Experiment 19

Molar Mass Determination by Depression of the Freezing Point

The most common liquid we encounter in our daily lives is water. In this experiment we will study the equilibria that can exist between pure water and its aqueous solutions, and ice, the solid form of water. (Water is the only substance for which we have a separate name for the solid.)

If we take some ice cubes from the refrigerator and put them into a glass of water from the tap, we find that the water temperature falls and some ice melts. This occurs because heat will always tend to flow from a higher to a lower temperature. Heat from the water flows into the ice. It takes heat, called the heat of fusion, to melt ice. If there is enough ice present, the water temperature will ultimately fall to 0°C, and stay there. At that point, ice and water are in equilibrium, at the freezing point of water. At the freezing point, T_f°, the vapor pressures of ice and water must be equal, and that condition fixes the temperature. (See Fig. 19.1.)

Now let us consider what happens if we add a soluble liquid or solid to the equilibrium mixture of ice and water. Rather surprisingly, we find that the temperature of the ice and the solution falls as equilibrium is reestablished. The reason this happens is that in the solution the vapor pressure of water at 0°C is less than that of the pure liquid. So the vapor pressure of ice at 0°C is higher than that of the solution, and some ice melts. This requires heat, which comes from the solution and from the ice, and the temperature falls. The vapor pressures of the ice and the solution both fall, but that of the ice falls faster, and at some temperature T_f below 0°C equilibrium is established at the new freezing point. The situation is shown in Figure 19.1.

The change in the freezing point that is observed is called the freezing point depression, ΔT_f, equal to $T_f^\circ - T_f$. It is observed with solutions of any solvent. The freezing point depression is one of the colligative properties of solutions. Others are the boiling point elevation for non-volatile solutes, the osmotic pressure, and the vapor pressure lowering. The colligative properties of solutions depend on the number of solute particles present in a given amount of solvent and not on the kinds of particles dissolved, be they molecules, atoms, or ions.

When working with colligative properties it is convenient to express the solute concentration in terms of its molality m as defined by the equation:

$$\text{molality of } A = m_A = \frac{\text{no. of moles } A \text{ dissolved}}{\text{no. of kg solvent in the soln}} \tag{1}$$

For this unit of concentration, the boiling point elevation, $T_b - T_b^\circ$, or ΔT_b, and the freezing point depression, $T_f^\circ - T_f$, or ΔT_f, in °C at very low concentrations are given by the equations:

$$\Delta T_b = k_b m \quad \text{and} \quad \Delta T_f = k_f m \tag{2}$$

where k_b and k_f are characteristic of the solvent used. For water, $k_b = 0.52$ and $k_f = 1.86$. For benzene, $k_b = 2.53$ and $k_f = 5.10$. In this experiment we will assume that Equation 2 is valid, even though our solutions are moderately concentrated.

One of the classic uses of colligative properties was in connection with finding molar masses of unknown substances. With organic molecules, molar masses by FP depression agreed with those found by other methods. With ionic salts, like NaCl, molar masses were lower than the formula masses. On the basis of such experiments Arrhenius suggested that ionic substances exist as ions in aqueous solution, consistent with the observation that such solutions conduct an electric current. Arrhenius' general idea turned out to be correct, and is now a basic part of modern chemical theory.

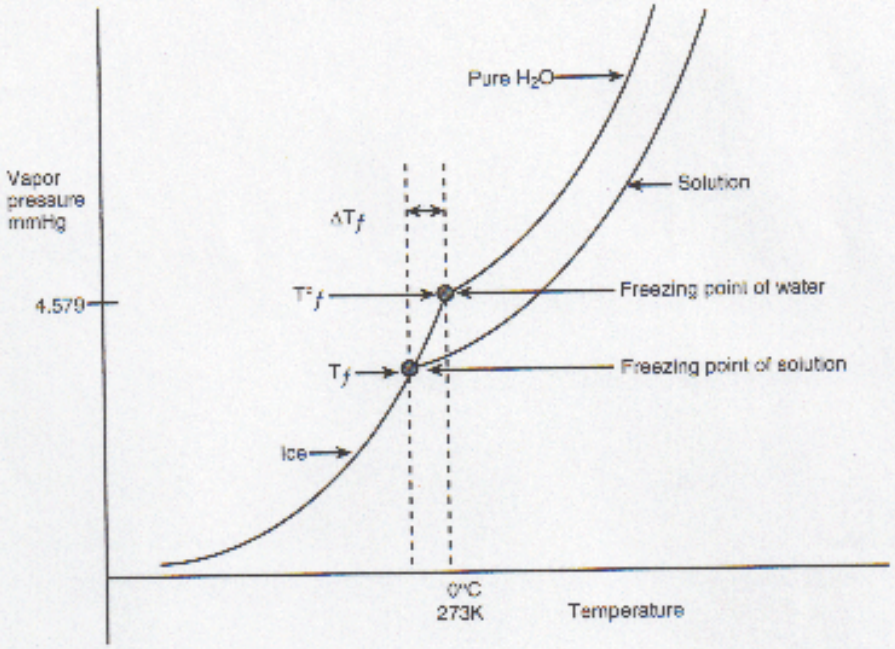

Figure 19.1

Discussion of the Method

In this experiment we will study the freezing point behavior of some aqueous solutions. First you will measure the freezing point of pure water, using a slurry of ice and water. Then you'll add a known mass of an unknown to the slurry, and find the freezing point of the solution, thus determining the freezing point depression, ΔT_f. That allows you to find the molality of the solution. Finally, you separate the solution from the ice in the mixture, and weigh the solution, which will contain all of the solute. This information furnishes you with the composition of the solution, and lets you calculate the mass of solute in 1 kg of water. The molar mass follows from Equations 1 and 2.

WEAR YOUR SAFETY GLASSES WHILE PERFORMING THIS EXPERIMENT

Experimental Procedure

You may work in pairs on this experiment. Both members of the pair must submit a report. From the stock room obtain a digital thermometer, an insulated cup, and two unknowns, one liquid and one solid. The actual molar mass of the solid will be furnished to you.

A. Finding the Freezing Point of Water

You will first need to determine the freezing point of pure water. Prepare a water-ice mixture in your insulated cup, using more ice than water. Stir well, and record the lowest temperature you observe for that mixture. (Since your thermometer may not be properly calibrated, that temperature may not be 0.0°C.)

B. Finding the Freezing Point of a Solution of Liquid Unknown

To the water-ice mixture you need to add a known amount of one of your unknowns. Let's work first with the liquid unknown. To estimate the mass of your liquid to add to the mixture, assume that you will have about 100 g of water in the final solution, that the molality of the solute will be about 2 m, and that the molar mass

of the solute is 50 g. Tare the insulated cup on the top loading-balance, and add the estimated mass by pouring it down a stirring rod on to the center of the ice-water mix. Record the mass. Then record the lowest temperature you observe after stirring the ice + solution mixture. You should obtain a freezing point depression of at least 4°C. If you need to, add more of the liquid unknown, weighing the amount added. Stir well and measure the lowest temperature of the mixture that you observe. Then promptly separate the solution from the ice by pouring it through a wire screen into a tared beaker on the top-loading balance. (Place the screen over the cup, and pour out the solution, keeping a corner of the screen down.) Record the mass of the solution.

Make a second molar mass measurement for your liquid unknown. This is easily done if you pour the decanted solution back into the cup once you have found its mass. Add some water and ice to the ice + solution mixture, thereby lowering the molality of the solute. Measure the new freezing point for that mixture. Pour off and weigh the solution.

When you have finished this part of the experiment, dispose of the mixture of ice and solution as directed by your instructor.

Determine molar masses as described in the Discussion.

C. Finding the Freezing Point of a Solution of Solid Unknown

With solid unknowns, you can use the same general procedure as with liquids. First, make a solution of the solid in water, using the same total mass of solid as you did with the liquid. You can do this by taring a small dry beaker on the top-loading balance, and adding the solid, noting its mass. Add a minimum amount of water to dissolve the solid (use at least 20 g of water). Stir until solution is complete. Add the entire solution of the solid to a new ice + water mix, noting the lowest temperature you obtain. Decant and weigh the solution as you did with the liquid unknown.

Again, make measurements at two different solute concentrations.

If the molar mass you find for your solid is less than the actual molar mass, you have an ionic solid. The ratio of the true molar mass to the value you find is equal to a quantity called the van't Hoff factor, i. This factor can be related to the apparent percentage dissociation of the salt you are studying. For a 1:1 salt,

$$\% \text{ dissociation} = (i - 1) \times 100\% \tag{3}$$

It turns out that Equation 3 works well for weak electrolytes like acetic acid, but is not correct for salts like NaCl, which modern theory assumes are completely ionized in aqueous solution.

In your report, note all the masses observed and the temperatures of the equilibrium mixtures. Report the average molar masses you calculate and show how you obtained them. If you have an ionic solid, find i and the % dissociation as predicted by the Arrhenius theory.

When you are finished with the experiment, pour the solution and the contents of the cup into the sink. Return the digital thermometer and the insulated cup to the stock room.