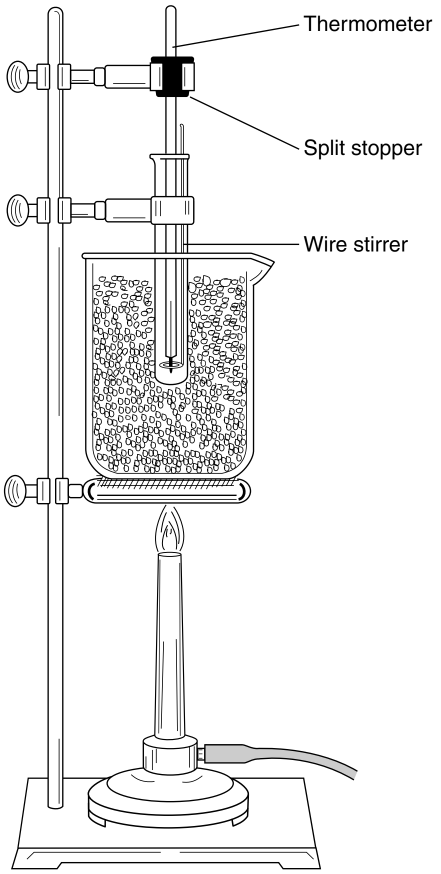



**Figure 17.3**
*Apparatus for determining freezing point*

**B.** Weigh an empty test tube to ±0.01 g on a centigram balance. Add about 10 g of naphthalene and weigh again.

**C.** Insert the thermometer in the test tube and place the unit in the water bath. Heat the water bath until the naphthalene completely melts. Be sure the entire thermometer bulb is submerged in the molten naphthalene and is not touching the bottom or walls of the test tube.

**D.** Discontinue heating, remove the water bath, and allow the liquid to cool slowly. Beginning at about 90°C, record the temperature to ±0.1 °C every 30 seconds for 10 minutes. Stir continuously during this period by raising and lowering the wire stirrer.

**2. The Freezing Point of the Solution**

**A.** Place a 1.0- to 1.3 g sample of unknown solute into a test tube and weigh them to the nearest 0.01 g on a centigram balance. Transfer the unknown to the test tube containing naphthalene (Part 1). Again weigh the empty test tube with any powder of the unknown that may not have been transferred, to determine the mass of the solute dissolved.

**B.** Heat the mixture in the water bath until all the naphthalene is melted and the unknown is completely dissolved. With constant stirring, determine the freezing point of the solution exactly the same way as you determined the freezing point of the pure naphthalene.

**C.** If time permits, remelt the solution and repeat the freezing cycle.

**3. Clean-Up**

To clean your equipment, melt the solution in the test tube and pour it onto a paper towel folded to several thicknesses. The test tube may be cleaned with hexane, acetone, or some other suitable solvent.

**CAUTION**

**Do *not* pour melted naphthalene solutions into the sink. They freeze and clog drains. Many cleaning solvents are flammable and should not be used near an open flame. Clean the equipment in a hood. Do not breathe vapors.**

## FREEZING-POINT DETERMINATION

Estimate to ±0.1 °C the freezing point of pure naphthalene from your data. According to Figure 17.1, the freezing point of a pure substance is the constant temperature at which the substance freezes. With due allowance for supercooling, if any, this temperature should be apparent from the table. Record it on the work page.

To estimate the freezing temperature of the solution of the unknown in naphthalene, plot the temperature vs. time on the graph paper provided. The freezing point of the solution *of the concentration you prepared* is the point where it first begins to freeze if there is no supercooling. If supercooling does occur, the freezing point may be estimated from the graph by extrapolating the curve during freezing (from A to B in Figure 17.2) back to its intersection with the cooling line for the liquid (point C). The temperature corresponding to point C is the temperature at which freezing would have begun in the absence of supercooling—the freezing point of your solution at its initial concentration. Record the freezing temperature of the solution on the work page.

## CALCULATIONS

From the observed freezing points of pure naphthalene and the solution, calculate the freezing-point depression. Record $\Delta T_F$ in the Results table on the work page.

Using Equation 17.1 and the molal freezing-point constant of naphthalene ($K_F = 6.9°C/m$), find the molality of your solution. Record $m$ in the Results table on the work page.

Determine and record the kilograms of naphthalene and grams of solute in your solution.

Using Equation 17.2 and the results already determined, calculate and record the molar mass of your unknown.

Name Date Section

# Experiment 17

## Advance Study Assignment

**1.** Define colligative properties.

**2.** Calculate the molality of the solution obtained when 10.3 g of sugar, $C_6H_{12}O_6$, are dissolved in 275 g of water.

**3.** Calculate the freezing-point depression for a solution prepared by dissolving 25.0 g of $C_8H_{18}$ in 175 g of benzene. ($K_F$ = 4.90°C/$m$ for benzene.)

**4.** If 2.6 g of unknown solute are dissolved in 28 g of water, the freezing-point depression is 2.7°C.

**a.** Calculate the molality of the solution if $K_F$ = 1.86°C/$m$ for water.

**b.** Calculate the molar mass of the solute.

*Name* ______ *Date* ______ *Section* ______

# Experiment 17

## Work Page

## Data

### Time-Temperature Readings (Read to ±0.1 °C)

| *Time (Minutes)* | *Naphthalene* | *Naphthalene + Unknown* | | | |
|---|---|---|---|---|---|
| 0 | | | | | |
| $\frac{1}{2}$ | | | | | |
| 1 | | | | | |
| $1\frac{1}{2}$ | | | | | |
| 2 | | | | | |
| $2\frac{1}{2}$ | | | | | |
| 3 | | | | | |
| $3\frac{1}{2}$ | | | | | |
| 4 | | | | | |
| $4\frac{1}{2}$ | | | | | |
| 5 | | | | | |
| $5\frac{1}{2}$ | | | | | |
| 6 | | | | | |
| $6\frac{1}{2}$ | | | | | |
| 7 | | | | | |
| $7\frac{1}{2}$ | | | | | |
| 8 | | | | | |
| $8\frac{1}{2}$ | | | | | |
| 9 | | | | | |
| $9\frac{1}{2}$ | | | | | |
| 10 | | | | | |

Name ______________________ Date ____________ Section ____________

# Experiment 17

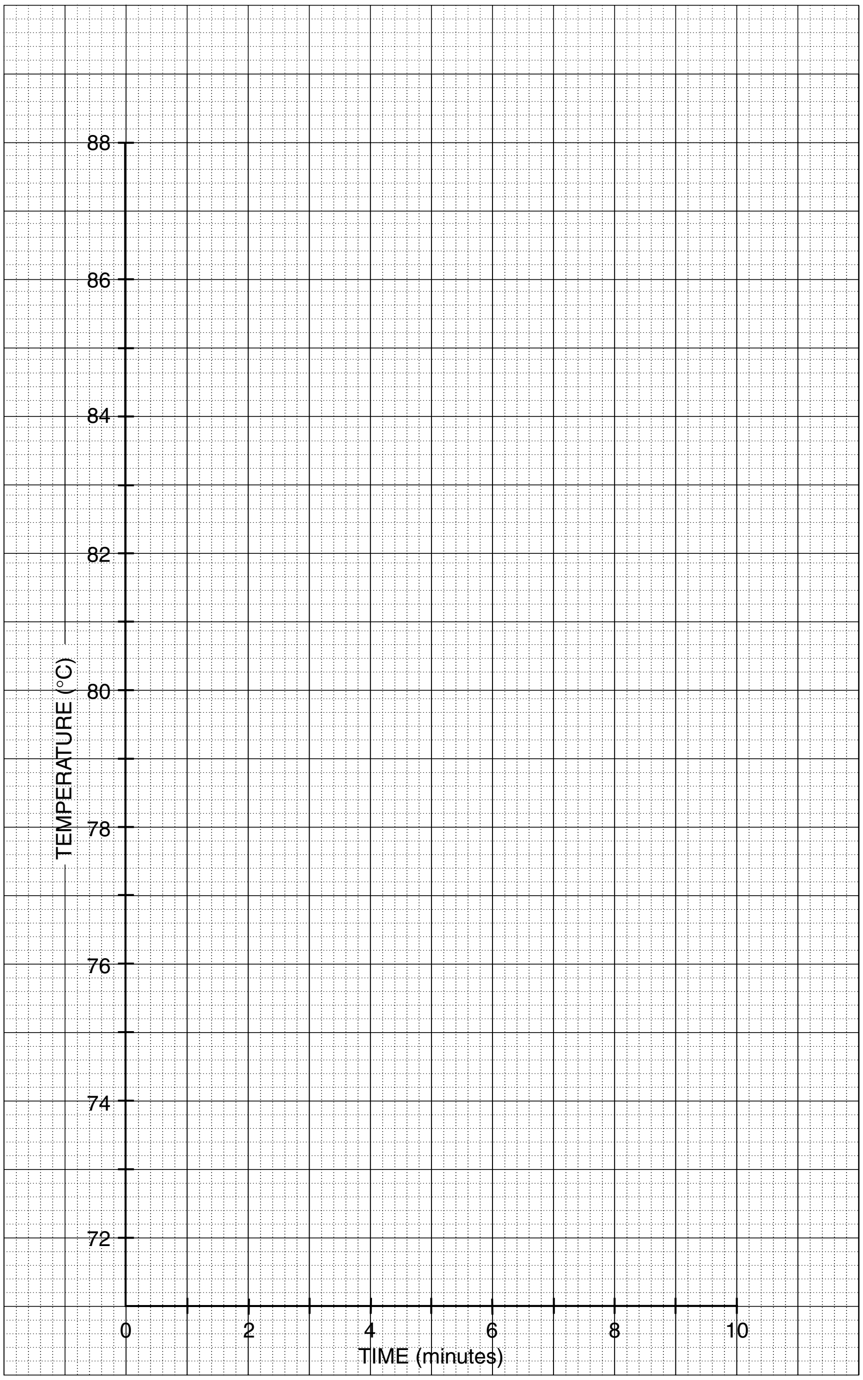
## Work Page

### Data

| | | | |
|---|---|---|---|
| Mass of test tube (g) | | | |
| Mass of test tube and naphthalene (g) | | | |
| Mass of test tube and unknown ________ (g) | | | |
| Mass of test tube after transfer (g) | | | |
| Freezing point of naphthalene (°C) | | | |
| Freezing point of solution (from curve) (°C) | | | |

### Results

| | | | |
|---|---|---|---|
| Freezing-point depression, $\Delta T_F$ (°C) | | | |
| Molality, $m$ (mole solute/kg solvent) | | | |
| Mass of naphthalene (g) | | | |
| Mass of unknown ________ (g) | | | |
| Molar mass of unknown (g/mole) | | | |




Cooling curve of solution

*Name* | *Date* | *Section*

# Experiment 17

## Report Sheet

## Data

### Time-Temperature Readings (Read to ±0.1 °C)

| *Time (Minutes)* | *Naphthalene* | *Naphthalene + Unknown* | | | |
|---|---|---|---|---|---|
| 0 | | | | | |
| $\frac{1}{2}$ | | | | | |
| 1 | | | | | |
| $1\frac{1}{2}$ | | | | | |
| 2 | | | | | |
| $2\frac{1}{2}$ | | | | | |
| 3 | | | | | |
| $3\frac{1}{2}$ | | | | | |
| 4 | | | | | |
| $4\frac{1}{2}$ | | | | | |
| 5 | | | | | |
| $5\frac{1}{2}$ | | | | | |
| 6 | | | | | |
| $6\frac{1}{2}$ | | | | | |
| 7 | | | | | |
| $7\frac{1}{2}$ | | | | | |
| 8 | | | | | |
| $8\frac{1}{2}$ | | | | | |
| 9 | | | | | |
| $9\frac{1}{2}$ | | | | | |
| 10 | | | | | |

Name ______________________ Date ____________ Section ____________

# Experiment 17

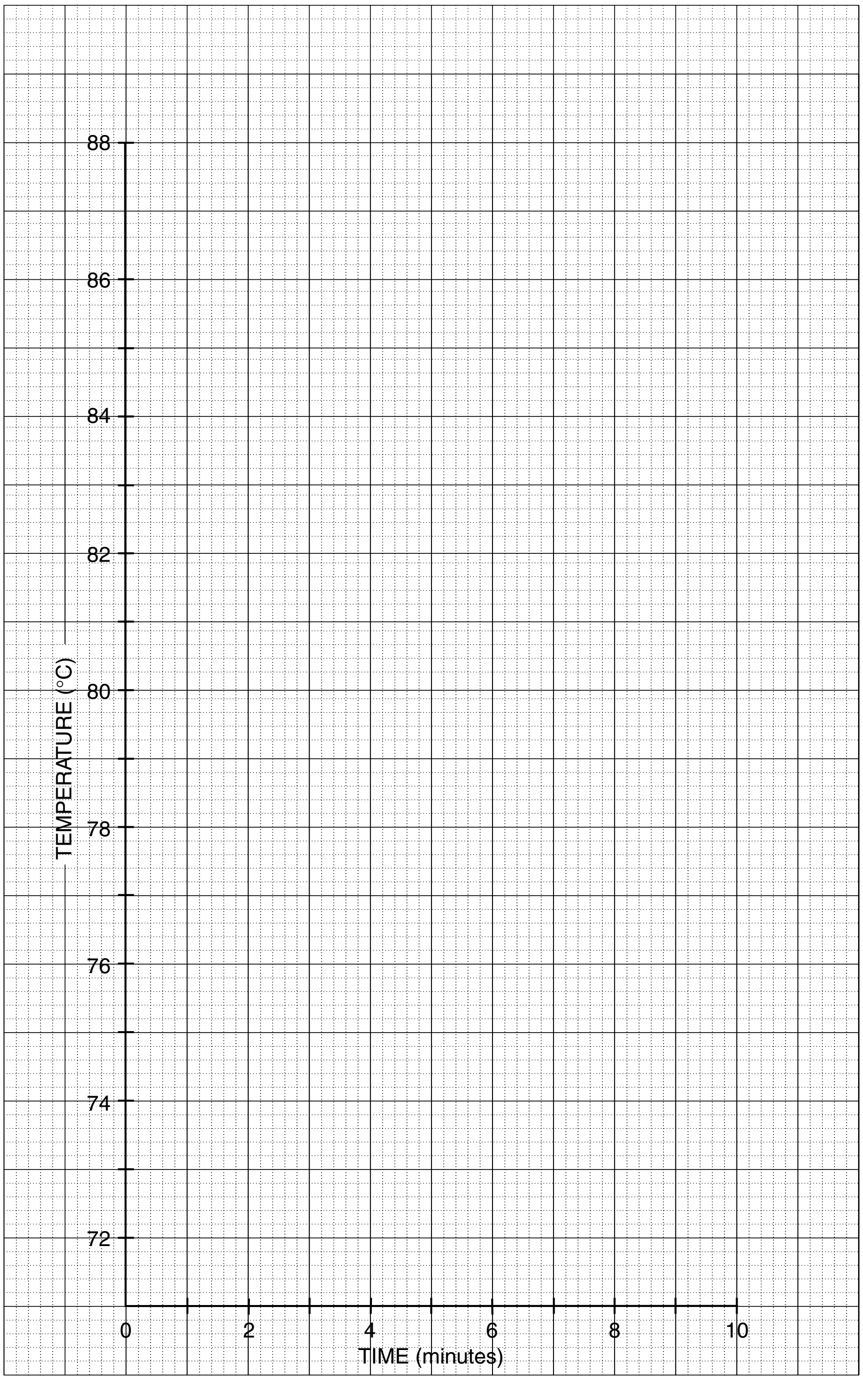
## Report Sheet

### Data

| | | | |
|---|---|---|---|
| Mass of test tube (g) | | | |
| Mass of test tube and naphthalene (g) | | | |
| Mass of test tube and unknown ________ (g) | | | |
| Mass of test tube after transfer (g) | | | |
| Freezing point of naphthalene (°C) | | | |
| Freezing point of solution (from curve) (°C) | | | |

### Results

| | | | |
|---|---|---|---|
| Freezing-point depression, $\Delta T_F$ (°C) | | | |
| Molality, $m$ (mole solute/kg solvent) | | | |
| Mass of naphthalene (g) | | | |
| Mass of unknown ________ (g) | | | |
| Molar mass of unknown (g/mole) | | | |




Cooling curve of solution