

## 13.7: Colligative Properties of Strong Electrolyte Solutions

At the beginning of [Section 13.6](#), we saw that colligative properties depend on the number of dissolved particles and that we therefore must treat electrolytes slightly differently than nonelectrolytes when determining colligative properties. For example, the freezing point depression of a 0.10-*m* sucrose solution is  $\Delta T_f = 0.186^\circ\text{C}$ . However, the freezing point depression of a 0.10-*m* sodium chloride solution is nearly twice this large. Why? Because 1 mol of sodium chloride dissociates into nearly 2 mol of ions in solution. The ratio of moles of particles in solution to moles of formula units dissolved is called the **van't Hoff factor (*i*)**:

$$i = \frac{\text{moles of particles in solution}}{\text{moles of formula units dissolved}}$$

Because 1 mol of NaCl produces 2 mol of particles in solution, we expect the van't Hoff factor for NaCl to be exactly 2. In reality, this expected factor only occurs in very dilute solutions. For example, the van't Hoff factor for a 0.10-*m* NaCl solution is 1.87, and that for a 0.010-*m* NaCl solution is 1.94. The van't Hoff factor approaches the expected value at infinite dilution (as the concentration approaches zero). [Table 13.7](#) lists the actual and expected van't Hoff factors for a number of solutes.

**Table 13.7 Van't Hoff Factors at 0.05-*m* Concentration in Aqueous Solution**

Solute	<i>i</i> Expected	<i>i</i> Measured
Nonelectrolyte	1	1
NaCl	2	1.9
MgSO <sub>4</sub>	2	1.3
MgCl <sub>2</sub>	3	2.7
K <sub>2</sub> SO <sub>4</sub>	3	2.6
FeCl <sub>3</sub>	4	3.4

The van't Hoff factor does not exactly equal the expected value because some ions effectively pair in solution. We expect the dissociation of an ionic compound to be complete in solution. In reality, however, the dissociation is not complete—at any given moment, some cations are pairing with anions ([Figure 13.17](#)), slightly reducing the number of particles in solution.

**Figure 13.17 Ion Pairing**

In solutions, hydrated anions and cations may get close enough together to effectively pair, lowering the concentration of particles more than would be expected.



To calculate freezing point depression, boiling point elevation, and osmotic pressure of ionic solutions, we use the van't Hoff factor in each equation as follows:

$$\Delta T_f = im \times K_f \text{ (freezing point depression)}$$

$$\Delta T_b = im \times K_b \text{ (boiling point elevation)}$$

$$\Pi = iMRT \text{ (osmotic pressure)}$$

### Conceptual Connection 13.8 Colligative Properties

#### Example 13.11 Van't Hoff Factor and Freezing Point Depression

The freezing point of an aqueous 0.050-*m* CaCl<sub>2</sub> solution is -0.27 °C. What is the van't Hoff factor (*i*) for CaCl<sub>2</sub> at this concentration? How does it compare to the expected value of *i*?

**SORT** You are given the molality of a solution and its freezing point. You are asked to find the value of *i*—the van't Hoff factor—and compare it to the expected value.

**GIVEN:** 0.050-*m* CaCl<sub>2</sub> solution,  $\Delta T_f = -0.27^\circ\text{C}$

**FIND:** *i*

**STRATEGIZE** To solve this problem, use the freezing point depression equation including the van't Hoff factor.

**CONCEPTUAL PLAN**

$$\Delta T_f = im \times K_f$$

**SOLVE** Solve the freezing point depression equation for *i*, substituting in the given quantities to calculate its value.

The expected value of *i* for CaCl<sub>2</sub> is 3 because calcium chloride forms 3 mol of ions for each mole of calcium chloride that dissolves. The experimental value is slightly less than 3, probably because of ion pairing.

**SOLUTION**

$$\begin{aligned} \Delta T_f &= im \times K_f \\ i &= \frac{\Delta T_f}{m \times K_f} \\ &= \frac{0.27^\circ\text{C}}{0.050\cancel{m} \times \frac{1.86^\circ\text{C}}{\cancel{m}}} \\ &= 2.9 \end{aligned}$$

**CHECK** The answer has no units, as expected, as *i* is a ratio. The magnitude is about right because it is close to the value you would expect upon complete dissociation of CaCl<sub>2</sub>.

#### FOR PRACTICE 13.11

Calculate the freezing point of an aqueous 0.10-*m* FeCl<sub>3</sub> solution using a van't Hoff factor of 3.2.

## Strong Electrolytes and Vapor Pressure

Just as the freezing point depression of a solution containing an electrolyte solute is greater than that of a solution containing the same concentration of a nonelectrolyte solute, so the vapor pressure lowering is greater (for the same reasons). The vapor pressure for a sodium chloride solution, for example, decreases about twice as much as it does for a nonelectrolyte solution of the same concentration. To calculate the vapor pressure of a solution containing an ionic solute, we need to account for the dissociation of the solute when we calculate the mole fraction of the solvent, as demonstrated in [Example 13.12](#).

### Example 13.12 Calculating the Vapor Pressure of a Solution Containing an Ionic Solute

A solution contains 0.102 mol  $\text{Ca}(\text{NO}_3)_2$  and 0.927 mol  $\text{H}_2\text{O}$ . Calculate the vapor pressure of the solution at 55 °C. The vapor pressure of pure water at 55 °C is 118.1 torr. (Assume that the solute completely dissociates.)

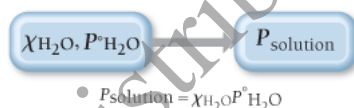
**SORT** You are given the number of moles of each component of a solution and asked to find the vapor pressure of the solution. You are also given the vapor pressure of pure water at the appropriate temperature.

0.102 mol  $\text{Ca}(\text{NO}_3)_2$   
**GIVEN:** 0.927 mol  $\text{H}_2\text{O}$   
 $P_{\text{H}_2\text{O}}^\circ = 118.1 \text{ torr (at } 55^\circ\text{C)}$

**FIND:**  $P_{\text{solution}}$

**STRATEGIZE** To solve this problem, use Raoult's law as you did in [Example 13.6](#). Calculate  $\chi_{\text{solvent}}$  from the given amounts of solute and solvent.

#### CONCEPTUAL PLAN

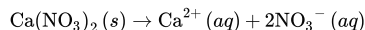


**SOLVE** The key to solving this problem is understanding the dissociation of calcium nitrate. Write an equation showing the dissociation.

Since 1 mol of calcium nitrate dissociates into 3 mol of dissolved particles, you must multiply the number of moles of calcium nitrate by 3 when you calculate the mole fraction.

Use the mole fraction of water and the vapor pressure of pure water to calculate the vapor pressure of the solution.

#### SOLUTION



$$\begin{aligned} \chi_{\text{H}_2\text{O}} &= \frac{n_{\text{H}_2\text{O}}}{3 \times n_{\text{Ca}(\text{NO}_3)_2} + n_{\text{H}_2\text{O}}} \\ &= \frac{0.927 \text{ mol}}{3(0.102 \text{ mol}) + 0.927 \text{ mol}} \\ &= 0.7518 \end{aligned}$$

$$\begin{aligned} P_{\text{solution}} &= \chi_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^\circ \\ &= 0.7518 (118.1 \text{ torr}) \\ &= 88.8 \text{ torr} \end{aligned}$$

**CHECK** The units of the answer are correct. The magnitude also seems right because the calculated

vapor pressure of the solution is significantly less than that of the pure solvent, as you would expect for a solution with a significant amount of solute.

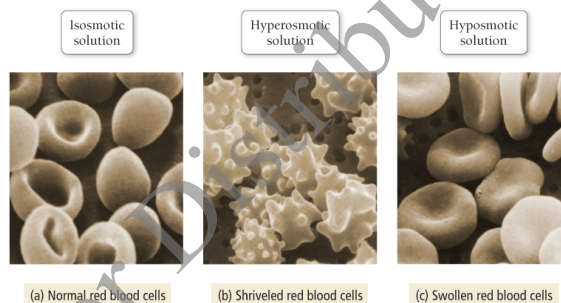
**FOR PRACTICE 13.12** A solution contains 0.115 mol  $\text{H}_2\text{O}$  and an unknown number of moles of sodium chloride. The vapor pressure of the solution at 30 °C is 25.7 torr. The vapor pressure of pure water at 30 °C is 31.8 torr. Calculate the number of moles of sodium chloride in the solution.

## Colligative Properties and Medical Solutions

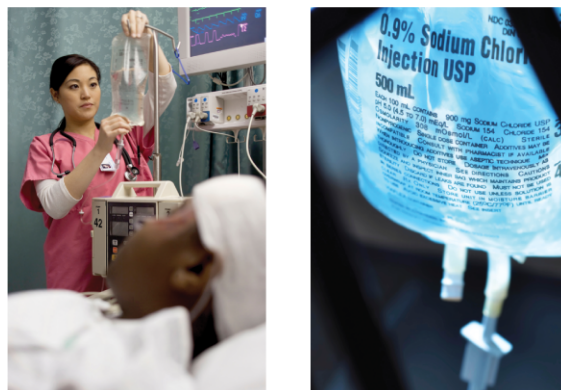
Doctors and other health care workers often administer solutions to patients. The osmotic pressure of these solutions is controlled to ensure the desired effect on the patient. Intravenous (IV) solutions—those that are administered directly into a patient's veins—must have osmotic pressures equal to those of body fluids. These solutions are called *isosmotic* (or *isotonic*) (Figure 13.18(a)□). Solutions having osmotic pressures greater than those of body fluids are *hyperosmotic*. These solutions take water out of cells and tissues. When a human cell is placed in a hyperosmotic solution, it tends to shrivel as it loses water to the surrounding solution (Figure 13.18(b)□). Solutions having osmotic pressures less than those of body fluids are *hyposmotic*. These solutions pump water into cells. When a human cell is placed in a hyposmotic solution—such as pure water, for example—water enters the cell, sometimes causing it to burst (Figure 13.18(c)□).

**Figure 13.18 Red Blood Cells and Osmosis**

(a) In an isosmotic solution, red blood cells have the normal shape shown here. In a hyperosmotic solution (b), they lose water and shrivel. In a hyposmotic solution (c), they swell up and may burst as water flows into the cell.



When intravenous fluids are given in a hospital, the majority of the fluid is usually an isosmotic saline solution—a solution containing 0.9 g NaCl per 100 mL of solution. In medicine and in other health-related fields, solution concentrations are often reported in units that indicate the mass of the solute per given volume of solution. Also common is percent mass to volume—which is the mass of the solute in grams divided by the volume of the solution in milliliters times 100%. In these units, the concentration of an isotonic saline solution is 0.9% mass/volume.



Fluids used for intravenous transfusion must be isosmotic with bodily fluids—that is, they must have the

same osmotic pressure.

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