

# *Ions in Aqueous Solutions and Colligative Properties*

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*These formations were made by the precipitation of ionic compounds from an aqueous solution.*

# Compounds in Aqueous Solutions

## SECTION 14-1

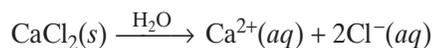
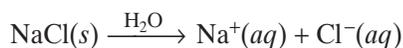
### OBJECTIVES

- Write equations for the dissolution of soluble ionic compounds in water.
- Predict whether a precipitate will form when solutions of soluble ionic compounds are combined, and write net ionic equations for precipitation reactions.
- Compare dissociation of ionic compounds with ionization of molecular compounds.
- Draw the structure of the hydronium ion, and explain why it is used to represent the hydrogen ion in solution.
- Distinguish between strong electrolytes and weak electrolytes.

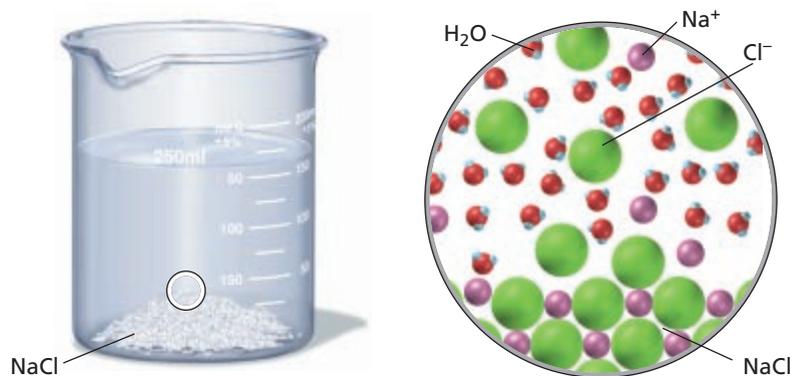
As you have learned, solid compounds can be ionic or molecular. In an ionic solid, a crystal structure is made up of charged particles held together by ionic attractions. In a molecular solid, molecules are composed of covalently bonded atoms held together by intermolecular forces. When they dissolve in water, ionic compounds and molecular compounds behave differently.

### Dissociation

When a compound that is made of ions dissolves in water, the ions separate from one another, as shown in Figure 14-1. *This separation of ions that occurs when an ionic compound dissolves is called dissociation.* For example, dissociation of sodium chloride and calcium chloride in water can be represented by the following equations. (As usual, *(s)* indicates a solid species and *(aq)* indicates a species in an aqueous solution. Note that the equation is balanced for charge as well as for atoms.)

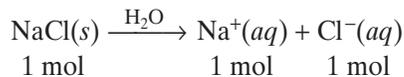


Notice the number of ions produced per formula unit in the equations above. One formula unit of sodium chloride gives two ions in solution, whereas one formula unit of calcium chloride gives three ions in solution.

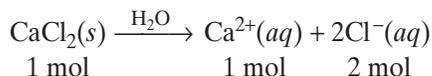


**FIGURE 14-1** When NaCl dissolves in water, the ions separate as they leave the crystal.

Assuming 100% dissociation, a solution that contains 1 mol of sodium chloride contains 1 mol of  $\text{Na}^+$  ions and 1 mol of  $\text{Cl}^-$  ions. In this book, you can assume 100% dissociation for all soluble ionic compounds. The dissociation of  $\text{NaCl}$  can be represented as follows.



A solution that contains 1 mol of calcium chloride contains 1 mol of  $\text{Ca}^{2+}$  ions and 2 mol of  $\text{Cl}^-$  ions—a total of 3 mol of ions.



### SAMPLE PROBLEM 14-1

Write the equation for the dissolution of aluminum sulfate,  $\text{Al}_2(\text{SO}_4)_3$ , in water. How many moles of aluminum ions and sulfate ions are produced by dissolving 1 mol of aluminum sulfate? What is the total number of moles of ions produced by dissolving 1 mol of aluminum sulfate?

#### SOLUTION

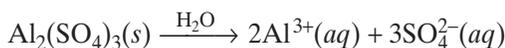
##### 1 ANALYZE

**Given:** amount of solute = 1 mol  $\text{Al}_2(\text{SO}_4)_3$   
solvent identity = water

**Unknown:** a. moles of aluminum ions and sulfate ions  
b. total number of moles of solute ions produced

##### 2 PLAN

The coefficients in the balanced dissociation equation will reveal the mole relationships, so you can use the equation to determine the number of moles of solute ions produced.



##### 3 COMPUTE

a. 1 mol  $\text{Al}_2(\text{SO}_4)_3 \rightarrow 2 \text{ mol Al}^{3+} + 3 \text{ mol SO}_4^{2-}$   
b. 2 mol  $\text{Al}^{3+} + 3 \text{ mol SO}_4^{2-} = 5 \text{ mol of solute ions}$

##### 4 EVALUATE

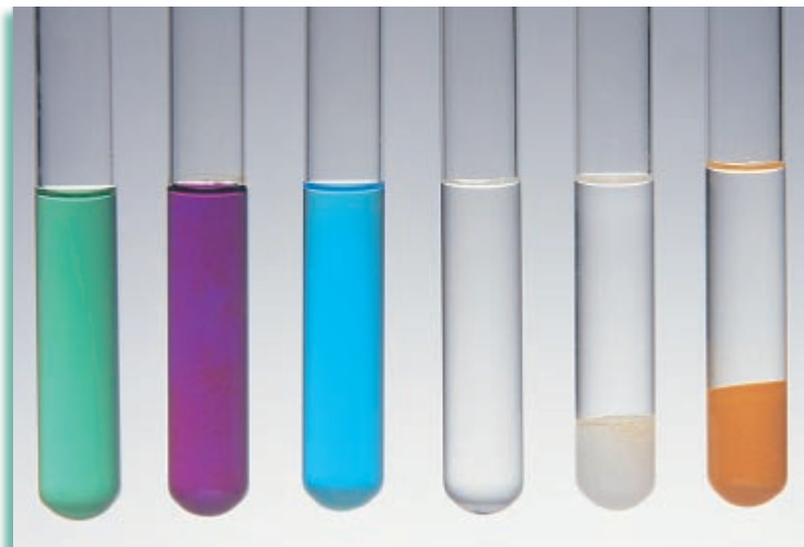
The equation is correctly balanced. Because one formula unit of  $\text{Al}_2(\text{SO}_4)_3$  produces 5 ions, 1 mol of  $\text{Al}_2(\text{SO}_4)_3$  produces 5 mol of ions.

#### PRACTICE

- Write the equation for the dissolution of each of the following in water, and then determine the number of moles of each ion produced as well as the total number of moles of ions produced.
  - 1 mol ammonium chloride
  - 1 mol sodium sulfide
  - 0.5 mol barium nitrate

*Answer*

- $\text{NH}_4\text{Cl}(s) \xrightarrow{\text{H}_2\text{O}} \text{NH}_4^+(aq) + \text{Cl}^-(aq)$ ;  
1 mol  $\text{NH}_4^+$ , 1 mol  $\text{Cl}^-$ , 2 mol ions
- $\text{Na}_2\text{S}(s) \xrightarrow{\text{H}_2\text{O}} 2\text{Na}^+(aq) + \text{S}^{2-}(aq)$ ;  
2 mol  $\text{Na}^+$ , 1 mol  $\text{S}^{2-}$ , 3 mol ions
- $\text{Ba}(\text{NO}_3)_2(s) \xrightarrow{\text{H}_2\text{O}} \text{Ba}^{2+}(aq) + 2\text{NO}_3^-(aq)$ ;  
0.5 mol  $\text{Ba}^{2+}$ , 1 mol  $\text{NO}_3^-$ , 1.5 mol ions



**FIGURE 14-2** Ionic compounds can be soluble or insoluble in water.  $\text{NiCl}_2$ ,  $\text{KMnO}_4$ ,  $\text{CuSO}_4$ , and  $\text{Pb}(\text{NO}_3)_2$  are soluble in water.  $\text{AgCl}$  and  $\text{CdS}$  are insoluble in water.

## Precipitation Reactions

Although no compound is completely insoluble, compounds of very low solubility can be considered insoluble for most practical purposes. Some examples of ionic compounds that are soluble and insoluble in water are shown in Figure 14-2. It is difficult to write solubility rules that cover all possible conditions. However, we can write some general guidelines to help predict whether a compound made of a certain combination of ions is soluble. These general solubility guidelines are given in Table 14-1.

By looking at the table you can tell that most sodium compounds are soluble. Sodium carbonate,  $\text{Na}_2\text{CO}_3$ , is soluble because it contains sodium. Its dissociation equation is as follows.



**TABLE 14-1** General Solubility Guidelines

1. Most sodium, potassium, and ammonium compounds are soluble in water.
2. Most nitrates, acetates, and chlorates are soluble.
3. Most chlorides are soluble, except those of silver, mercury(I), and lead. Lead(II) chloride is soluble in hot water.
4. Most sulfates are soluble, except those of barium, strontium, and lead.
5. Most carbonates, phosphates, and silicates are insoluble, except those of sodium, potassium, and ammonium.
6. Most sulfides are insoluble, except those of calcium, strontium, sodium, potassium, and ammonium.

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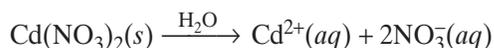
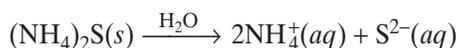
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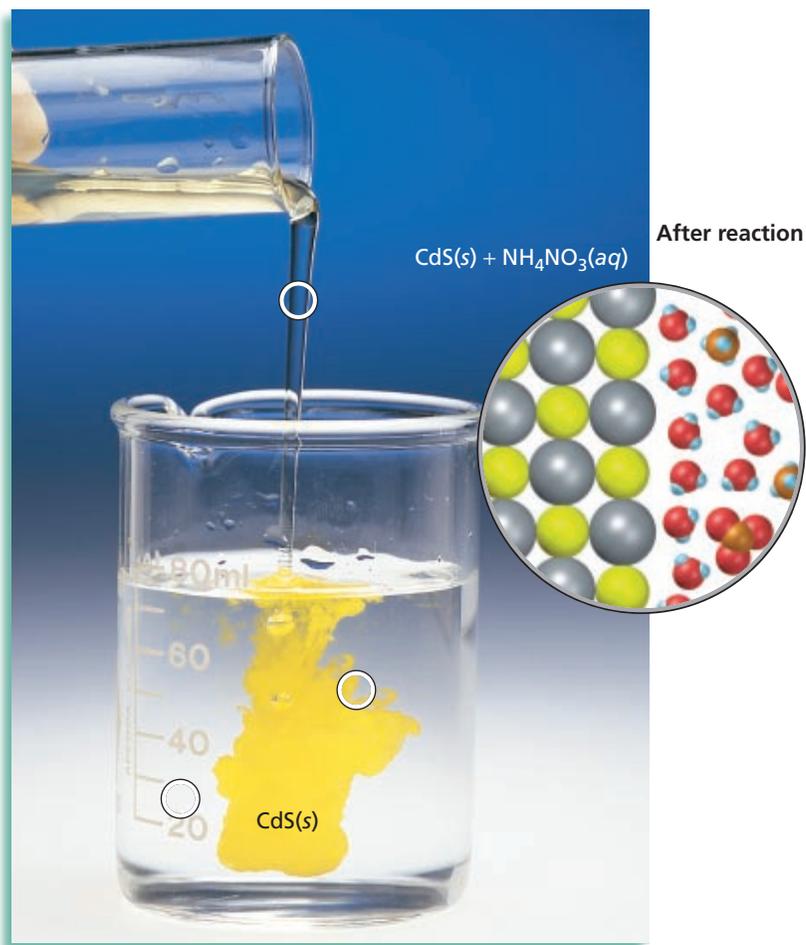
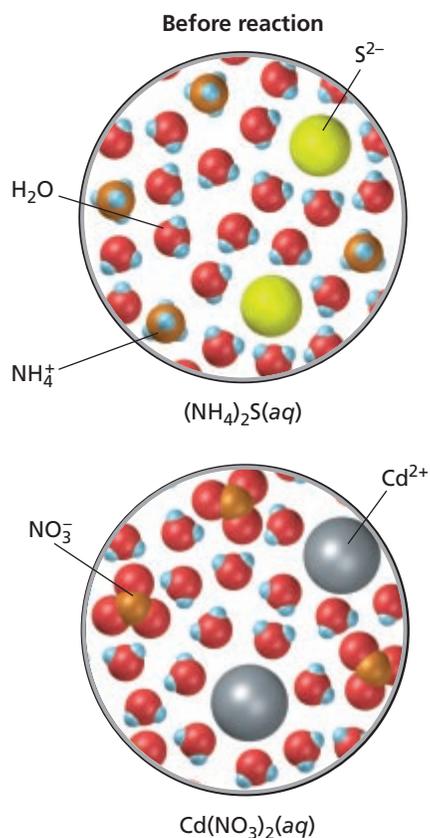
Is calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , soluble or insoluble? According to Table 14-1, most phosphates are insoluble. Calcium phosphate is not one of the exceptions listed, so it is insoluble. Dissociation equations cannot be written for insoluble compounds.

The information in Table 14-1 is also useful in predicting what will happen if solutions of two different soluble compounds are mixed. If the mixing results in a combination of ions that forms an insoluble compound, a double-replacement reaction and precipitation will occur. Precipitation occurs because the attraction between the ions is greater than the attraction between the ions and surrounding water molecules.

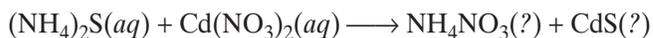
Will a precipitate form when solutions of ammonium sulfide and cadmium nitrate are combined? By using the table, you can tell that cadmium nitrate,  $\text{Cd}(\text{NO}_3)_2$ , is soluble because it is a nitrate and all nitrates are soluble. You can also tell that ammonium sulfide,  $(\text{NH}_4)_2\text{S}$ , is soluble. It is one of the sulfides listed in the table as being soluble. Their dissociation equations are as follows.



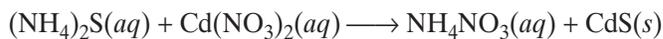
**FIGURE 14-3** Ammonium sulfide is a soluble compound that dissociates in water to form  $\text{NH}_4^+$  and  $\text{S}^{2-}$  ions. Cadmium nitrate is a soluble compound that dissociates in water to form  $\text{NO}_3^-$  and  $\text{Cd}^{2+}$  ions. Precipitation of cadmium sulfide occurs when the two solutions are mixed.



The two possible products of a double-replacement reaction between  $(\text{NH}_4)_2\text{S}$  and  $\text{Cd}(\text{NO}_3)_2$  are ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , and cadmium sulfide,  $\text{CdS}$ . (The question marks indicate that the states are unknown.)

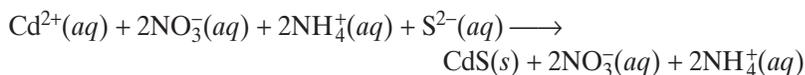


To decide whether a precipitate can form, you must know the solubilities of these two compounds. Consulting Table 14-1, you can see that  $\text{NH}_4\text{NO}_3$  is soluble in water. However,  $\text{CdS}$  is insoluble. You can therefore predict that when solutions of ammonium sulfide and cadmium nitrate are combined, ammonium nitrate will not precipitate and cadmium sulfide will. As illustrated in Figure 14-3, crystals of  $\text{CdS}$  form when the solutions are mixed. In the following equation, the designations  $(aq)$  and  $(s)$  show that ammonium nitrate remains in solution and cadmium sulfide precipitates.



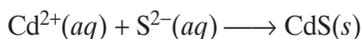
## Net Ionic Equations

Reactions of ions in aqueous solution are usually represented by net ionic equations rather than formula equations. A **net ionic equation** includes only those compounds and ions that undergo a chemical change in a reaction in an aqueous solution. To write a net ionic equation, you first convert the chemical equation into an overall ionic equation. All soluble ionic compounds are shown as dissociated ions in solution. The precipitates are shown as solids. The precipitation of cadmium sulfide described previously can be shown by the following overall ionic equation.



Notice that the ammonium ion,  $\text{NH}_4^+$ , and the nitrate ion,  $\text{NO}_3^-$ , appear on both sides of this equation. Therefore, they have not undergone any chemical change and are still present in their original form. *Ions that do not take part in a chemical reaction and are found in solution both before and after the reaction are **spectator ions**.*

To convert an ionic equation into a net ionic equation, the spectator ions are canceled on both sides of the equation. Eliminating the  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ions from the overall ionic equation above gives the following net ionic equation.



This net ionic equation applies not only to the reaction between  $(\text{NH}_4)_2\text{S}$  and  $\text{Cd}(\text{NO}_3)_2$  but also to *any* reaction in which a precipitate of cadmium sulfide forms when the ions are combined in solution. For example, it is also the net ionic equation for the precipitation of  $\text{CdS}$  when  $\text{CdSO}_4$  and  $\text{H}_2\text{S}$  react.

## SAMPLE PROBLEM 14-2

**Identify the precipitate that forms when aqueous solutions of zinc nitrate and ammonium sulfide are combined. Write the equation for the possible double-replacement reaction. Then write the formula equation, overall ionic equation, and net ionic equation for the reaction.**

### SOLUTION

#### 1 ANALYZE

**Given:** identity of reactants: zinc nitrate and ammonium sulfide  
reaction medium: aqueous solution

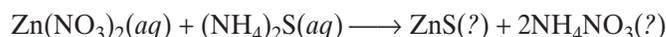
**Unknown:** **a.** equation for the possible double-replacement reaction **b.** identity of the precipitate **c.** formula equation **d.** overall ionic equation **e.** net ionic equation

#### 2 PLAN

Write the possible double-replacement reaction between  $\text{Zn}(\text{NO}_3)_2$  and  $(\text{NH}_4)_2\text{S}$ . Use Table 14-1 to determine if any of the products are insoluble and will precipitate. Write a formula equation and an overall ionic equation, then cancel the spectator ions to produce a net ionic equation.

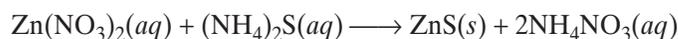
#### 3 COMPUTE

**a.** The equation for the possible double-replacement reaction is as follows.

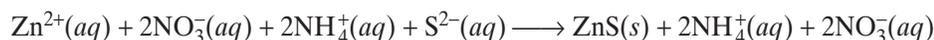


**b.** Table 14-1 reveals that zinc sulfide is not a soluble sulfide and is therefore a precipitate. Ammonium nitrate is soluble according to the table.

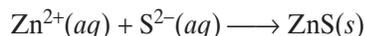
**c.** The formula equation is as follows.



**d.** The overall ionic equation is as follows.



**e.** The ammonium and nitrate ions appear on both sides of the equation as spectator ions. The net ionic equation is as follows.



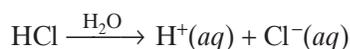
### PRACTICE

- |  |  |
|--|--|
| 1. Will a precipitate form if solutions of potassium sulfate and barium nitrate are combined? If so, write the net ionic equation for the reaction.              | <p style="margin: 0;"><i>Answer</i></p> <p style="margin: 0;">Yes;</p> $\text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq) \longrightarrow \text{BaSO}_4(s)$  |
| 2. Will a precipitate form if solutions of potassium nitrate and magnesium sulfate are combined? If so, write the net ionic equation for the reaction.           | <p style="margin: 0;"><i>Answer</i></p> <p style="margin: 0;">No</p>   |
| 3. Will a precipitate form if solutions of barium chloride and sodium sulfate are combined? If so, identify the spectator ions and write the net ionic equation. | <p style="margin: 0;"><i>Answer</i></p> <p style="margin: 0;">Yes; <math>\text{Na}^+</math> and <math>\text{Cl}^-</math>;</p> $\text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq) \longrightarrow \text{BaSO}_4(s)$ |
| 4. Write the net ionic equation for the precipitation of nickel(II) sulfide.   | <p style="margin: 0;"><i>Answer</i></p> $\text{Ni}^{2+}(aq) + \text{S}^{2-}(aq) \longrightarrow \text{NiS}(s)$   |

## Ionization

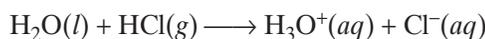
Some molecular compounds can also form ions in solution. Usually such compounds are polar. *Ions are formed from solute molecules by the action of the solvent in a process called **ionization**.* The more general meaning of this term is the creation of ions where there were none. Note that *ionization* is different from *dissociation*. When an ionic compound dissolves, the ions that were already present separate from one another. When a molecular compound dissolves and ionizes in a polar solvent, ions are formed where none existed in the undissolved compound. Like all ions in aqueous solution, the ions formed by such a molecular solute are hydrated. The heat released during the hydration of the ions provides the energy needed to break the covalent bonds.

In general, the extent to which a solute ionizes in solution depends on the strength of the bonds within the molecules of the solute and the strength of attraction between the solute and solvent molecules. If the strength of a bond within the solute molecule is weaker than the attractive forces of the solvent molecules, then the covalent bond of the solute breaks and the molecule is separated into ions. Hydrogen chloride, HCl, is a molecular compound that ionizes in aqueous solution. It contains a highly polar bond. The attraction between a polar HCl molecule and the polar water molecules is strong enough to break the HCl bond, forming hydrogen ions and chloride ions.



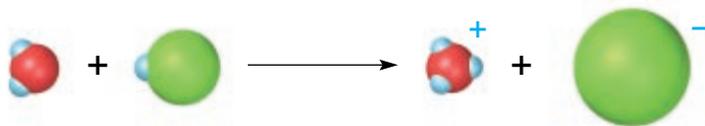
### The Hydronium Ion

The  $\text{H}^+$  ion attracts other molecules or ions so strongly that it does not normally exist alone. The ionization of hydrogen chloride in water is better described as a chemical reaction in which a proton is transferred directly from HCl to a water molecule, where it becomes covalently bonded to oxygen and forms  $\text{H}_3\text{O}^+$ .



This process is represented in Figure 14-4. *The  $\text{H}_3\text{O}^+$  ion is known as the **hydronium ion**.*

The hydration of the  $\text{H}^+$  ion to form the hydronium ion is a highly exothermic reaction. The energy released makes a large contribution to the energy needed to ionize a molecular solute. Many molecular compounds that ionize in an aqueous solution contain hydrogen and form  $\text{H}_3\text{O}^+$ .

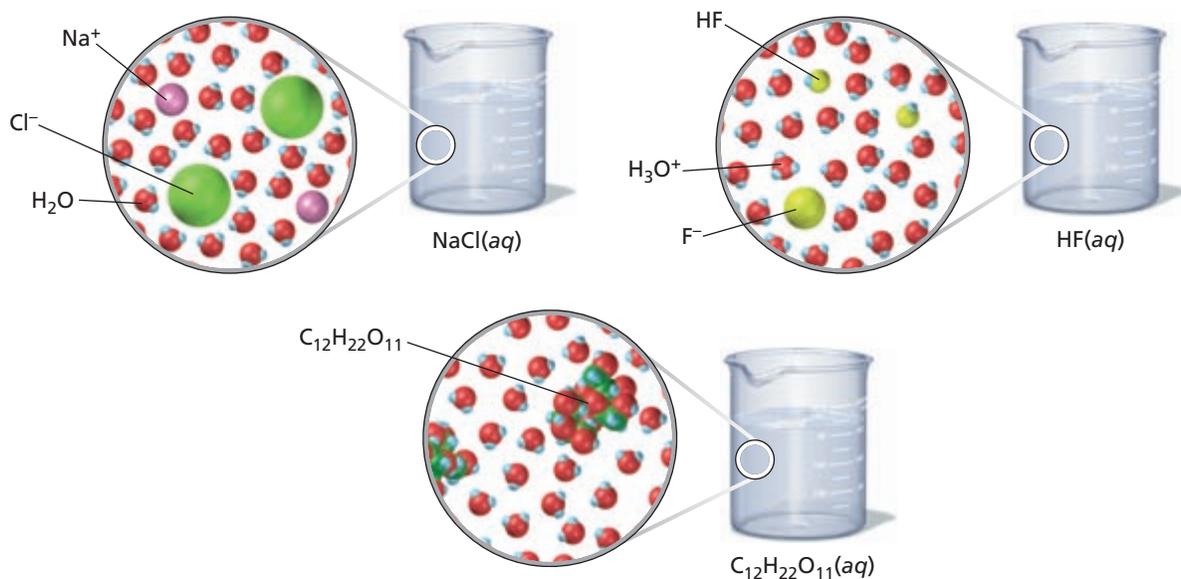


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**FIGURE 14-4** When hydrogen chloride gas dissolves in water, it ionizes to form an  $\text{H}^+$  ion and a  $\text{Cl}^-$  ion. The  $\text{H}^+$  ion immediately bonds to a water molecule, forming a hydronium ion. The aqueous solution of hydrogen chloride is called hydrochloric acid.



**FIGURE 14-5** Strong electrolytes, such as NaCl, yield only ions when they dissolve in aqueous solution. Weak electrolytes, such as HF, exist as both ions and unionized molecules in aqueous solution. Nonelectrolytes, such as sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , do not form any ions in aqueous solution.

## Strong and Weak Electrolytes

As discussed in Chapter 13, substances that yield ions and conduct an electric current in solution are electrolytes. Substances that do not yield ions and do not conduct an electric current in solution are nonelectrolytes. Hydrogen chloride is one of a series of compounds composed of hydrogen and the members of Group 17 (known as the halogens). The hydrogen halides are all molecular compounds with single polar-covalent bonds. All are gases, all are very soluble in water, and all are electrolytes. Hydrogen chloride, hydrogen bromide, and hydrogen iodide strongly conduct an electric current in an aqueous solution. However, hydrogen fluoride only weakly conducts an electric current at the same concentration. The strength with which substances conduct an electric current is related to their ability to form ions in solution, as shown in Figure 14-5.

### Strong Electrolytes

Hydrogen chloride, hydrogen bromide, and hydrogen iodide are 100% ionized in dilute aqueous solution. A **strong electrolyte** is any compound whose dilute aqueous solutions conduct electricity well; this is due to the presence of all or almost all of the dissolved compound in the form of ions. Hydrogen chloride, hydrogen bromide, and hydrogen iodide are all acids in aqueous solution. These acids, several other acids, and all soluble ionic compounds are strong electrolytes.

The distinguishing feature of strong electrolytes is that, to whatever extent they dissolve in water, they yield only ions. For example, an ionic compound may be highly soluble in water and dissociate into ions in solution, such as NaCl. Other ionic compounds may not dissolve much,

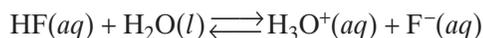


**Module 8:** Strong and Weakly Ionized Species, pH, and Titrations

but the amount that does dissolve exists solely as hydrated ions in solution.

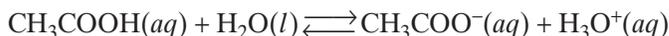
## Weak Electrolytes

An aqueous solution of some molecular compounds contains not only dissolved ions but also some dissolved molecules that are not ionized. Hydrogen fluoride, HF, dissolves in water to give an acid solution known as hydrofluoric acid. However, the hydrogen-fluorine bond is much stronger than the bonds between hydrogen and the other halogens. When hydrogen fluoride dissolves, some molecules ionize. But the reverse reaction—the transfer of  $\text{H}^+$  ions back to  $\text{F}^-$  ions to form hydrogen fluoride molecules—also takes place.



Thus, the concentration of dissolved unionized HF molecules remains high and the concentration of  $\text{H}_3\text{O}^+$  and  $\text{F}^-$  ions remains low.

Hydrogen fluoride is an example of a *weak electrolyte*. A **weak electrolyte** is any compound whose dilute aqueous solutions conduct electricity poorly; this is due to the presence of a small amount of the dissolved compound in the form of ions. This is in contrast to a non-electrolyte, of which none of the dissolved compound exists as ions. Another example of a weak electrolyte is acetic acid,  $\text{CH}_3\text{COOH}$ . Only a small percentage of the acetic acid molecules ionize in aqueous solution.



The description of an electrolyte as strong or weak must not be confused with the description of a solution as concentrated or dilute. Strong and weak electrolytes differ in the *degree of ionization or dissociation*. Concentrated and dilute solutions differ in the *amount of solute dissolved* in a given quantity of a solvent. Hydrochloric acid is always a strong electrolyte. This is true even in a solution that is 0.000 01 M—a very dilute solution. By contrast, acetic acid is always considered a weak electrolyte, even in a 10 M solution—a fairly concentrated solution.

## SECTION REVIEW

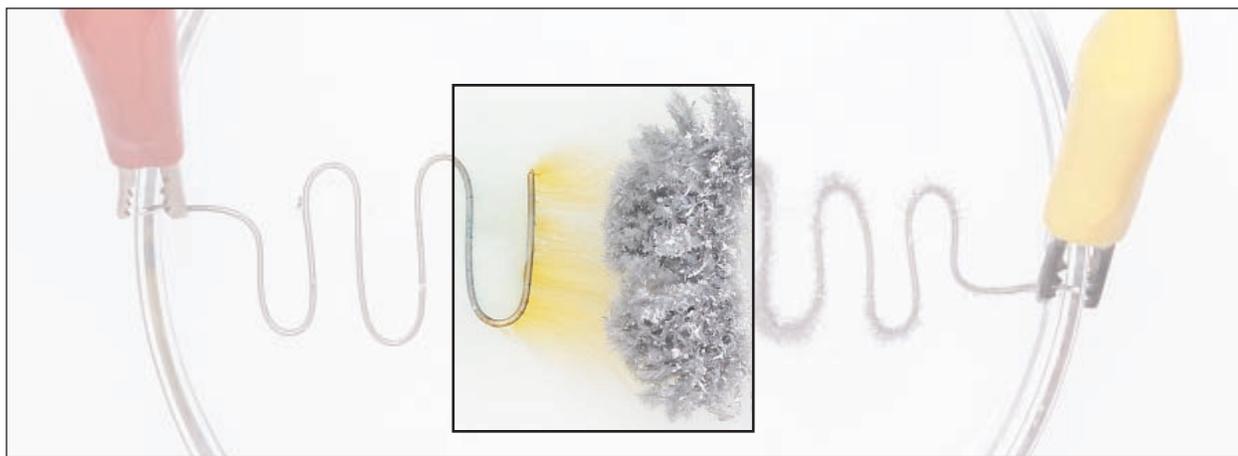
1. Write the equation for the dissolution of  $\text{Sr}(\text{NO}_3)_2$  in water. How many moles of strontium ions and nitrate ions are produced by dissolving 0.5 mol of strontium nitrate?
2. Will a precipitate form if solutions of magnesium acetate and strontium chloride are combined?
3. What determines whether a molecular compound will be ionized in a polar solvent?
4. How is a hydronium ion formed when a compound like HCl dissolves in water? What is its net charge?
5. Explain why HCl is a strong electrolyte and HF is a weak electrolyte.



# The Riddle of Electrolysis

## HISTORICAL PERSPECTIVE

*When Michael Faraday performed his electrochemical experiments, little was known about the relationship between matter and electricity. Chemists were still debating the existence of atoms, and the discovery of the electron was more than 50 years away. Combining his talents in electrical and chemical investigation, Faraday pointed researchers to the intimate connection between chemical reactions and electricity while setting the stage for the development of a new branch of chemistry.*



Chlorine being produced by electrolysis.

### Electrifying Experiments

In 1800, the Italian physicist Alessandro Volta introduced his “voltaic pile,” better known as the battery. The stack of alternating zinc and silver disks provided scientists with a source of electric current for the first time, and, in the words of the famous English chemist Humphry Davy, it acted as “an alarm-bell to experimenters in every part of Europe.”

That same year, chemists discovered a new phenomenon using Volta’s device. They immersed

the two poles of a battery at different locations in a container of water. As current flowed, the water decomposed into its elemental components, with hydrogen evolving at the positive pole of the battery and oxygen evolving at the negative pole. Similar experiments using solutions of certain solids dissolved in water resulted in the decomposition of the solids, with the two products of their breakdown also evolving at opposite poles of the battery. This electrochemical decomposition was later named electrolysis.

### The Roots of Electrolytic Theory

The discovery of electrolysis led two pioneering chemists to ponder the connection between chemical forces and electricity. One of them was Davy:

*Is not what has been called chemical affinity merely the union . . . of particles in naturally opposite states? And are not chemical attractions of particles and electrical attractions of masses owing to one property and governed by one simple law?*

The Swedish chemist Jöns Jacob Berzelius took Davy's idea a step further. He postulated that matter consisted of combinations of "electropositive" and "electronegative" substances, classifying the parts by the pole at which they accumulated during electrolysis.

These ideas inspired two early electrolytic theories, each of which ultimately proved incorrect but which contributed to our present understanding of the phenomenon. The "contact theory" proposed that electrolytic current was due merely to the contact of the battery's metals with the electrolytic solution. The "chemical theory," on the other hand, attributed the flow of current to undefined changes in the solution's components.

### Faraday Provides a Spark

Although Michael Faraday is best remembered for his work in electromagnetism, he began his career as Humphry Davy's laboratory assistant at the Royal Institution, in London, and went on to be the professor of chemistry there for over 30 years. In the 1830s, Faraday devised several ingenious experiments to determine whether the flow of current in an electrolytic

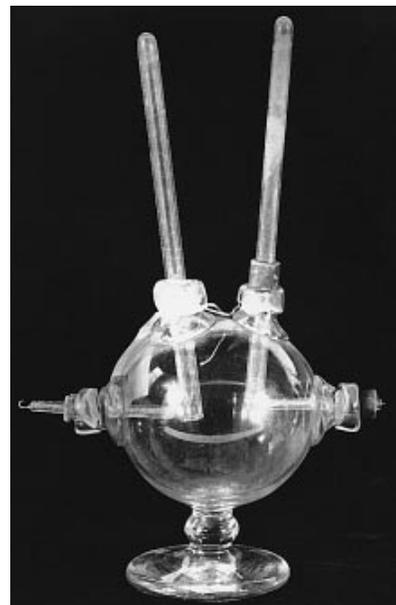
solution is dependent solely on the contact of the battery's poles with the solution. In a typical setup, one of the poles was separated from the solution and electricity was permitted to enter it by way of a spark. In all cases, Faraday observed current to flow in the electrolytic cell despite one or both of the poles not being in direct contact with the electrolytic solution. In 1833 he wrote the following:

*I conceive the effects [of electrolysis] to arise from forces which are internal, relative to the matter under decomposition, and not external, as they might be considered, if directly dependent on the poles. I suppose that the effects are due to a modification, by the electric current, of the chemical affinity of the particles through or by which the current is passing.*

Although the battery's poles were, in fact, later shown to play a part in the flow of the current, Faraday had established the active role of the electrolytic solution in electrolysis. And in realizing that electricity affected the chemical nature of the solution, he anticipated the ideas of oxidation and reduction—despite the fact that the concepts of electrons and ions were half a century away.

### Faraday's Legacy

Faraday continued to study the role of the electrolytic solution, or *electrolyte*, as he named it, in electrolysis. (He also coined most



Instrument used by Michael Faraday in his studies of electrolysis.

of the other modern terms of electrolysis, for example, *electrode*, *ion*, *anode*, *cathode*, *anion*, and *cation*.) These investigations culminated in the discovery of his basic laws of electrolysis.

Still valid today, these principles not only put electrolysis on a quantitative footing, leading to our current understanding of the phenomenon, but also bolstered the atomic theory, which was still seriously contested by many chemists at the time. And perhaps most important, Faraday's experiments inspired his successors to further clarify the chemical nature of solutions. This ultimately led to Svante Arrhenius's theory of electrolytic dissociation and the evolution of a new division in the chemical field, known today as physical chemistry.

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## SECTION 14-2

### OBJECTIVES

- List four colligative properties, and explain why they are classified as colligative properties.
- Calculate freezing-point depression, boiling-point elevation, and solution molality of nonelectrolytic solutions.
- Calculate the expected changes in freezing point and boiling point of an electrolytic solution.
- Discuss causes of the differences between expected and experimentally observed colligative properties of electrolytic solutions.

# Colligative Properties of Solutions

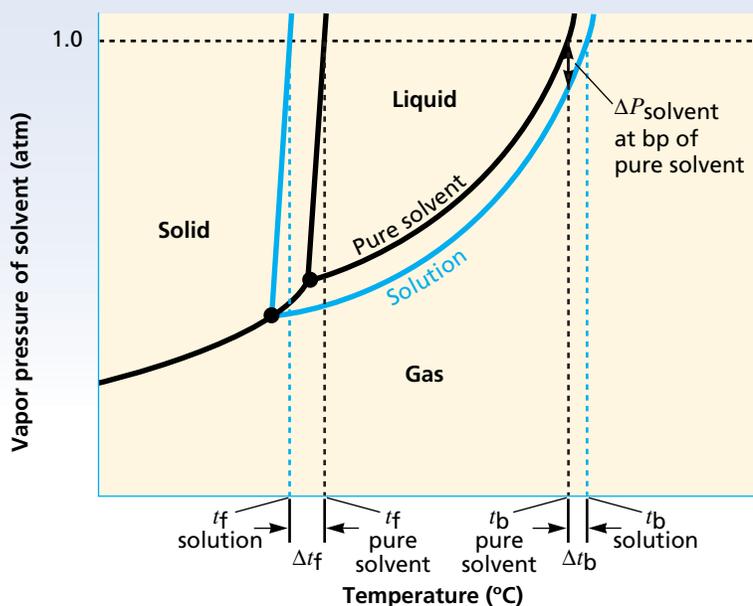
The presence of solutes affects the properties of the solutions. Some of these properties are not dependent on the nature of the dissolved substance but only on how many dissolved particles are present. *Properties that depend on the concentration of solute particles but not on their identity are called **colligative properties**.* In calculations involving some colligative properties, the concentration is given in terms of molality,  $m$ .

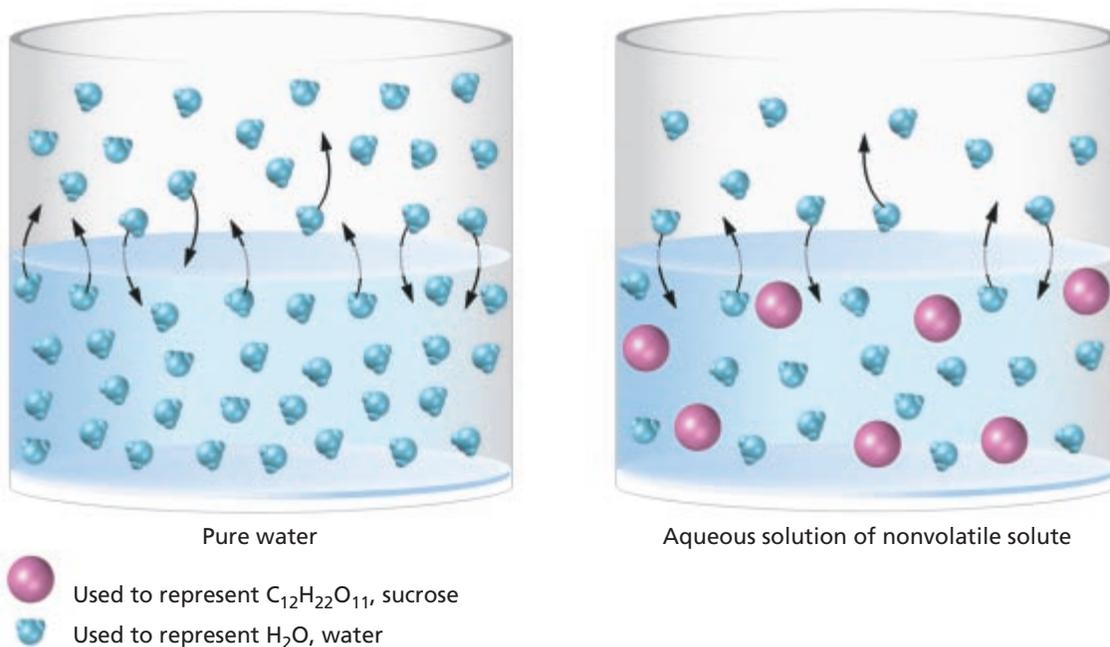
## Vapor-Pressure Lowering

The boiling point and freezing point of a solution differ from those of the pure solvent. The graph in Figure 14-6 shows that a nonvolatile solute raises the boiling point and lowers the freezing point. A **non-volatile substance** is one that has little tendency to become a gas under existing conditions.

**FIGURE 14-6** Vapor pressure as a function of temperature is shown for a pure solvent, a solution of that solvent, and a nonvolatile solute. The vapor pressure of the solution is lower than the vapor pressure of the pure solvent. (This can be seen by noting the decrease in pressure between the pure solvent and the solution at the temperature that is the boiling point of the pure solvent.) The solute thus reduces the freezing point and elevates the boiling point.

**Vapor Pressure vs. Temperature for a Pure Solvent and a Solution with a Nonvolatile Solute**





**FIGURE 14-7** The vapor pressure of water over pure water is greater than the vapor pressure of water over an aqueous solution containing a nonvolatile solute, such as sucrose.

To understand why a nonvolatile solute changes the boiling point and freezing point, you must consider equilibrium vapor pressure, which was discussed in Chapter 12. Vapor pressure is the pressure caused by molecules that have escaped from the liquid phase to the gaseous phase. Experiments show that the vapor pressure of a solvent containing a nonvolatile solute is lower than the vapor pressure of the pure solvent at the same temperature, as shown in Figure 14-7. Notice the liquid-vapor boundaries. Vapor pressure can be thought of as a measure of the tendency of molecules to escape from a liquid. Addition of sucrose, a nonvolatile solute, lowers the concentration of water molecules at the surface of the liquid. This lowers the tendency of water molecules to leave the solution and enter the vapor phase. Thus, the vapor pressure of the solution is lower than the vapor pressure of pure water.

Nonelectrolyte solutions of the same molality have the same concentration of particles. Dilute solutions of the same solvent and equal molality of any nonelectrolyte solute lower vapor pressure equally. For example, a 1 *m* aqueous solution of the nonelectrolyte glucose,  $C_6H_{12}O_6$ , lowers the vapor pressure of water  $5.5 \times 10^{-4}$  atm at 25°C. A 1 *m* solution of sucrose,  $C_{12}H_{22}O_{11}$ , another nonelectrolyte, also lowers the vapor pressure  $5.5 \times 10^{-4}$  atm. Because vapor-pressure lowering depends on the concentration of a nonelectrolyte solute and is independent of solute identity, it is a colligative property.

Refer to the graph in Figure 14-6. Because the vapor pressure has been lowered, the solution remains liquid over a larger temperature range. This lowers the freezing point and raises the boiling point. It follows that changes in boiling point and freezing point also depend on the concentration of solute and are therefore colligative properties.

## Freezing-Point Depression

The freezing point of a 1-molal solution of any nonelectrolyte solute in water is found by experiment to be  $1.86^{\circ}\text{C}$  lower than the freezing point of water. That is, when 1 mol of a nonelectrolyte solute is dissolved in 1 kg of water, the freezing point of the solution is  $-1.86^{\circ}\text{C}$  instead of  $0.00^{\circ}\text{C}$ . When 2 mol of a nonelectrolyte solute is dissolved in 1 kg of water, the freezing point of the solution is  $-3.72^{\circ}\text{C}$ . This is  $2 \times -1.86^{\circ}\text{C}$ . In fact, for any concentration of a nonelectrolyte solute in water, the decrease in freezing point can be determined by using the value of  $-1.86^{\circ}\text{C}/m$ . This value, called the **molal freezing-point constant ( $K_f$ )**, is the freezing-point depression of the solvent in a 1-molal solution of a nonvolatile, nonelectrolyte solute.

Each solvent has its own characteristic molal freezing-point constant. The values of  $K_f$  for some common solvents are given in Table 14-2. These values are most accurate for dilute solutions at 1 atmosphere of pressure. Some variations are introduced in the value of  $K_f$  at other pressures and with more-concentrated solutions. The table also shows the values of a related quantity called  $K_b$ , which you will study next.

As stated earlier, the freezing point of a solution containing 1 mol of a nonelectrolyte solute in water is  $1.86^{\circ}\text{C}$  lower than the normal freezing point of water. The **freezing-point depression,  $\Delta t_f$** , is the difference between the freezing points of the pure solvent and a solution of a nonelectrolyte in that solvent, and it is directly proportional to the molal concentration of the solution. As shown by the previous example, if the molal concentration is doubled, the freezing-point depression is doubled. Freezing-point depression can be calculated by the following equation.

$$\Delta t_f = K_f m$$

$K_f$  is expressed as  $^{\circ}\text{C}/m$ ,  $m$  is expressed in mol solute/kg solvent (molality), and  $\Delta t_f$  is expressed in  $^{\circ}\text{C}$ . Sample Problems 14-3 and 14-4 show how this relationship can be used to determine the freezing-point depression and molal concentration of a solution.

**TABLE 14-2** Molal Freezing-Point and Boiling-Point Constants

Solvent	Normal f.p. ( $^{\circ}\text{C}$ )	Molal f.p. constant, $K_f$ ( $^{\circ}\text{C}/m$ )	Normal b.p. ( $^{\circ}\text{C}$ )	Molal b.p. constant, $K_b$ ( $^{\circ}\text{C}/m$ )
Acetic acid	16.6	-3.90	117.9	3.07
Camphor	178.8	-39.7	207.4	5.61
Ether	-116.3	-1.79	34.6	2.02
Naphthalene	80.2	-6.94	217.7	5.80
Phenol	40.9	-7.40	181.8	3.60
Water	0.00	-1.86	100.0	0.51

### SAMPLE PROBLEM 14-3

What is the freezing-point depression of water in a solution of 17.1 g of sucrose,  $C_{12}H_{22}O_{11}$ , and 200. g of water? What is the actual freezing point of the solution?

#### SOLUTION

##### 1 ANALYZE

**Given:** solute mass and chemical formula = 17.1 g  $C_{12}H_{22}O_{11}$   
solvent mass and identity = 200.0 g water

**Unknown:** a. freezing-point depression  
b. freezing point of the solution

##### 2 PLAN

Find the molal freezing-point constant,  $K_f$ , for water in Table 14-2. To use the equation for freezing-point depression,  $\Delta t_f = K_f m$ , you need to determine the molality of the solution.

$$\text{mass of solute (g)} \times \frac{1 \text{ mol solute}}{\text{molar mass of solute (g)}} = \text{amount of solute (mol)}$$

$$\frac{\text{amount of solute (mol)}}{\text{mass of solvent (g)}} \times \frac{1000 \text{ g water}}{1 \text{ kg water}} = \text{molality}$$

$$\Delta t_f = K_f m$$

$$\text{f.p. solution} = \text{f.p. solvent} + \Delta t_f$$

##### 3 COMPUTE

$$17.1 \text{ g } C_{12}H_{22}O_{11} \times \frac{1 \text{ mol } C_{12}H_{22}O_{11}}{342.34 \text{ g } C_{12}H_{22}O_{11}} = 0.0500 \text{ mol } C_{12}H_{22}O_{11}$$

$$\frac{0.0500 \text{ mol } C_{12}H_{22}O_{11}}{200. \text{ g water}} \times \frac{1000 \text{ g water}}{\text{kg water}} = \frac{0.250 \text{ mol } C_{12}H_{22}O_{11}}{\text{kg water}} = 0.250 \text{ } m$$

a.  $\Delta t_f = 0.250 \text{ } m \times (-1.86^\circ\text{C}/m) = -0.465^\circ\text{C}$

b.  $\text{f.p. solution} = 0.000^\circ\text{C} + (-0.465^\circ\text{C}) = -0.465^\circ\text{C}$

### SAMPLE PROBLEM 14-4

A water solution containing an unknown quantity of a nonelectrolyte solute is found to have a freezing point of  $-0.23^\circ\text{C}$ . What is the molal concentration of the solution?

#### SOLUTION

##### 1 ANALYZE

**Given:** freezing point of solution =  $-0.23^\circ\text{C}$

**Unknown:** molality of the solution

##### 2 PLAN

Water is the solvent, so you will need the value of  $K_f$ , the molal-freezing-point constant for water, from Table 14-2. The  $\Delta t_f$  for this solution is the difference between the f.p. of water and the f.p. of the solution. Use the equation for freezing-point depression to calculate molality.

$$\Delta t_f = \text{f.p. of solution} - \text{f.p. of pure solvent}$$

$$\Delta t_f = K_f m \quad \text{Solve for molality, } m.$$

$$m = \frac{\Delta t_f}{K_f}$$

**3 COMPUTE**

$$\Delta t_f = -0.23^\circ\text{C} - 0.00^\circ\text{C} = -0.23^\circ\text{C}$$

$$m = \frac{-0.23^\circ\text{C}}{-1.86^\circ\text{C}/m} = 0.12\ m$$

**4 EVALUATE**

As shown by the unit cancellation, the answer gives the molality, as desired. The answer is properly limited to two significant digits.

**PRACTICE**

- |  |   |
|--|---|
| 1. A solution consists of 10.3 g of the nonelectrolyte glucose, $\text{C}_6\text{H}_{12}\text{O}_6$ , dissolved in 250. g of water. What is the freezing-point depression of the solution? | <i>Answer</i><br>$-0.426^\circ\text{C}$ |
| 2. In a laboratory experiment, the freezing point of an aqueous solution of glucose is found to be $-0.325^\circ\text{C}$ . What is the molal concentration of this solution?              | <i>Answer</i><br>$0.175\ m$             |
| 3. If 0.500 mol of a nonelectrolyte solute are dissolved in 500.0 g of ether, what is the freezing point of the solution?  | <i>Answer</i><br>$-118.1^\circ\text{C}$ |
| 4. The freezing point of an aqueous solution that contains a nonelectrolyte is $-9.0^\circ\text{C}$ .  | <i>Answer</i>                           |
| a. What is the freezing-point depression of the solution?  | a. $-9.0^\circ\text{C}$                 |
| b. What is the molal concentration of the solution?  | b. $4.8\ m$                             |

## Boiling-Point Elevation

As you learned in Chapter 12, the boiling point of a liquid is the temperature at which the vapor pressure of the liquid is equal to the prevailing atmospheric pressure. Therefore, a change in the vapor pressure of the liquid will cause a corresponding change in the boiling point. As stated earlier, the vapor pressure of a solution containing a nonvolatile solute is lower than the vapor pressure of the pure solvent. This means that more heat will be required to raise the vapor pressure of the solution to equal the atmospheric pressure. Thus, the boiling point of a solution is higher than the boiling point of the pure solvent.

The **molal boiling-point constant** ( $K_b$ ) is the boiling-point elevation of the solvent in a 1-molal solution of a nonvolatile, nonelectrolyte solute. The boiling-point elevation of a 1-molal solution of any nonelectrolyte solute in water has been found by experiment to be  $0.51^\circ\text{C}$ . Thus, the molal boiling-point constant for water is  $0.51^\circ\text{C}/m$ .

For different solvents, the boiling-point elevations of 1-molal solutions have different values. Some other values for  $K_b$  are included in Table 14-2. Like the freezing-point constants, these values are most accurate for dilute solutions.

The **boiling-point elevation**,  $\Delta t_b$ , is the difference between the boiling points of the pure solvent and a nonelectrolyte solution of that solvent,

and it is directly proportional to the molal concentration of the solution. Boiling-point elevation can be calculated by the following equation.

$$\Delta t_b = K_b m$$

When  $\Delta t_b$  is expressed in  $^{\circ}\text{C}/m$  and  $m$  is expressed in mol of solute/kg of solvent,  $\Delta t_b$  is the boiling-point elevation in  $^{\circ}\text{C}$ .

### SAMPLE PROBLEM 14-5

**What is the boiling-point elevation of a solution made from 20.0 g of a nonelectrolyte solute and 400.0 g of water? The molar mass of the solute is 62.0 g.**

#### SOLUTION

##### 1 ANALYZE

**Given:** solute mass = 20.0 g  
 solute molar mass = 62.0 g  
 solvent mass and identity = 400.0 g of water  
**Unknown:** boiling-point elevation

##### 2 PLAN

Find the molal boiling-point constant,  $K_b$ , for water in Table 14-2. To use the equation for boiling-point elevation,  $\Delta t_b = K_b m$ , you need to determine the molality of the solution.

$$\text{mass of solute (g)} \times \frac{1 \text{ mol solute}}{\text{molar mass of solute (g)}} = \text{amount of solute (mol)}$$

$$\frac{\text{amount of solute (mol)}}{\text{mass of solvent (g)}} \times \frac{1000 \text{ g water}}{1 \text{ kg water}} = \text{molality}$$

$$\Delta t_b = K_b m$$

##### 3 COMPUTE

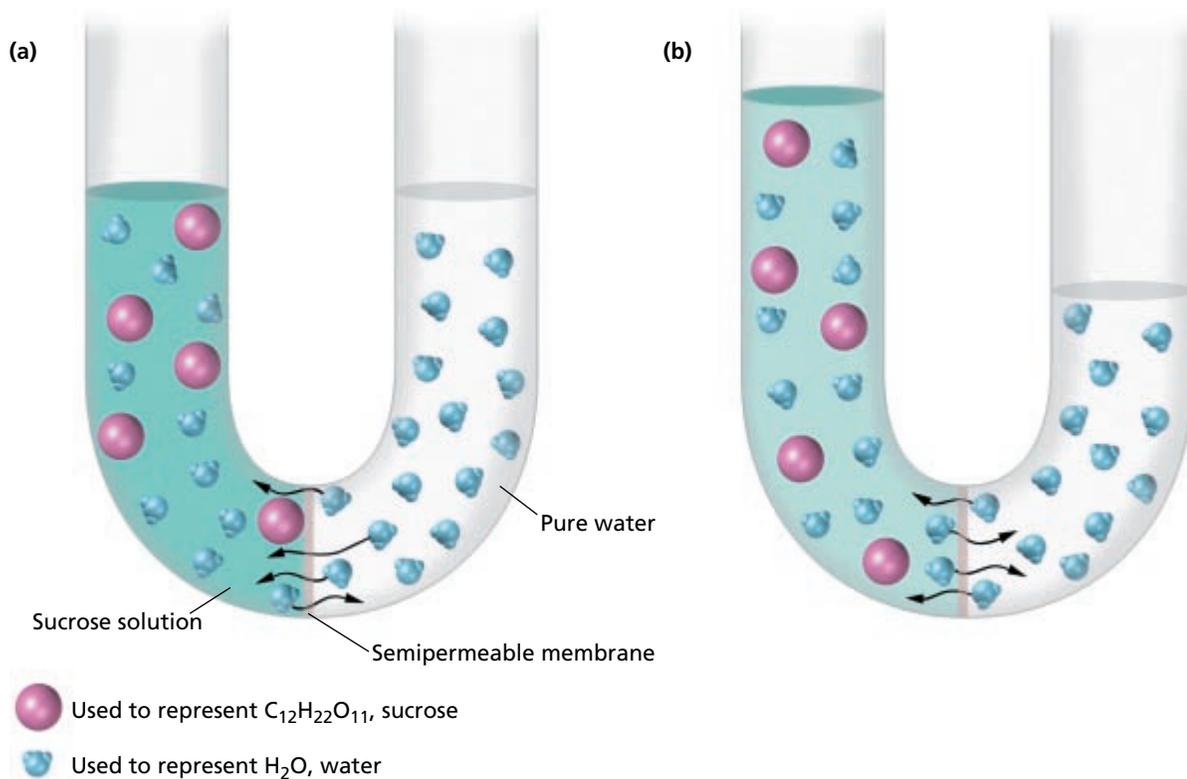
$$20.0 \text{ g of solute} \times \frac{1 \text{ mol solute}}{62.0 \text{ g of solute}} = 0.323 \text{ mol of solute}$$

$$\frac{0.323 \text{ mol of solute}}{400.0 \text{ g water}} \times \frac{1000 \text{ g water}}{1 \text{ kg water}} = 0.808 \frac{\text{mol solute}}{\text{kg water}} = 0.808 m$$

$$\Delta t_b = 0.51^{\circ}\text{C}/m \times 0.808 m = 0.41^{\circ}\text{C}$$

#### PRACTICE

1. A solution contains 50.0 g of sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , a nonelectrolyte, dissolved in 500.0 g of water. What is the boiling-point elevation? *Answer* 0.15 $^{\circ}\text{C}$
2. A solution contains 450.0 g of sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , a nonelectrolyte, dissolved in 250 g of water. What is the boiling point of the solution? *Answer* 102.7 $^{\circ}\text{C}$
3. If the boiling point elevation of an aqueous solution containing a nonvolatile electrolyte is 1.02 $^{\circ}\text{C}$ , what is the molality of the solution? *Answer* 2.0  $m$
4. The boiling point of an aqueous solution containing a nonvolatile electrolyte is 100.75 $^{\circ}\text{C}$ . *Answer*  
 a. What is the boiling-point elevation?  
 b. What is the molality of the solution? *Answer* a. 0.75 $^{\circ}\text{C}$   
 b. 1.5  $m$



**FIGURE 14-8** (a) When pure water and an aqueous sucrose solution are separated by a semipermeable membrane, the net movement of water molecules through the membrane is from the pure water side into the aqueous solution. (b) The level of the solution rises until pressure exerted by the height of the solution equals the osmotic pressure, at which point no net movement of water molecules occurs.

## Osmotic Pressure

Figure 14-8 illustrates another colligative property. In the figure, an aqueous sucrose solution is separated from pure water by a semipermeable membrane. **Semipermeable membranes** allow the movement of some particles while blocking the movement of others. The level of the sucrose solution will rise until a certain height is reached. What causes the level of the solution to rise?

The semipermeable membrane allows water molecules, but not sucrose molecules, to pass through. The sucrose molecules on the solution side allow fewer water molecules to strike the membrane than strike on the pure water side in the same amount of time. Thus, the rate at which water molecules leave the pure water side is greater than the rate at which they leave the solution. This causes the level of the solution to rise. The level rises until the pressure exerted by the height of the solution is large enough to force water molecules back through the membrane from the solution at a rate equal to that at which they enter from the pure water side.

The movement of solvent through a semipermeable membrane from the side of lower solute concentration to the side of higher solute concentration is **osmosis**. Osmosis occurs whenever two solutions of different concentrations are separated by a semipermeable membrane. **Osmotic pressure** is the external pressure that must be applied to stop osmosis. In the example given above, osmosis caused the level of the solution to rise until the height of the solution provided the pressure necessary to stop osmosis. Because osmotic pressure is dependent on the concentration of

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solute particles and not on the type of solute particles, it is a colligative property. The greater the concentration of a solution, the greater the osmotic pressure of the solution.

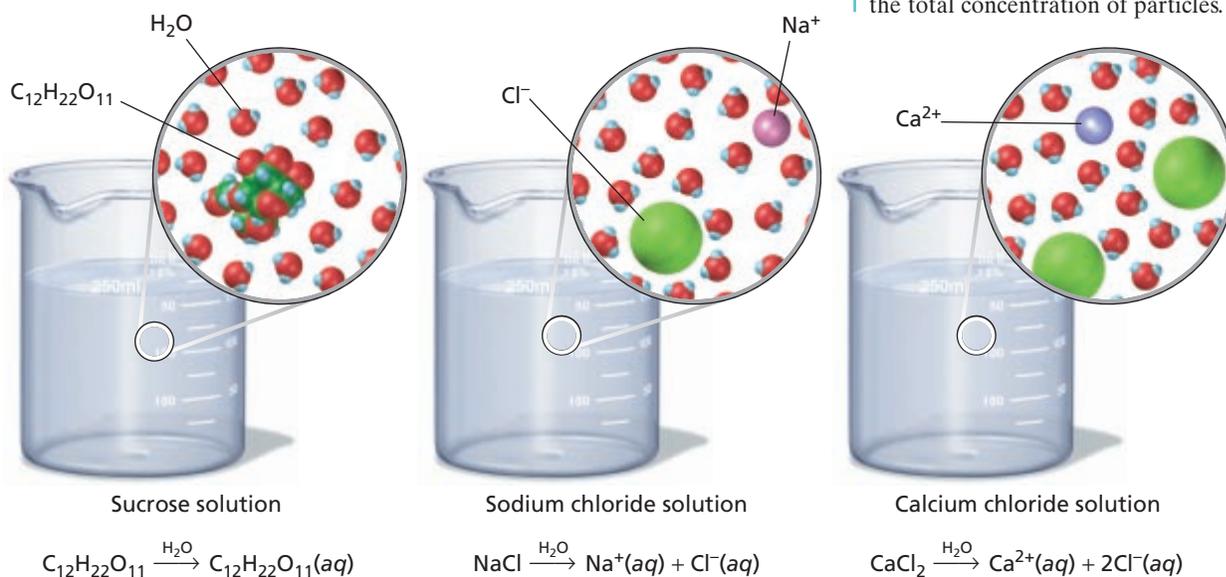
Regulation of osmosis is vital to the life of a cell because cell membranes are semipermeable. Cells lose water and shrink when placed in a solution of higher concentration. They gain water and swell when placed in a solution of lower concentration. In vertebrates, cells are protected from swelling and shrinking by blood and lymph that surround the cells. Blood and lymph are equal in concentration to the concentration inside the cell.

## Electrolytes and Colligative Properties

Early investigators were puzzled by experiments in which certain substances depressed the freezing point or elevated the boiling point of a solvent more than expected. For example, a 0.1 *m* solution of sodium chloride, NaCl, lowers the freezing point of the solvent nearly twice as much as a 0.1 *m* solution of sucrose. A 0.1 *m* solution of calcium chloride, CaCl<sub>2</sub>, lowers the freezing point of the solvent nearly three times as much as a 0.1 *m* solution of sucrose. The effect on boiling points is similar.

To understand why this is so, contrast the behavior of sucrose with that of sodium chloride in aqueous solutions. Each sucrose molecule dissolves to produce only one particle in solution. So 1 mol of sucrose dissolves to produce only 1 mol of particles in solution. Sugar is a nonelectrolyte. NaCl, however, is a strong electrolyte. Each mole of NaCl dissolves to produce 2 mol of particles in solution: 1 mol of sodium ions and 1 mol of chloride ions. Figure 14-9 compares the production of particles in solution for three different solutes. As you can see, electrolytes produce more than 1 mol of solute particles for each mole of compound dissolved.

**FIGURE 14-9** Compare the number of particles produced per formula unit for these three solutes. Colligative properties depend on the total concentration of particles.



## Calculated Values for Electrolyte Solutions

Remember that colligative properties depend on the total concentration of solute particles regardless of their identity. So electrolytes cause changes in colligative properties proportional to the total molality in terms of all dissolved particles instead of formula units. For the same molal concentrations of sucrose and sodium chloride, you would expect the effect on colligative properties to be twice as large for sodium chloride as for sucrose. What about barium nitrate,  $\text{Ba}(\text{NO}_3)_2$ ? Each mole of barium nitrate yields 3 mol of ions in solution.



You would expect a  $\text{Ba}(\text{NO}_3)_2$  solution of a given molality to lower the freezing point of its solvent three times as much as a nonelectrolytic solution of the same molality.

### SAMPLE PROBLEM 14-6

**What is the expected change in the freezing point of water in a solution of 62.5 g of barium nitrate,  $\text{Ba}(\text{NO}_3)_2$ , in 1.00 kg of water?**

#### SOLUTION

##### 1 ANALYZE

**Given:** solute mass and formula = 62.5 g  $\text{Ba}(\text{NO}_3)_2$   
solvent mass and identity = 1.00 kg water  
 $\Delta t_f = K_f m$

**Unknown:** expected freezing-point depression

##### 2 PLAN

The molality can be calculated by converting the solute mass to moles and then dividing by the number of kilograms of solvent. That molality is in terms of formula units of  $\text{Ba}(\text{NO}_3)_2$  and must be converted to molality in terms of dissociated ions in solution. It must be multiplied by the number of moles of ions produced per mole of formula unit. This adjusted molality can then be used to calculate the freezing-point depression.

$$\frac{\text{mass of solute (g)}}{\text{mass of solvent (kg)}} \times \frac{1 \text{ mol solute}}{\text{molar mass of solute (g)}} = \text{molality of solution} \left( \frac{\text{mol}}{\text{kg}} \right)$$

$$\text{molality of solution} \left( \frac{\text{mol}}{\text{kg}} \right) \times \text{molality conversion} \left( \frac{\text{mol ions}}{\text{mol}} \right) \times K_f \left( \frac{^\circ\text{C} \cdot \text{kg H}_2\text{O}}{\text{mol ions}} \right) \\ = \text{expected freezing-point depression (}^\circ\text{C)}$$

This problem is similar to Sample Problem 14-5, except that the solute is ionic rather than a nonionizing molecular solute. The number of particles in solution will therefore equal the number of ions of the solute.

##### 3 COMPUTE

$$\frac{62.5 \text{ g } \text{Ba}(\text{NO}_3)_2}{1.00 \text{ kg H}_2\text{O}} \times \frac{\text{mol } \text{Ba}(\text{NO}_3)_2}{261.35 \text{ g } \text{Ba}(\text{NO}_3)_2} = \frac{0.239 \text{ mol } \text{Ba}(\text{NO}_3)_2}{\text{kg H}_2\text{O}}$$



Each formula unit of barium nitrate yields three ions in solution.

$$\frac{0.239 \text{ mol Ba}(\text{NO}_3)_2}{\text{kg H}_2\text{O}} \times \frac{3 \text{ mol ions}}{\text{mol Ba}(\text{NO}_3)_2} \times \frac{-1.86^\circ\text{C} \cdot \text{kg H}_2\text{O}}{\text{mol ions}} = -1.33^\circ\text{C}$$

#### 4 EVALUATE

The units cancel properly to give the desired answer in  $^\circ\text{C}$ . The answer is correctly given to three significant digits. The mass of the solute is approximately one-fourth its molar mass and would give 0.75 mol of ions in the 1 kg of solvent, so the estimated answer of  $0.75 \times -1.86^\circ\text{C} = -1.4^\circ\text{C}$  supports our computation.

#### PRACTICE

1. What is the expected freezing-point depression for a solution that contains 2.0 mol of magnesium sulfate dissolved in 1.0 kg of water? *Answer*  $-7.4^\circ\text{C}$
2. What is the expected boiling-point elevation of water for a solution that contains 150 g of sodium chloride dissolved in 1.0 kg of water? *Answer*  $2.7^\circ\text{C}$
3. The freezing point of an aqueous sodium chloride solution is  $-20.0^\circ\text{C}$ . What is the molality of the solution? *Answer*  $5.4 \text{ m NaCl}$

### Actual Values for Electrolyte Solutions

It is important to remember that the values just calculated are only *expected* values. As stated earlier, a 0.1 *m* solution of sodium chloride lowers the freezing point *nearly* twice as much as a 0.1 *m* solution of sucrose. The actual values of the colligative properties for all strong electrolytes are *almost* what would be expected based on the number of particles they produce in solution. Some specific examples are given in Table 14-3. The freezing-point depression of a compound that produces two ions per formula unit is almost twice that of a nonelectrolytic solution. The freezing-point depression of a compound that produces three ions per formula unit is almost three times that of a nonelectrolytic solution.

**TABLE 14-3** Molal Freezing-Point Depressions for Aqueous Solutions of Ionic Solutes

Solute	Concentration (m)	$\Delta t_f$ , observed ( $^\circ\text{C}$ )	$\Delta t_f$ , nonelectrolyte solution ( $^\circ\text{C}$ )	$\frac{\Delta t_f, \text{observed}}{\Delta t_f, \text{nonelectrolyte solution}}$
KCl	0.1	-0.345	-0.186	1.85
	0.01	-0.0361	-0.0186	1.94
	0.001	-0.00366	-0.00186	1.97
MgSO <sub>4</sub>	0.1	-0.225	-0.186	1.21
	0.01	-0.0285	-0.0186	1.53
	0.001	-0.00338	-0.00186	1.82
BaCl <sub>2</sub>	0.1	-0.470	-0.186	2.53
	0.01	-0.0503	-0.0186	2.70
	0.001	-0.00530	-0.00186	2.84



**FIGURE 14-10** The salts applied to icy roads are electrolytes. They lower the freezing point of water and melt the ice.

Look at the values given for KCl solutions in Table 14-3. The freezing-point depression of a 0.1 *m* KCl solution is only 1.85 times greater than that of a nonelectrolyte solution. However, as the concentration decreases, the freezing-point depression comes closer to the value that is twice that of a nonelectrolytic solution.

The differences between the expected and calculated values are caused by the attractive forces that exist between dissociated ions in aqueous solution. The attraction between the hydrated ions in the solution is small compared with those in the crystalline solid. However, forces of attraction do interfere with the movements of the aqueous ions. The more concentrated a solution is, the closer together the ions are, and the greater the attraction between ions is. Only in very dilute solutions is the average distance between the ions large enough and the attraction between ions small enough for the solute ions to move about almost completely freely.

Peter Debye and Erich Hückel introduced a theory in 1923 to account for this attraction between ions in dilute aqueous solutions. According to this theory, the attraction between dissociated ions of ionic solids in dilute aqueous solutions is caused by an ionic atmosphere that surrounds each ion. This means that each ion is, on average, surrounded by more ions of opposite charge than of like charge. This clustering effect hinders the movements of solute ions. A cluster of hydrated ions can act as a single unit rather than as individual ions. Thus, the effective total concentration is less than expected, based on the number of ions known to be present.

Ions of higher charge attract other ions very strongly. They therefore cluster more and have lower effective concentrations than ions with smaller charge. For example, ions formed by  $\text{MgSO}_4$  have charges of 2+ and 2-. Ions formed by KCl have charges of 1+ and 1-. Note in Table 14-3 that  $\text{MgSO}_4$  in a solution does not depress the freezing point as much as the same concentration of KCl.

## SECTION REVIEW

1. What colligative properties are displayed by each of the following situations?
  - a. Antifreeze is added to a car's cooling system to prevent freezing when the air temperature is below 0°C.
  - b. Ice melts on sidewalks after salt has been spread on them.
2. Two moles of a nonelectrolytic solute are dissolved in 1 kg of an unknown solvent. The solution freezes at 7.8°C *below* its normal freezing point. What is the molal freezing-point constant of the unknown solvent? What is your prediction for the identity of the solvent?
3. If two solutions of equal amounts in a U-tube are separated by a semipermeable membrane, will the level of the more-concentrated solution or the less-concentrated solution rise?
4.
  - a. Calculate the expected freezing-point depression of a 0.2 *m*  $\text{KNO}_3$  solution.
  - b. Will the value you calculated match the actual freezing-point depression for this solution? Why or why not?

# CHAPTER 14 REVIEW

## CHAPTER SUMMARY

- 14-1**
- The separation of ions that occurs when an ionic solid dissolves is called dissociation.
  - When two different ionic solutions are mixed, a precipitate may form if ions from the two solutions react to form an insoluble compound.
  - A net ionic equation for a reaction in aqueous solution includes only compounds and ions that change chemically in the reaction. Spectator ions are ions that do not take part in such a reaction.
  - Formation of ions from solute molecules is called ionization. A molecular compound may ionize in a water solution if the attraction of the polar water molecules is strong enough to break the polar-covalent bonds of the solute molecules.
  - An  $\text{H}_3\text{O}^+$  ion is called a hydronium ion.
  - All, or almost all, of a dissolved strong electrolyte exists as ions in an aqueous solution, whereas a relatively small amount of a dissolved weak electrolyte exists as ions in an aqueous solution.

### Vocabulary

dissociation (425)

ionization (431)

spectator ions (429)

weak electrolyte (433)

hydronium ion (431)

net ionic equation (429)

strong electrolyte (432)

- 14-2**
- Colligative properties of solutions depend only on the total number of solute particles present. Boiling-point elevation, freezing-point depression, vapor-pressure lowering, and osmotic pressure are all colligative properties.
  - The molal boiling-point and freezing-point constants are used to calculate boiling-point elevations and freezing-point depressions of solvents containing nonvolatile solutes.
  - Electrolytes have a greater effect on the freezing and boiling points of solvents than do nonelectrolytes.
  - Except in very dilute solutions, the values of colligative properties of electrolytic solutions are less than expected because of the attraction between ions in solution.

### Vocabulary

boiling-point elevation,  $\Delta t_b$  (440)

molal boiling-point constant,  $K_b$  (440)

nonvolatile substance (436)

osmotic pressure (442)

colligative properties (436)

molal freezing-point constant,  $K_f$  (438)

osmosis (442)

semipermeable membranes (442)

freezing-point depression,  $\Delta t_f$  (438)

## REVIEWING CONCEPTS

1. How many moles of ions are contained in 1 L of a 1 M solution of KCl? of  $\text{Mg}(\text{NO}_3)_2$ ? (14-1)
2. Use Table 14-1 to predict whether each of the following compounds is considered soluble or insoluble:
  - a. KCl
  - b.  $\text{NaNO}_3$
  - c. AgCl
  - d.  $\text{BaSO}_4$
  - e.  $\text{Ca}_3(\text{PO}_4)_2$
  - f.  $\text{Pb}(\text{ClO}_3)_2$
  - g.  $(\text{NH}_4)_2\text{S}$
  - h.  $\text{PbCl}_2$  (in cold water)
  - i. FeS
  - j.  $\text{Al}_2(\text{SO}_4)_3$  (14-1)
3. What is a net ionic equation? (14-1)
4.
  - a. What is ionization?
  - b. Distinguish between ionization and dissociation. (14-1)

5. a. Define and distinguish between strong electrolytes and weak electrolytes.  
b. Give two examples of each type. (14-1)
6. What determines the strength with which a solute acts as an electrolyte? (14-1)
7. Distinguish between the use of the terms *strong* and *weak* and the use of the terms *dilute* and *concentrated* when used to describe electrolyte solutions. (14-1)
8. How does the presence of a nonvolatile solute affect each of the following properties of the solvent into which the solute is dissolved?  
a. vapor pressure  
b. freezing point  
c. boiling point  
d. osmotic pressure (14-2)
9. Using Figure 14-6 as a guide, make a sketch of a vapor pressure-versus-temperature curve that shows the comparison of pure water, a solution with  $x$  amount of solute, and a solution with  $2x$  the amount of solute. What is the relationship between  $\Delta t_f$  for the  $x$  curve and  $\Delta t_f$  for the  $2x$  curve? (14-2)
10. a. Why does the level of the more-concentrated solution rise when two solutions of different concentrations are separated by a semipermeable membrane?  
b. When does the level of the solution stop rising?  
c. When the level stops rising, what is the net movement of water molecules across the membrane? (14-2)
11. a. Compare the effects of nonvolatile electrolytes with the effects of nonvolatile nonelectrolytes on the freezing and boiling points of solvents in which they are dissolved.  
b. Why are such differences observed? (14-2)
12. Why does the actual freezing-point depression of an electrolytic solution differ from the freezing-point depression calculated on the basis of the concentration of particles? (14-2)

## PROBLEMS

## Dissociation

13. Write the equation for the dissolution of each of the following ionic compounds in water. (Hint: See Sample Problem 14-1.)  
a. KI  
b.  $\text{NaNO}_3$   
c.  $\text{MgCl}_2$   
d.  $\text{Na}_2\text{SO}_4$
14. For the compounds listed in the previous problem, determine the number of moles of each ion produced as well as the total number of moles of ions produced when 1 mol of each compound dissolves in water.
15. Write the equation for the dissolution of each of the following in water, and then indicate the total number of moles of solute ions formed.  
a. 0.50 mol strontium nitrate  
b. 0.50 mol sodium phosphate

## Precipitation Reactions

16. Using Table 14-1, write the balanced chemical equation, write the overall ionic equation, identify the spectator ions and possible precipitates, and write the net ionic equation for each of the following reactions. (Hint: See Sample Problem 14-2.)  
a. mercury(II) chloride ( $aq$ ) + potassium sulfide ( $aq$ )  $\longrightarrow$   
b. sodium carbonate ( $aq$ ) + calcium chloride ( $aq$ )  $\longrightarrow$   
c. copper(II) chloride ( $aq$ ) + ammonium phosphate ( $aq$ )  $\longrightarrow$
17. Identify the spectator ions in the reaction between  $\text{KCl}$  and  $\text{AgNO}_3$  in an aqueous solution.
18. Copper(II) chloride and lead(II) nitrate react in aqueous solutions by double replacement. Write the balanced chemical equation, the overall ionic equation, and the net ionic equation for this reaction. If 13.45 g of copper(II) chloride react, what is the maximum amount of precipitate that could be formed?

### Freezing-Point Depression of Nonelectrolytes

- Determine the freezing-point depression of  $\text{H}_2\text{O}$  in each of the following solutions. (Hint: See Sample Problem 14-3.)
  - 1.50 *m* solution of  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  (sucrose) in  $\text{H}_2\text{O}$
  - 171 g of  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  in 1.00 kg  $\text{H}_2\text{O}$
  - 77.0 g of  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  in 400. g  $\text{H}_2\text{O}$
- Determine the molality of each solution of an unknown nonelectrolyte in water, given the following freezing-point depressions. (Hint: See Sample Problem 14-4.)
  - $-0.930^\circ\text{C}$
  - $-3.72^\circ\text{C}$
  - $-8.37^\circ\text{C}$
- A solution contains 20.0 g of  $\text{C}_6\text{H}_{12}\text{O}_6$  (glucose) in 250. g of water.
  - What is the freezing-point depression of the solvent?
  - What is the freezing point of the solution?
- How many grams of antifreeze,  $\text{C}_2\text{H}_4(\text{OH})_2$ , would be required per 500. g of water to prevent the water from freezing at a temperature of  $-20.0^\circ\text{C}$ ?
- Pure benzene,  $\text{C}_6\text{H}_6$ , freezes at  $5.45^\circ\text{C}$ . A solution containing 7.24 g of  $\text{C}_2\text{Cl}_4\text{H}_2$  in 115 g of benzene (specific gravity = 0.879) freezes at  $3.55^\circ\text{C}$ . Based on these data, what is the molal freezing-point constant for benzene?
- If 1.500 g of a solute having a molar mass of 125.0 g were dissolved in 35.00 g of camphor, what would be the resulting freezing point of the solution?

### Boiling-Point Elevation of Nonelectrolytes

- Determine the boiling-point elevation of  $\text{H}_2\text{O}$  in each of the following solutions. (Hint: See Sample Problem 14-5.)
  - 2.5 *m* solution of  $\text{C}_6\text{H}_{12}\text{O}_6$  (glucose) in  $\text{H}_2\text{O}$
  - 3.20 g  $\text{C}_6\text{H}_{12}\text{O}_6$  in 1.00 kg  $\text{H}_2\text{O}$
  - 20.0 g  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  (sucrose) in 500. g  $\text{H}_2\text{O}$
- Determine the molality of each water solution given the following boiling points:
  - $100.25^\circ\text{C}$
  - $101.53^\circ\text{C}$
  - $102.805^\circ\text{C}$

### Colligative Properties of Electrolytes

- Given 1.00 *m* aqueous solutions of each of the following electrolytic substances, what is the expected change in the freezing point of the solvent? (Hint: See Sample Problem 14-6.)
  - KI
  - $\text{CaCl}_2$
  - $\text{Ba}(\text{NO}_3)_2$
- What is the expected change in the freezing point of water for an aqueous solution that is 0.015 *m*  $\text{AlCl}_3$ ?
- What is the expected freezing point of a solution containing 85.0 g of NaCl dissolved in 450. g of water?
- Determine the expected boiling point of a solution made by dissolving 25.0 g of barium chloride in 0.150 kg of water.
- The change in the boiling point of water for an aqueous solution of potassium iodide is  $0.65^\circ\text{C}$ . Determine the apparent molal concentration of potassium iodide.
- The freezing point of an aqueous solution of barium nitrate is  $-2.65^\circ\text{C}$ . Determine the apparent molal concentration of barium nitrate.
- Calculate the expected freezing point of a solution containing 1.00 kg of  $\text{H}_2\text{O}$  and 0.250 mol of NaCl.
- Experimental data for a 1.00 *m*  $\text{MgI}_2$  aqueous solution indicate an actual change in the freezing point of water of  $-4.78^\circ\text{C}$ . Determine the expected change in the freezing point of water. Suggest a possible reason for discrepancies between the experimental and the expected values.

## MIXED REVIEW

- Given 0.01 *m* aqueous solutions of each of the following, arrange the solutions in order of increasing change in the freezing point of the solution.
  - NaI
  - $\text{CaCl}_2$
  - $\text{K}_3\text{PO}_4$
  - $\text{C}_6\text{H}_{12}\text{O}_6$  (glucose)

36. What is the molal concentration of an aqueous calcium chloride solution that freezes at  $-2.43^{\circ}\text{C}$ ?
37. a. Write the balanced formula equation that shows the possible products of a double replacement reaction between calcium nitrate and sodium chloride.  
b. Using Table 14-1, determine if there is a precipitate.
38. Write a balanced equation to show what occurs when hydrogen bromide dissolves and reacts with water. Include a hydronium ion in the equation.
39. Write the equation for the dissolution of each of the following in water, and then indicate the total number of moles of solute ions formed.  
a. 0.275 mol potassium sulfide  
b. 0.15 mol aluminum sulfate
40. Calculate the expected change in the boiling point of water in a solution made up of 131.2 g of silver nitrate,  $\text{AgNO}_3$ , in 2.00 kg of water.
41. Nitrous acid,  $\text{HNO}_2$ , is a weak electrolyte. Nitric acid,  $\text{HNO}_3$ , is a strong electrolyte. Write equations to represent the ionization of each in water. Include the hydronium ion, and show the appropriate kind of arrow in each case.
42. Find the boiling point of an aqueous solution containing a nonelectrolyte that freezes at  $-6.51^{\circ}\text{C}$ .
43. Write a balanced equation for the dissolution of sodium carbonate,  $\text{Na}_2\text{CO}_3$ , in water. Find the number of moles of each ion produced when 0.20 mol of sodium carbonate dissolves. Then find the total number of moles of ions.
44. Given the reaction below and the information in Table 14-1, write the net ionic equation for the reaction.  
potassium phosphate (*aq*) + lead (II) nitrate (*aq*)
45. Find the expected freezing point of a water solution that contains 268 g of aluminum nitrate,  $\text{Al}(\text{NO}_3)_3$ , in 8.50 kg of water.

## CRITICAL THINKING

## 46. Applying Models

- a. You are conducting a freezing-point determination in the laboratory using an aqueous solution of  $\text{KNO}_3$ . The observed freezing point of the solution is  $-1.15^{\circ}\text{C}$ . Using a pure water sample, you recorded the freezing point of the pure solvent on the same thermometer as  $0.25^{\circ}\text{C}$ . Determine the molal concentration of  $\text{KNO}_3$ . Assume that there are no forces of attraction between ions.
- b. You are not satisfied with the result in part (a) because you suspect that you should not ignore the effect of ion interaction. You take a 10.00 mL sample of the solution. After carefully evaporating the water from the solution, you obtain a mass of 0.415 g  $\text{KNO}_3$ . Determine the actual molal concentration of  $\text{KNO}_3$  and the percentage difference between the predicted concentration and the actual concentration of  $\text{KNO}_3$ . Assume that the solution's density is 1.00 g/mL.

47. Analyzing Information The observed freezing-point depression for electrolyte solutions is sometimes less than the calculated value. Why does this occur? Is the difference greater for concentrated solutions or dilute solutions?

48. Analyzing Information The osmotic pressure of a dilute solution can be calculated as follows.

$$\pi = MRT$$

$\pi$  = osmotic pressure

$M$  = concentration in moles per liter

$R$  = ideal gas constant

$T$  = absolute temperature of the solution

How does the osmotic-pressure equation compare with the ideal gas law?

**HANDBOOK SEARCH**

- 49.** Common reactions for Group 13 elements are found in the *Elements Handbook*. Review this material and answer the following.
- Write net ionic equations for each of the example reactions shown on page 751.
  - Which reactions did not change when written in net ionic form? Why?
- 50.** Common reactions for Group 14 elements are found in the *Elements Handbook*. Review this material and answer the following.
- Write net ionic equations for each of the example reactions shown on page 755.
  - Which reactions did not change when written in net ionic form? Why?

**RESEARCH & WRITING**

- 51.** Find out how much salt a large northern city, such as New York City or Chicago, uses on its streets in a typical winter. What environmental problems result from this use of salt? What substitutes for salt are being used to melt ice and snow?
- 52.** Research the role of electrolytes and electrolytic solutions in your body. Find out how electrolytes work in the functioning of nerves and muscles. What are some of the health problems that can arise from an imbalance of electrolytes in body fluids?

**ALTERNATIVE ASSESSMENT**

- 53. Performance** Determine the freezing point of four different mixtures of water and ethylene glycol (use commercial antifreeze). What mixture shows the lowest freezing point?
- 54. Performance** Find the optimum mixture of salt and ice for reducing the temperature of the chilling bath for an ice-cream freezer. Use your data to write a set of instructions on how to prepare the chilling bath for making ice cream.
- 55. Performance** Using a low-voltage dry cell, assemble a conductivity apparatus. Secure several unknown aqueous solutions of equal molality from your instructor, and use the apparatus to distinguish the electrolytes from the nonelectrolytes. Among those identified as electrolytes, rank their relative strengths as conductors from good to poor.
- 56. Performance** Using equal volumes of the unknown solutions from the preceding activity, explain how you could use the freezing-point depression concept to distinguish the electrolytes from the nonelectrolytes. Explain how you could determine the number of ions contained per molecule among the solutes identified as electrolytes. Design and conduct an experiment to test your theories.