

Colligative Properties

The Molar Mass of a Soluble Substance by Freezing-Point Depression

PURPOSE

To explore one of the colligative properties of a solution, the freezing-point depression. To use this property to determine the molar mass of an unknown substance.

Pre-Lab Preparation

When a nonvolatile solute is dissolved in a solvent, the solution properties change from those of the pure solvent. Relative to the pure solvent, the solution has a lower vapor pressure, a lower freezing point, and a higher boiling point. These effects are called *colligative* properties of the solution because they are linked together by a common feature: They all depend primarily on the ratio of the number of solute particles to the number of solvent particles. The size of the particles or whether they are molecules or ions makes little difference; it is the *relative number of particles* that is important.¹

Vapor-pressure lowering, freezing-point depression, and boiling-point elevation—all of these charac-

teristics are observed in both aqueous and nonaqueous solutions. For example, a solution of a nonvolatile solute like sucrose or ethylene glycol in water shows the same kind of effects as a solution of aspirin dissolved in cyclohexanol or sulfur in naphthalene.

We make practical use of the colligative properties of an aqueous solution of ethylene glycol by putting it in the cooling system of an automobile. Because antifreeze—an aqueous solution of ethylene glycol—has both a lower freezing point and a higher boiling point than pure water, the solution protects the car's cooling system against both freezing and boiling over. Boil-over protection is increased by using a spring-loaded pressure cap, which allows the system to operate above atmospheric pressure. Increases in pressure further raise the boiling point of the solution.

The origin of the freezing-point depression and boiling-point elevation of an aqueous solution can be understood with the setup shown in Figure 22-1. The phase diagram shown in Figure 22-2 describes what takes place in the apparatus. This diagram shows that solvent vapor pressure is lowered when a nonvolatile solute is dissolved in the solvent. Note that the vapor-pressure curve for the solution (shown by the dotted curve) is lower than the vapor-pressure curve for pure water (shown by the solid curve). Recall that the boiling point is the temperature at which the equilibrium vapor pressure equals the atmospheric pressure. The equilibrium vapor pressure of the solvent over the solution is *less* than that of the pure solvent at the same temperature. Therefore, the solution must be heated to a higher

¹These statements are quantitatively true for ideal solutions, in which the forces between molecules are small and for molecules having moderate molecular weights (< 500 g/mol). For real solutions, except at great dilution, there is always some deviation. For polar or ionic substances or for solutions of high-molecular-weight polymers, this deviation may be considerable. In particular, ions cannot move independently because of the strong electric forces between them. When measuring the colligative properties, we therefore try to use as dilute a solution as will allow satisfactory experimental precision.

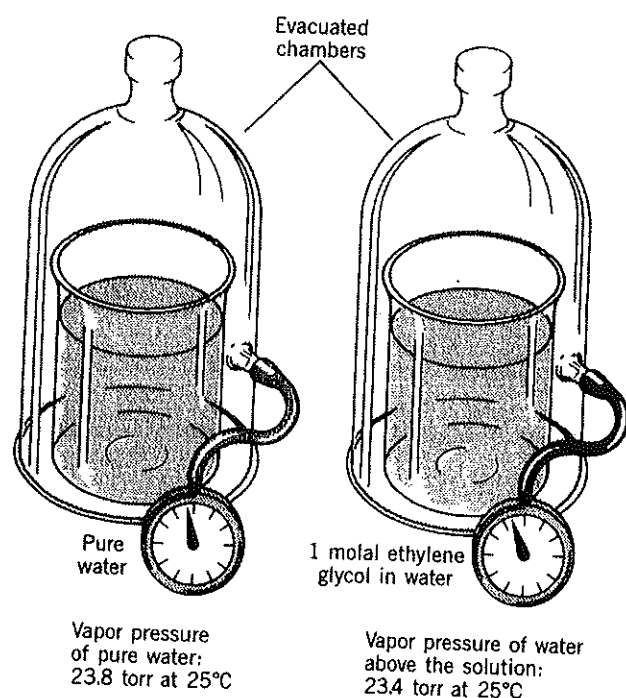


FIGURE 22-1 An illustration of the phenomenon of vapor pressure. If a beaker of a volatile liquid such as water is placed in an evacuated chamber, some of the liquid evaporates to fill the chamber with vapor. The pressure of this vapor is determined solely by the temperature of the liquid. When a nonvolatile solvent, such as ethylene glycol, is added to the pure solvent, the resulting solution has a vapor pressure less than the pure solvent at each temperature.

temperature than the pure solvent in order to reach atmospheric pressure. That means that the boiling point of the solution is higher than that of the pure solvent. Increasing the pressure above atmospheric pressure, as is done when you use a pressure cap on your auto radiator, raises the boiling point even further. (If you drew a horizontal line at $P = 2$ atm, it would intersect the vapor pressure curve at a higher temperature.)

When the temperature of most solutions is lowered to the freezing point, the solid that separates out is mainly pure solvent. Lowering the vapor pressure of a solvent by adding a nonvolatile solute causes the equilibrium vapor-pressure curve to intersect the sublimation-pressure curve at a lower temperature than the curve for the pure solvent (see Figure 22-2). The freezing-point curves for the solution and the pure solvent begin at the intersections of the sublimation-pressure and vapor-pressure curves, that is, at the *triple points* (shown in Figure 22-2), where all three phases (solid, liquid, and gas) simul-

taneously coexist. (The liquid phase is either the pure solvent or the solution containing added solute.) Therefore, the freezing-point curve for the solution lies at a *lower* temperature than the freezing-point curve of the pure solvent.

The freezing-point-depression effect has several important scientific uses. It allows us to compare the freezing-point depressions of a known and unknown substance in the same solvent in order to determine the molar mass of the unknown. This type of comparison is called *cryoscopy*, the stem *cryo-* coming from the Greek word meaning *icy* or *cold*. In this experiment you will determine the molecular weight of an unknown dissolved in cyclohexane by the cryoscopic method.

Cryoscopy is also used in the clinical laboratory to measure the total concentration of solutes in urine, making use of the fact that the freezing-point depression is proportional to the sum of the concentrations of all dissolved particles. The urine that initially is formed within the kidney has a much lower concentration of solutes than the urine that leaves the kidney. This is because the kidney conserves body water by recovering much of the water in urine as it passes through the kidney tubules. The kidney's ability to concentrate urine is one of this organ's most important functions, and when the renal tubules are damaged, this ability is one of the first functions to be lost. Thus a cryoscopic measurement of the solute content of urine is an indication of kidney function.

Raoult's Law

The equation that quantitatively describes vapor-pressure lowering is called *Raoult's law*. It is expressed as

$$P_1 = X_1 P_1^0 \quad (1)$$

where P_1 is the vapor pressure of the solvent above the solution, P_1^0 is the vapor pressure of the pure solvent, and X_1 is the mole fraction of the solvent in the solution. The mole fraction is a dimensionless concentration unit that expresses the fraction of the total number of molecules (or moles) that are solvent molecules:

$$X_1 = \frac{n_1}{n_1 + n_2} \quad (2)$$

where n_1 is the number of moles of solvent and n_2 is the number of moles of solute. This justifies the earlier statement that the colligative properties depend only on the relative numbers of solvent and solute molecules.

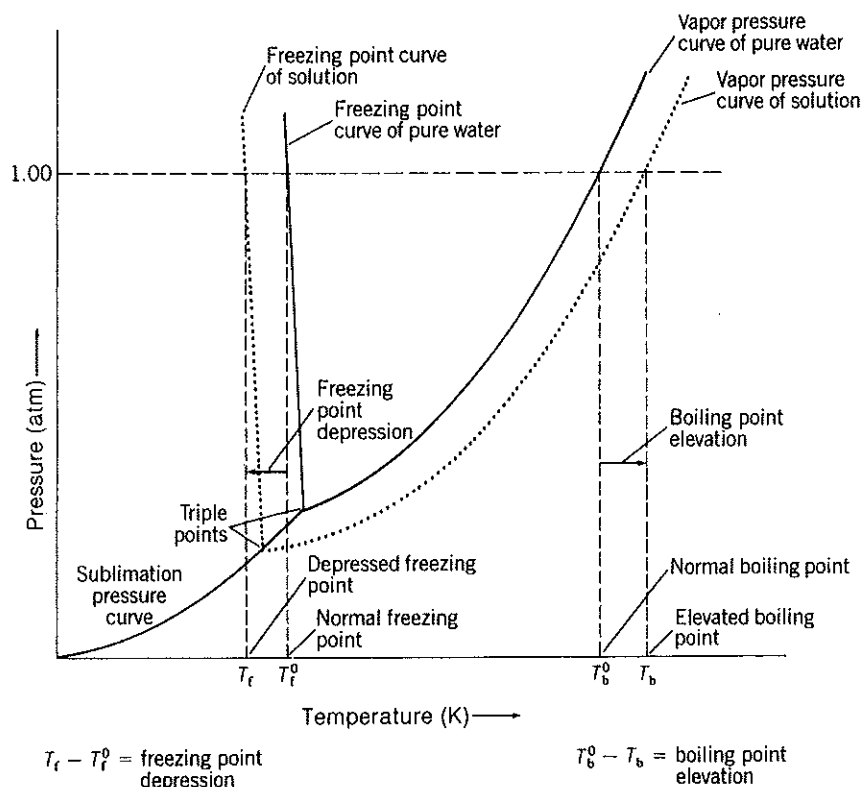


FIGURE 22-2 Phase diagrams for pure water (solid line), and for water containing a nonvolatile solute (dotted line). The presence of the solute lowers the vapor pressure of the solvent. The reduced vapor pressure of the solvent gives rise to an *increase* in the boiling point of the solution relative to pure water, $T_b - T_b^0 > 0$, and to a *decrease* in the freezing point of the solution

relative to pure water, $T_f - T_f^0 < 0$. (When the temperature of an aqueous solution is lowered to the freezing point, the solid that separates out is almost always pure ice, so the sublimation-pressure curve is assumed to remain unchanged.) The extent of vapor-pressure lowering is exaggerated in the diagram to show the effects more clearly.

It is convenient in working with the colligative properties of solutions to introduce the *molality concentration scale* for solutes. We define the molality, m , of a solute as the number of moles of the solute per 1000 g of solvent:

$$\text{Molality} = \frac{\text{moles of solute}}{1000 \text{ g of solvent}} = \frac{\text{moles of solute}}{\text{kilogram of solvent}} \quad (3)$$

For example, a solution prepared by dissolving 1.00 mol of KCl (74.55 g) in 1.00 kg of water is 1.00 molal in KCl. The "particle molality" would be 2.00 molal, because KCl dissociates into two ions, K^+ and Cl^- .

For dilute solutions the molality is proportional to the mole fraction. Both molality and mole fraction are temperature-independent concentration scales, in contrast to the molar concentration, which changes with temperature because of expansion or contraction of the solution volume.

The Freezing-Point Depression

The equation describing the freezing-point depression is²

$$\Delta T_f = K_f m$$

The symbol ΔT_f represents the freezing-point depression: $\Delta T_f = T_f^0 - T_f$, where T_f^0 is the freezing point of the pure solvent and T_f is the freezing point of the solution. This quantity is directly proportional to the concentration of particles expressed as the molality, m , of the particles in the solution. The proportionality constant, K_f , is called the *molal freezing-point-*

²Some texts write the freezing-point-depression equation with a minus sign, $-\Delta T_f = K_f m$, because ΔT_f defined as $\Delta T_f = T_f - T_f^0$ is a negative quantity, so that the minus signs will cancel. For simplicity, we are ignoring the minus signs.

depression constant. By using a solute of known molar mass, we can determine K_f for a particular solvent. The molality (and molar mass) of an unknown compound can then be determined by measuring the freezing-point depression of a solution of the unknown in the same solvent.

Note the phrase *particle molality* used in discussing the molality of an ionic solute, KCl. If the solute does not dissociate into two or more particles, the particle molality equals the molality of the solute. This will be true for all the solutions we will study in this experiment, solutions of *p*-dichlorobenzene and organic compounds dissolved in cyclohexane. The distinction between particle molality and solute molality is important to keep in mind when dealing with aqueous solutions. A 0.1 *m* KCl solution would lower the freezing point of water approximately twice as much as a 0.1 *m* sucrose solution. (Sucrose, ordinary table sugar, does not dissociate in water.) Does this help to explain why CaCl_2 is often used in northern climates to melt ice on roads and sidewalks?

The freezing-point depression for a 1 *m* solution in water (the molal freezing-point constant) is 1.86 °C, and the corresponding boiling-point rise (the *molal boiling-point constant*) is 0.52 °C. The same principles apply for solutions in other solvents. For cyclohexane, which we will use in this experiment, the freezing point is 6.5 °C, with an ideal molal freezing-point constant of 20.2 °C/*m*.

These constants apply to measurements in quite dilute solution. For the more concentrated solutions (0.5 *m*) that we must use, the freezing-point constant may deviate slightly from the ideal value. This is the reason we will first determine the constant under the conditions of the experiment, and then use this value for determining molar mass.

Calculations of Molar Mass

Either boiling point or freezing point may be used to determine the molar mass of a soluble substance. For the latter, it is necessary only to determine the freezing point of a solution containing a known mass of the solute in a known mass of the solvent and to compare this with the freezing point of the pure solvent, as follows.

1. Use the measured freezing-point depression and the molal freezing-point constant in Equation (1) to determine the molality of the unknown cyclohexane solution.
2. This molality is equal to the moles of unknown divided by the kilograms of the solvent, cyclohexane; so if we multiply the

molality by the mass of cyclohexane (in kilograms), we will know the number of moles of unknown that the solution contains.

3. The molar mass is the number of grams per mole, so dividing the mass of the unknown by the number of moles (which we just determined in Step 2) gives the molar mass of the unknown.

Experimental Procedure

Special Supplies: Thermometer (1 °C divisions are suitable; electronic thermometers with 0.1 °C resolution are more convenient to read and give better precision);¹ 27 cm of 1/16-in. diameter brass rod (brazing rod available from welding supply companies is ideal); 20 mm × 150 mm test tube; No. 2 solid stopper; No. 2 one-hole stopper.

Chemicals: Cyclohexane, ~~*p*-dichlorobenzene~~, solid organic compounds for use as unknowns for molar mass determination, salt (NaCl; see following note), ice. **STEARIC ACID***
 WE WILL USE STEARIC ACID IN PLACE OF
~~*p*-dichlorobenzene~~



NOTES TO THE INSTRUCTOR

If an electronic thermometer with 0.1 °C resolution is used, a smaller 15 × 125 mm test tube may be used, omitting the rubber stopper, and the amount of cyclohexane may be decreased to 5 mL and the solute mass to 0.25–0.30 g.

Some grades of salt (NaCl) contain anticaking additives that cloud the ice–water solution, making it more difficult to see the crystals of cyclohexane as they form. It is best to use a grade of salt that does not contain these additives.



SAFETY PRECAUTIONS: Cyclohexane is flammable. No open flames should be in the laboratory while this experiment is in progress. Keep the cyclohexane containers stoppered as much as possible, or use the fume hood to minimize odors.

¹Moderately priced electronic digital thermometers (cost, approximately \$30) with a 4-in. stainless steel temperature sensing probe and 1-m cable, a range of –50 to +150 °C, and temperature resolution of 0.1 °C, are available from Hanna Instruments Inc. (Model Checktemp 1C) or Flinn Scientific (Catalog No. AP8559).



WASTE COLLECTION: The cyclohexane solutions should be disposed of in a properly labeled container. This container should be in a fume hood if possible.

1. The Freezing Point of Cyclohexane. Figure 22-3 illustrates the simple apparatus required. Using a sharp razor blade, a 45° pie-shaped sector is cut longitudinally from a No. 2 one-hole rubber stopper. The split stopper easily holds a thermometer in position without danger of breakage. A circular stirrer, fashioned from 1/16-in. diameter brazing rod (or 14-gauge copper wire), is fitted through the notch at the side of the stopper.

Weigh the empty 20 × 150 mm test tube with the solid stopper to ±0.01 g on a balance. (You can stand the test tube up in a beaker.) Add about 10 mL of cyclohexane (C₆H₁₂), and weigh the test tube apparatus again. Accurately weigh (to the nearest milligram) about 0.5 to 0.6 g of ~~p~~-dichlorobenzene, C₆H₄Cl₂ (molar mass 147.0), on a creased sheet of glazed weighing paper.

Clamp the 20 × 150 mm test tube with the cyclohexane in a water bath (550 mL of ice and water in a 600-mL beaker). The bottom of the test tube should be about 2 cm from the bottom of the beaker. Place

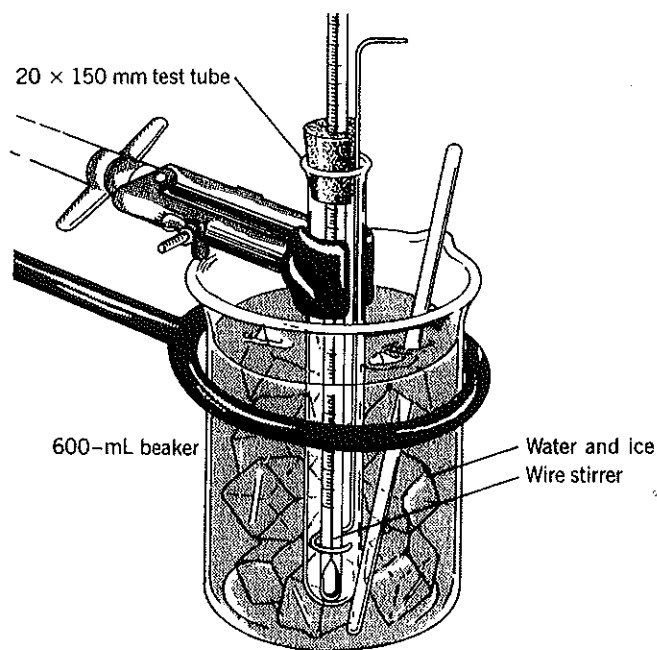


FIGURE 22-3 Freezing point apparatus for determination of molar mass.

the thermometer and stirrer in position, with the thermometer bulb about 2 to 3 mm above the bottom of the test tube, threaded through the ring of the stirrer. This arrangement ensures good stirring around the thermometer bulb. Stir the cyclohexane briskly and continuously. When crystals of solid cyclohexane begin to form and the temperature is constant, read the thermometer to the nearest 0.1 °C, and record this value. You may need to wipe condensation from the outside of the beaker in order to read the thermometer clearly. Warm the cyclohexane to room temperature; then repeat the cooling operation until you are certain of the freezing point (as accurately as your thermometer can be read). When reading the thermometer, be sure to have your eye on a level with the mercury meniscus, to avoid parallax in the reading.

2. The Molal Freezing Point Constant of Cyclohexane.

Remove the stopper and attached thermometer and stirrer (avoiding loss of cyclohexane), just far enough to add the sample of ~~p~~-dichlorobenzene. Weigh the glazed weighing paper to obtain, by difference, the weight of the ~~p~~-dichlorobenzene added. Warm the mixture, and stir it to dissolve the solute completely. Pour most of the water out of the 600-mL beaker, refill the beaker with ice, add 50 mL (approximately 65 g) of solid NaCl, and refill the beaker with water, leaving enough room for the test tube. Stir the mixture of salt and ice water to dissolve as much salt as possible, then lower the test tube into the ice-salt-water mixture and clamp it in place. Now stir briskly as before, and observe as accurately as possible the steady temperature at which a small amount of solid solvent is in equilibrium with the solution. There may be a small amount of supercooling before crystallization. Study Figure 22-4, noting especially that when a larger amount of solvent is

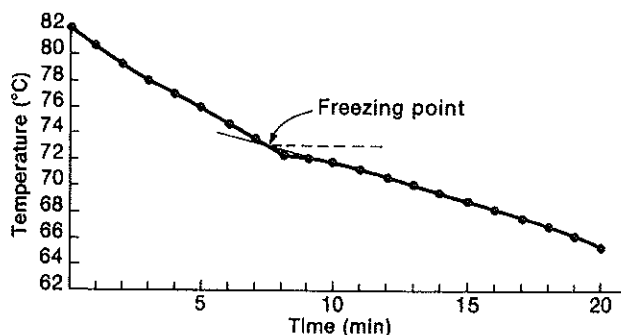



FIGURE 22-4 A typical freezing-point crystallization curve.

frozen out, the remaining solution is more concentrated and therefore gives a declining freezing point. This is why readings must be taken as soon as the first crystals appear in the solution, when only a very small amount of the solvent has frozen solid.⁴ Repeat this freezing-point measurement several times by warming the solution and allowing it to cool until you are certain of this equilibrium temperature, to within 0.1 °C if possible. When you have finished the measurements, pour the solution into the waste cyclohexane bottle provided. *Do not pour it into the sink.* Remove the last trace of solution by rinsing the tube with cyclohexane in the fume hood and drying the tube with a gentle stream of air in the hood.

From these data, calculate the molal freezing-point constant for cyclohexane—that is, the change in freezing point caused by 1 mol of *p*-dichlorobenzene per kilogram of cyclohexane. Compare your value with the literature value of 20.2 °C/m. (The literature value is an idealized value, extrapolated to zero concentration of solute.) If sufficient time is available, repeat the determination with a fresh cyclohexane sample and another weighed sample of *p*-dichlorobenzene. ~~STEARIC ACID~~

3. The Molar Mass of an Unknown Solid. Obtain from your instructor a sample of an unknown organic material. The freezing-point measurements for pure cyclohexane and for the unknown dissolved in the cyclohexane are made exactly as in Part 1, using a 0.5-g sample of unknown. From these data, calculate the molar mass of the unknown, using the molal freezing-point constant for cyclohexane determined in Part 2. Be sure to dispose of the cyclohexane solution in the proper container when you are finished. If your instructor so directs, repeat the measurement with a second sample of unknown.

 **CONSIDER THIS** Is the freezing-point depression a linear function of molality? Make a series of different concentrations of *p*-dichlorobenzene in cyclohexane and graph the freezing-point temperature versus concentration.

Why is the molality concentration scale used in the context of colligative properties

and not the more common molarity scale? Use the data in the *CRC Handbook of Chemistry and Physics* in a section entitled "Concentrative Properties of Aqueous Solutions: Conversion Tables") to plot ΔT_f versus molality and versus molarity in order to explore these relationships.

Most everyone has participated in the fun of making homemade ice cream. (If you haven't, do it soon!) A key feature of the process takes advantage of a colligative property. Describe why it is necessary to add salt to the ice that surrounds the ice-cream container in order to freeze the ice cream inside. This is an interesting system to explore. Place a quantity of ice in a Styrofoam-cup calorimeter. (See Experiment 14 or 15.) Monitor the temperature as you add salt to the system. How can the temperature drop if no heat can escape the system? How low can you get the temperature to go? Convert this temperature to °F. (Note: This was one of Fahrenheit's calibration points as he developed the thermometer. Why is the normal freezing point of pure water a better calibration point?)

Cool a clear plastic bottle of a soft drink in the freezer until it just begins to freeze. Take the cap off the bottle. (Over the sink is a good place to do this.) What happens? Explain in terms of the colligative properties that you explored in this experiment. Can you design an experiment to determine the carbon dioxide concentration in a soft drink using the freezing-point-depression property?

What has a lower freezing point, a diet soda or a regular version of the same soda? Why? Can you use the calorie content listed on the can to estimate the sugar concentration in the soda, then calculate an expected freezing point for the soda? What complications come into play?

⁴For precise determination, readings are taken every 30 to 60 s during the cooling process. A curve similar to Figure 22-4 is plotted, and the exact freezing point determined by extrapolation, as illustrated.

Colligative Properties

**The Molar Mass of a Soluble Substance
by Freezing Point Depression**

Name _____

Date _____

Section _____

Locker _____

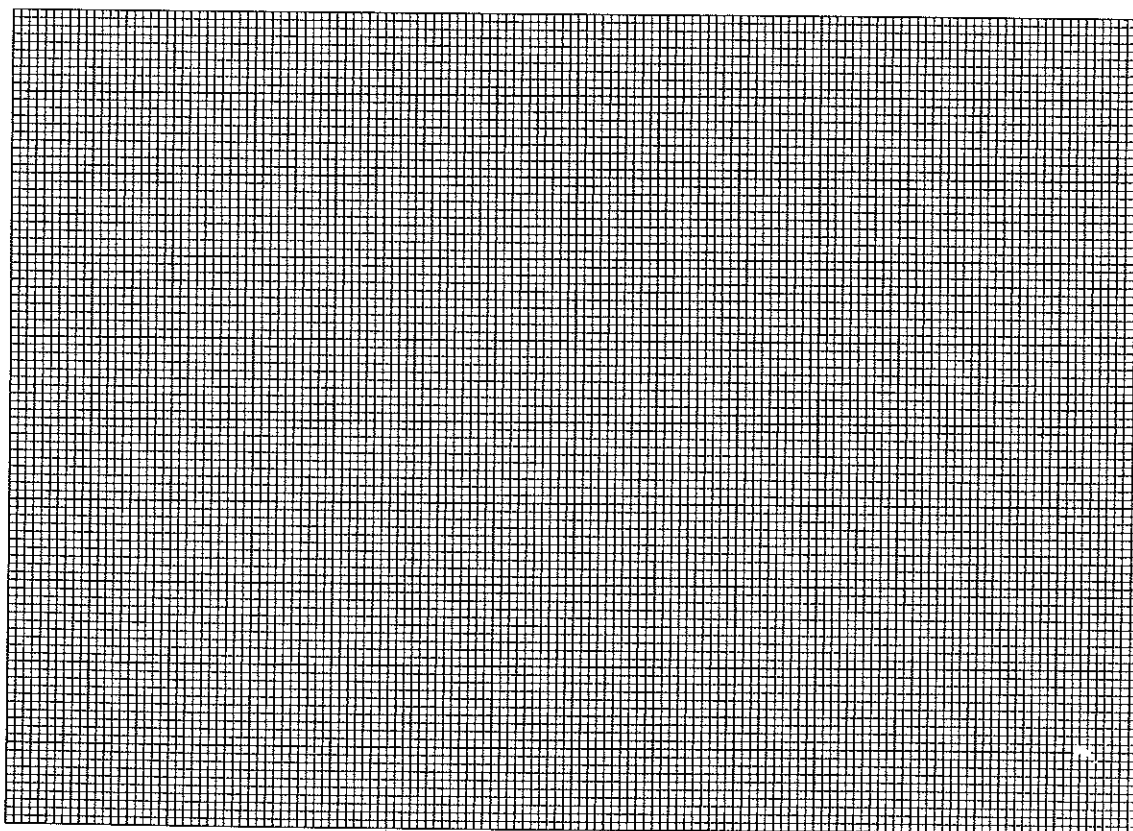
Instructor _____

1. Experimental Data

Sample or unknown no. _____

	<i>p</i> -dichlorobenzene		Unknown	
	Sample 1	Sample 2	Sample 1	Sample 2
Mass of cyclohexane + test tube + beaker	g	g	g	g
Mass of test tube + beaker	g	g	g	g
Mass of cyclohexane	g	g	g	g
Mass of sample + weighing paper	g	g	g	g
Mass of weighing paper	g	g	g	g
Mass of unknown	g	g	g	g
Freezing point of cyclohexane	°C	°C	°C	°C
Freezing point of solution	°C	°C	°C	°C

Use the graph below to plot the data from one of your cooling curves if so directed by your instructor.



2. Freezing Point Constant (Show a sample calculation.)

	Calculations	<i>p</i> -dichlorobenzene	
		Sample 1	Sample 2
Freezing point depression $\Delta T_f = T_f^0 - T_f$		°C	°C
Moles of solute, <i>p</i>-dichlorobenzene STEARIC ACID		mol	mol
Molality of solution = $\frac{\text{moles of solute}}{\text{kilograms of solvent}}$		mol/kg	mol/kg
Molal freezing-point constant, from $\Delta T_f = K_f m$		°C · kg/mol	°C · kg/mol

3. The Molar Mass of an Unknown Solid (Show a sample calculation.)

	Calculations	Unknown	
		Sample 1	Sample 2
Freezing point depression $\Delta T_f = T_f^0 - T_f$		°C	°C
Molality of unknown solution, from $\Delta T_f = K_f m$		mol/kg	mol/kg
Moles of unknown solute, from Molality of solution = $\frac{\text{moles of solute}}{\text{kilograms of solvent}}$		mol	mol
Molar mass of unknown = $\frac{\text{grams of unknown}}{\text{moles of unknown}}$		g/mol	g/mol
Percentage error = $\frac{\text{your value} - \text{actual value}}{\text{actual value}} \times 100$		%	%

Approval of Instructor: Your unknown is _____

Questions on Experimental Error

1. (a) Assume that you have a solution of an unknown solute in cyclohexane. If the solution has a freezing-point depression of $9.50\text{ }^{\circ}\text{C}$, what is the molality of this solution? (The molal freezing-point constant of cyclohexane is $20.2\text{ }^{\circ}\text{C}/m$.)

_____ m

- (b) Since the thermometer used has markings for each Celsius degree, assume that you can be certain of the freezing-point depression only to within $\pm 0.2\text{ }^{\circ}\text{C}$. If the freezing-point depression is measured as $9.7\text{ }^{\circ}\text{C}$, then what molality would be reported for this solution?

_____ m

- (c) What is the relative error in the molality that is introduced by this limitation in the thermometer? (Hint: The relative error in the molality will be the same as the relative error in the freezing-point depression.)

$$\left(\text{Relative error} = \frac{\text{measured value} - \text{actual value}}{\text{actual value}} \times 100 \right)$$

_____ %

2. The relative error can be reduced if a more precise thermometer is used. Assume that with the more precise thermometer you can determine the temperature to within $\pm 0.02\text{ }^{\circ}\text{C}$.

- (a) If the measured freezing-point depression with such a thermometer is $9.52\text{ }^{\circ}\text{C}$, what molality is determined for this solution?

_____ m

- (b) What is the relative error in the molality as determined with this more precise thermometer?

_____ %

Problems

1. Cyclohexanol, $\text{C}_6\text{H}_{11}\text{OH}$, is sometimes used as the solvent in molecular weight determinations by freezing-point depression. If 0.253 g of benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, dissolved in 12.45 g of cyclohexanol, lowered the freezing-point of pure cyclohexanol by $6.55\text{ }^{\circ}\text{C}$, what is the molal freezing-point constant of this solvent?

2. Since the freezing point of a solution depends on the relative number of *particles*, what would you calculate to be the freezing point of 0.1 *m* solutions in water of (a) NaCl, (b) BaCl₂? Assume that these salts are 100% ionized in solution. (Compare your answers with the actual respective freezing points: -0.348 °C and -0.470 °C. The difference is due to the decreased activity of the ions. Because of the attractive forces between the positively and negatively charged ions, they do not move completely independently of one another.)

(a) _____

(b) _____

3. How many grams of each of the following per kilogram of water in your car radiator are needed to give equal protection against freezing down to -10 °C? (a) Methyl alcohol, CH₃OH, b.p. 64.6 °C. (b) Ethylene glycol, C₂H₄(OH)₂, b.p. 197.2 °C. In spite of higher cost, what advantage does ethylene glycol possess over methyl alcohol as a winter antifreeze and/or summer coolant?

(a) _____

(b) _____



CONSIDER THIS

Is the freezing-point depression a linear function of molality? Make a series of different concentrations of *p*-dichlorobenzene in cyclohexane and graph the freezing-point temperature versus concentration.

Why is the molality concentration scale used in the context of colligative properties and not the more common molarity scale? Use the data in the *CRC Handbook of Chemistry and Physics* in a section entitled "Concentrative Properties of Aqueous Solutions: Conversion Tables") to plot ΔT_f versus molality and versus molarity in order to explore these relationships.