Experiment 11

FV-10/18//00

MOLAR MASS DETERMINATION BY FREEZING-POINT DEPRESSION

MATERIALS: 25 x 200 mm test tube, 600 mL beaker, 50 mL graduated cylinder, thermometer, cyclohexane, unknown solute, ice, NaCl, metal stirring rod.

PURPOSE: The purpose of this experiment is to determine the molar mass of a compound from freezing-point depression data.

LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Define solute, solvent, solution, and molality.
2. Interpret a phase diagram.
3. Experimentally determine the freezing points of pure liquids and solutions.
4. Calculate the approximate molar mass of a compound from freezing-point depression data.

DISCUSSION:

When a nonvolatile solute is added to a solvent, the vapor pressure of the resulting solution is lower than that of the pure solvent. In Figure 1, curve AB represents the temperature and pressure conditions at which a pure liquid solvent will be in equilibrium with its vapor (gaseous) phase. The equilibrium pressures are called "vapor pressures", and the equilibrium temperatures are called "boiling points." Curve AC represents the equilibrium between a pure solid solvent and its gas phase at their various equilibrium vapor pressures and "sublimation points." Curve CD represents the equilibrium between the vapor phase of the solvent and a liquid solution. The presence of the solute clearly shifts the line of the boiling point from AB (pure solvent) to CD (solution).

The *normal freezing point*, T_2, of the pure solvent is the temperature at which the vapor pressures of the solid and liquid phases of the solvent are equal under conditions where the total pressure of the system is 1 atm. The addition of a solute lowers the vapor pressure and reduces the freezing point to T_1, the temperature at which the vapor pressures of the solvent solid phase and solution are equal at 1 atm pressure.

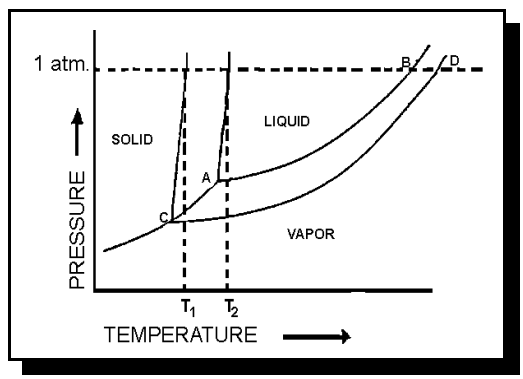


Figure 1: Phase Diagram

The magnitude of the vapor-pressure lowering of a solution depends only on the number of solute particles in the solution, not upon their identity. If one mole of nonvolatile solute particles is dissolved in 1000 grams of water, the freezing point is lowered 1.86 °C. If one mole of nonvolatile solute particles is dissolved in 1000 grams of cyclohexane, the freezing point is lowered 20.0 °C. This depression of freezing point by the addition of one mole of solute to 1000 grams of solvent is called the *molal freezing-point depression constant* and is given the symbol K_f. The value of K_f depends on the particular solvent. For dilute solutions, the freezing-point depression, ΔT_f, is directly proportional to the molality, m, of the solution. *Molality* is defined as the total number of moles of solute particles dissolved in 1000 grams or 1.000 kg of solvent.

$$\Delta T_f = K_f \cdot m \qquad \text{molality} = m = \frac{\text{moles solute}}{\text{kg solvent}}$$

PROCEDURE:

Safety Note: Cyclohexane is hazardous. Dispose of cyclohexane in the proper waste container.

1. Prepare an ice-water bath by adding ice and water to a 600 mL beaker. The ice-water level should be approximately to the 500 mL mark on the beaker.

2. Obtain a 50 mL graduated cylinder and a clean, dry, large test tube from the hood. Pour approximately 40 mL of cyclohexane into the graduated cylinder. Weigh the cylinder and its contents on a top-loading balance. Carefully pour the cyclohexane into the large test tube, then weigh the empty graduated cylinder. Record these masses in the Data Section. RETURN THE GRADUATED CYLINDER TO THE HOOD. (This procedure will insure that flammable cyclohexane vapors are vented from the lab.)

3. Place a thermometer and metal stirring rod into the test tube. Place the test tube into your ice-water bath. To ensure *slow* cooling of the liquid, move the metal stirring rod to keep the contents of the test tube in constant motion while in the ice-water bath. Remove the test tube from the ice-water bath as necessary to keep the temperature from dropping too fast. When the cyclohexane has reached its freezing point, snow-like crystals will appear in the liquid. (Some freezing on the interior walls of the tube should not be mistaken as the freezing point. Constant stirring of the cyclohexane should prevent this from happening.) Record the freezing point of the pure cyclohexane. Remove the test tube from the ice-water and allow it to warm until all the solid is melted.

4. Repeat the cooling process until consistent results for the freezing point of pure cyclohexane are obtained (two successive values should agree within 0.1 °C). Save the test tube of cyclohexane for the next step.

   If the contents of the test tube are not kept in constant motion during the cooling process or if the liquid is cooled too fast, it is possible to lower the temperature below the freezing point without having any solidification. In this case, the liquid is known as supercooled. More vigorous stirring will usually cause the liquid to solidify partially; this is accompanied by an abrupt rise in temperature to the normal freezing point.

5. Obtain a sample of an unknown solid from your instructor. Record the unknown number in the Data Section and weigh the small sample tube with its contents on an analytical balance. Pour approximately half of the sample into the test tube of cyclohexane and reweigh the sample tube. Record all masses in the Data Section. Stir the cyclohexane solution, using the metal stirring rod, until the solid (solute) is completely dissolved. Warming the solution with your hand will help the solute dissolve faster.

6. Determine the freezing point of this solution, Solution I, using the same method as that used for the pure cyclohexane. Again, two successive values must agree within 0.1ºC.

7. To prepare Solution II, pour the remaining unknown into Solution I and weigh the empty sample tube. Record this mass in the Data Section. Determine the freezing point of Solution II.

   If Solution II does not freeze in the ice bath, add some sodium chloride, NaCl, to the ice bath to lower its temperature below 0 °C.

Clean up:

1. Return the unknown sample tube, unwashed, to your instructor.
2. Pour Solution II into the waste container in the hood. Rinse the tube with about 2-4 mL of cyclohexane and pour the rinses into the container. DO NOT USE WATER. Place the large tube in the drying rack in the hood.
3. Wash all other glassware. Return all equipment to their proper locations.

Name _____ Section _____

Partner _____ Date _____

DATA SECTION
Experiment 11

Unknown number: _____

Mass of graduated cylinder + pure cyclohexane _____

Mass of empty graduated cylinder _____

Mass of pure cyclohexane _____

Mass of sample tube + original contents _____

Mass of sample tube + ½ original contents _____

Mass of empty sample tube _____

Mass of unknown in Solution I _____

Mass of *total* amount of unknown in Solution II _____

Trial Number	1	2	3	4	Average of last two trials
Freezing Point of cyclohexane					
Freezing Point of Solution I					
Freezing Point of Solution II					

Freezing-point depression of Solution I, ΔT_f _____

Freezing-point depression of Solution II, ΔT_f _____

DATA TREATMENT
Experiment 11

Be sure to include appropriate units and use the correct number of significant digits.

Solution I:

1. From your experimental data, calculate the molality of Solution I. The K_f of cyclohexane is 20.0°C·kg/mol. This can also be expressed as 20.0°C/molal.

Molality = _____

2. Calculate the number of moles and the molar mass of the unknown solute.

Number of moles = _____

Molar mass = _____

Solution II:

1. From your experimental data, calculate the molality of Solution II.

Molality = _____

2. Calculate the number of moles and the molar mass of the unknown solute.

Number of moles = _____

Molar mass = _____

3. Calculate the average molar mass of the unknown, determined from Solutions I and II.

Unknown number: _____ Average molar mass = _____

4. Optional: To check your results, enter them into the "Data Input and Feedback" section of MOLS at http://walnut.mathsci.usna.edu/~lomax/labs/login.html.

QUESTIONS
Experiment 11

1. If the thermometer consistently displays a temperature of 0.2 °C *lower* than the actual temperature throughout the experiment, what effect, *(i.e.*, too high, too low, or no effect) would this have on the calculated molar mass of the unknown? Explain your answer.

2. If the freezing point of the solution had been incorrectly read as 0.3 °C *lower* than its true freezing point and the freezing point of the pure solvent was correctly read, what effect (*i.e.*, too high, too low, or no effect) would this have on the calculated molar mass of the unknown? Explain.

3. Calcium chloride, $CaCl_2$, is commonly used as road salt. If one mole of $CaCl_2$ is dissolved in 1 kg of water, would the freezing point of the solution be greater than, less than, or the same as a solution prepared by dissolving one mole of table sugar (or sucrose), $C_{12}H_{22}O_{11}$, in 1 kg of water? Explain.

Name _____ Section _____

Date _____

PRE-LAB QUESTIONS
Experiment 11

1. Define the following terms:

   Solute

   Solvent

   Solution

2. a. Look up the safety information for cyclohexane (i.e., MSDS). Why is cyclohexane a hazard in our lab?
   http://chem.mathsci.usna.edu/plebechem/Safety.html

   b. Cyclohexane, C_6H_{12}, is a nonpolar solvent. Which of the following solutes would dissolve in cyclohexane? Circle your answer(s) and provide a brief explanation.

   NaCl $C_{10}H_8$ K_2SO_4 CH_3COOH

   Explanation:

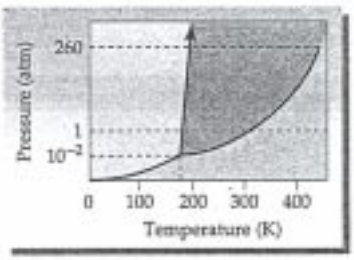
3. In an experiment carried out to determine the molar mass of a unknown compound, 1.07 g of the unknown was dissolved in 27.00 g of cyclohexane. The freezing point of pure cyclohexane was determined to be 6.50 °C and the freezing point of the solution was determined to be 0.700 °C.

   What is the molar mass of the compound? Show your work.

   Molar mass = _____

4. In the phase diagram, what is the normal boiling point? _____

   What is the normal freezing point? _____

   In what state is the material at 300K and 260 atm? _____

   Below what temperature and pressure conditions will the material sublime (s →g) rather than melt (s →l)? _____