

CHAPTER 13

Ions in Aqueous Solutions and Colligative Properties

BIG IDEA

Ionic compounds dissociate in aqueous solutions. Colligative properties of a solution depend only on the number of solute particles present.

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SECTION 1

Compounds in Aqueous Solutions

SECTION 2

Colligative Properties of Solutions

ONLINE LABS

- Testing Water for Ions
- Reacting Ionic Species in Aqueous Solution
- Colored Precipitates
- Diffusion and Cell Membranes
- Solubility and Chemical Fertilizers
- **S.T.E.M.** The Heat Is On!



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Colligative Properties

Compounds in Aqueous Solutions

Key Terms

dissociation

ionization

strong electrolyte

net ionic equation

hydronium ion

weak electrolyte

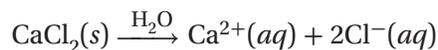
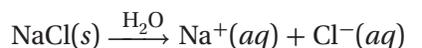
spectator ions

Solid compounds can be ionic or molecular. An ionic solid consists of oppositely charged ions. The attraction between the ions of opposite charge is responsible for its stability. In a molecular solid, molecules are composed of covalently bonded atoms. The solid is held together by noncovalent, intermolecular forces. When they dissolve in water, ionic compounds and molecular compounds behave differently.

▶ MAIN IDEA

Ions separate from each other when ionic compounds are dissolved in water.

When a compound that is made of ions dissolves in water, the ions separate from one another, as shown in **Figure 1.1**. **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 each 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.

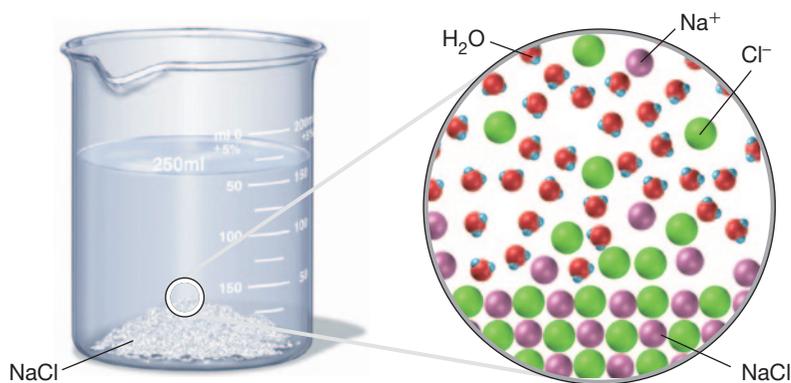
Main Ideas

- ▶ Ions separate from each other when ionic compounds are dissolved in water.
- ▶ A molecular compound ionizes in a polar solvent.
- ▶ An electrolyte's strength depends on how many dissolved ions it contains.

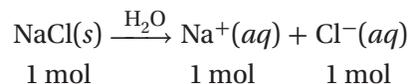
FIGURE 1.1

Dissociation

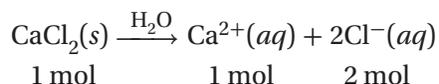
When NaCl dissolves in water, the ions separate as they leave the crystal.



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



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



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Calculating Moles of Dissolved Ions

Sample Problem A 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?

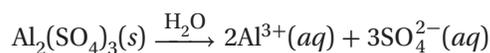
1 ANALYZE

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 SOLVE

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

4 CHECK YOUR WORK

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

Practice

Answers in Appendix E

- 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



FIGURE 1.2

Solubility of Ionic Compounds

Ionic compounds can be soluble or insoluble in water. NiCl_2 , KMnO_4 , CuSO_4 , and $\text{Pb}(\text{NO}_3)_2$ are soluble in water. AgCl and CdS are insoluble in water.

Precipitation Reactions

Although no ionic 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 1.2**. 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 **Figure 1.3**.

By looking at the table, you can tell that most sodium compounds are soluble. Sodium carbonate, Na_2CO_3 , is soluble because it contains sodium. Its dissociation equation is as follows.



FIGURE 1.3

GENERAL SOLUBILITY GUIDELINES

1. Sodium, potassium, and ammonium compounds are soluble in water.
2. 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, lead, calcium, and mercury(I).
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.

Is calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, soluble or insoluble? According to **Figure 1.3**, 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 **Figure 1.3** 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-displacement reaction with precipitation will occur. Precipitation occurs when the attraction between the ions is greater than the attraction between the ions and surrounding water molecules.

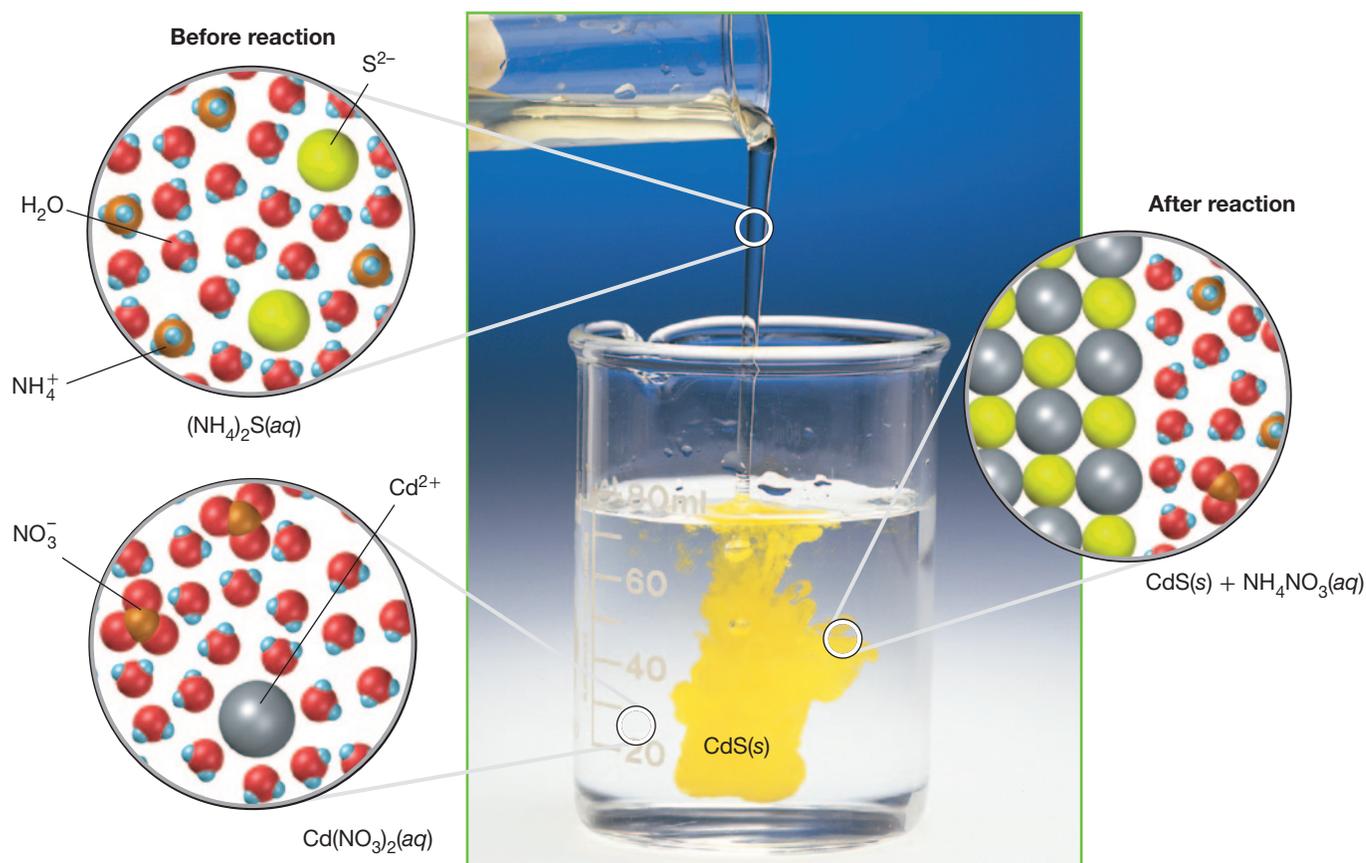
Will a precipitate form when solutions of ammonium sulfide and cadmium nitrate are combined? By using the table, you can tell that cadmium nitrate, $\text{Cd}(\text{NO}_3)_2$, is soluble because it is a nitrate and all nitrates are soluble. You can also tell that ammonium sulfide, $(\text{NH}_4)_2\text{S}$,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



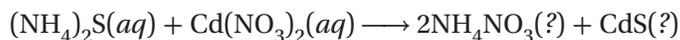
FIGURE 1.4

Precipitation Ammonium sulfide is a soluble compound that dissociates in water to form NH_4^+ and S^{2-} ions. Cadmium nitrate is a soluble compound that dissociates in water to form NO_3^- and Cd^{2+}

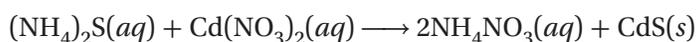
ions. Precipitation of cadmium sulfide occurs when the two solutions are mixed.



The two possible products of a double-displacement reaction between $(\text{NH}_4)_2\text{S}$ and $\text{Cd}(\text{NO}_3)_2$ are ammonium nitrate, NH_4NO_3 , and cadmium sulfide, CdS . The question marks indicate that the states are unknown.

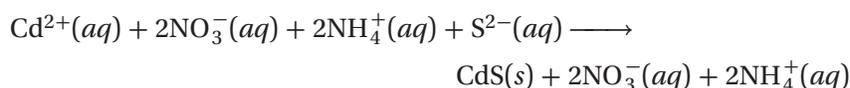


To decide whether a precipitate can form, you must know the solubilities of these two compounds. Consulting **Figure 1.3**, you can see that NH_4NO_3 is soluble in water. However, CdS is insoluble. You can therefore predict that when solutions of ammonium sulfide and cadmium nitrate are combined, ammonium nitrate will not precipitate and cadmium sulfide will. As illustrated in **Figure 1.4**, on the previous page, crystals of CdS form when the solutions are mixed. In the following equation, the designations (aq) and (s) show that $\text{NH}_4\text{NO}_3(aq)$ remains in solution and $\text{CdS}(s)$ precipitates.



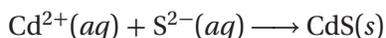
Net Ionic Equations

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.** They do not include any ions or substances that do not actually participate in the chemical reaction. To write a net ionic equation, you first convert the chemical equation into a complete 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 aqueous ammonium ion, $\text{NH}_4^+(aq)$, and the aqueous nitrate ion, $\text{NO}_3^-(aq)$, 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 NH_4^+ and 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 CdS when CdSO_4 and Na_2S react.

 **CHECK FOR UNDERSTANDING**
Interpret In your own words, state why it is helpful to write net ionic equations for chemical reactions.



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Writing Net Ionic Equations

Sample Problem B Identify the precipitate that forms when aqueous solutions of zinc nitrate and ammonium sulfide are combined. Write the equation for the possible double-displacement reaction. Then write the formula equation, complete ionic equation, and net ionic equation for the reaction.

1 ANALYZE

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

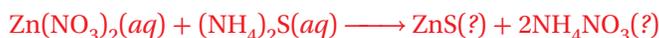
Unknown: a. equation for the possible double-displacement reaction
b. identity of the precipitate c. formula equation
d. complete ionic equation e. net ionic equation

2 PLAN

Write the possible double-displacement reaction between $\text{Zn}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{S}$. Use **Figure 1.3** to determine if any of the products are insoluble and will precipitate. Write a formula equation and a complete ionic equation, and then cancel the spectator ions to produce a net ionic equation.

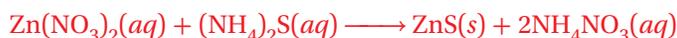
3 SOLVE

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

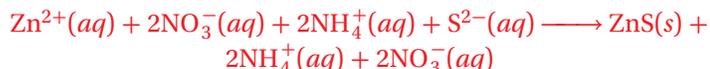


b. **Figure 1.3** reveals that because it is not soluble, **zinc sulfide is a precipitate**. Ammonium nitrate is soluble according to the table.

c. The formula equation is as follows.



d. The complete 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

Answers in Appendix E

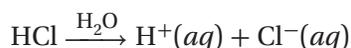
- Will a precipitate form if solutions of potassium sulfate and barium nitrate are combined? If so, write the net ionic equation for the reaction.
- Will a precipitate form if solutions of potassium nitrate and magnesium sulfate are combined? If so, write the net ionic equation for the reaction.
- Will 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.
- Write the net ionic equation for the precipitation of nickel(II) sulfide.

MAIN IDEA

A molecular compound ionizes in a polar solvent.

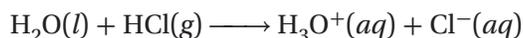
A few molecular compounds can form ions in solution. **Ions are formed from solute molecules by the action of the solvent in a process called ionization.** The more general meaning of this term is the creation of ions where there were none. Note that *ionization* is different from *dissociation*. When 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 energy to break the covalent bonds to form ions comes from the energy released as the ions become hydrated.

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. In aqueous solution, the HCl bond is broken, and a positively charged hydrogen ion and a negatively charged chloride ion are formed. The ions are each surrounded by water molecules, which enables them to stay separated.



The Hydronium Ion

Some molecular compounds, especially those that contain a hydrogen atom covalently bonded to an atom of high electronegativity, can ionize in an aqueous solution to release H^+ . The 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 H_3O^+ .



This process is represented in **Figure 1.5**. **The H_3O^+ ion is known as the hydronium ion.** The reaction of the H^+ ion to form the hydronium ion produces much of the energy needed to ionize a molecular solute.

FIGURE 1.5

Ionization When hydrogen chloride gas dissolves in water, it ionizes to form an H^+ ion and a Cl^- ion. The H^+ ion immediately bonds to a water molecule, forming a hydronium ion. The aqueous solution of hydrogen chloride is called hydrochloric acid.

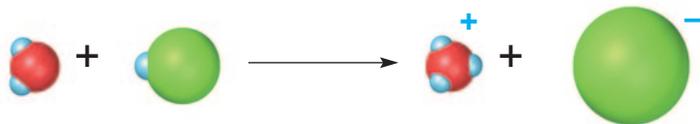
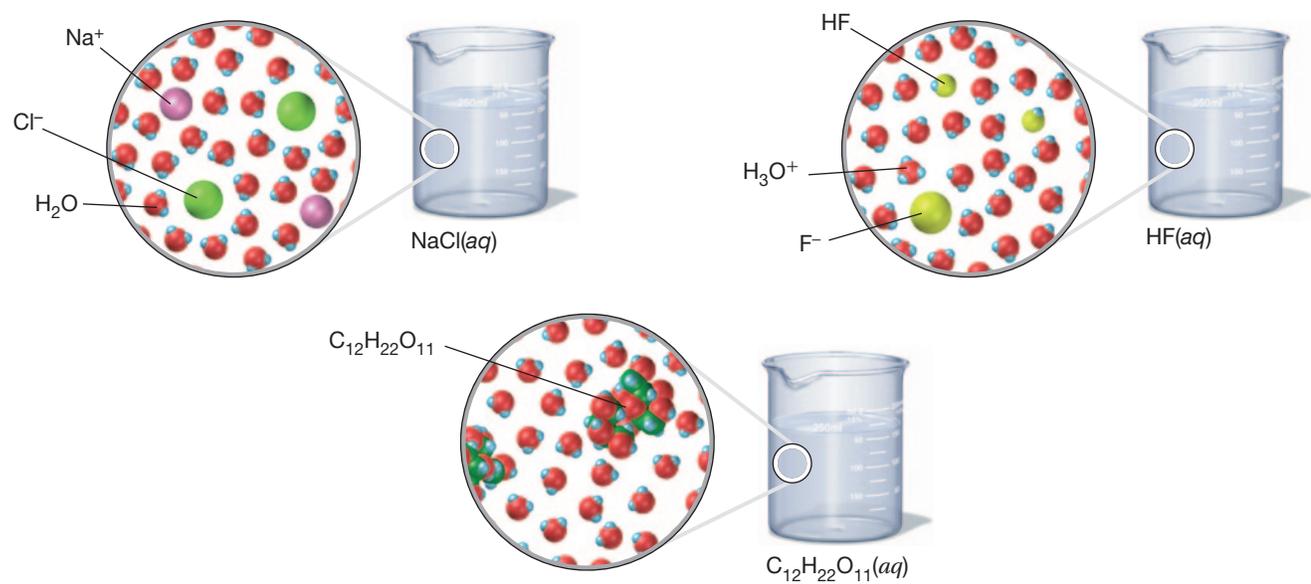


FIGURE 1.6

Electrolytes Strong electrolytes, such as NaCl, yield only ions when they dissolve in aqueous solution. Weak electrolytes, such as HF, exist as both ions and nonionized molecules in aqueous solution. Nonelectrolytes, such as sucrose, $C_{12}H_{22}O_{11}$, do not form any ions in aqueous solution.



MAIN IDEA

An electrolyte's strength depends on how many dissolved ions it contains.

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 1.6**.

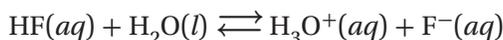
Strong Electrolytes

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.

All electrolytes that yield only ions when they dissolve are strong electrolytes. This includes all soluble ionic compounds, like NaCl, and a limited number of molecular compounds, like HCl.

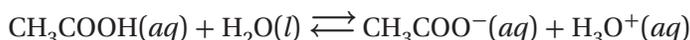
Weak Electrolytes

Some molecular compounds form aqueous solutions that contain dissolved ions and some dissolved molecules that are not ionized. Hydrogen fluoride, HF, dissolves in water to give an acidic 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 H^+ ions back to F^- ions to form hydrogen fluoride molecules—also takes place.



Thus, the concentration of dissolved intact HF is much greater than the concentration of H_3O^+ and F^- ions.

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 nonelectrolyte, such as the molecular compound sucrose, which dissolves but does not produce any ions in solution. Another example of a weak electrolyte is acetic acid, CH_3COOH . 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 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 very concentrated solution.



SECTION 1 FORMATIVE ASSESSMENT

▶ Reviewing Main Ideas

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 water?

4. Explain why HCl is a strong electrolyte and HF is a weak electrolyte.

✔ Critical Thinking

5. **PREDICTING OUTCOMES** For each of the following pairs, tell which solution contains the larger total concentration of ions.
 - a. 0.10 M HCl and 0.05 M HCl
 - b. 0.10 M HCl and 0.10 M HF
 - c. 0.10 M HCl and 0.10 M CaCl_2

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 in the future. 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.

Electrifying Experiments

In 1800, 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.

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. The current caused the water to decompose 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 the solids' 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 the chemists was Humphry Davy, who thought that chemical bonding must be driven by the same forces that drive electrical attractions.

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 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 current to undefined changes in the solution's components.

Chlorine being produced by electrolysis.



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 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 the solution by way of a spark. In all cases, Faraday observed current in the electrolytic cell despite one or both of the poles not being in direct contact with the electrolytic solution. In 1833, he made the hypothesis that the process of electrolysis was due to the intrinsic properties of the metals in solution and the effect of current on these properties.

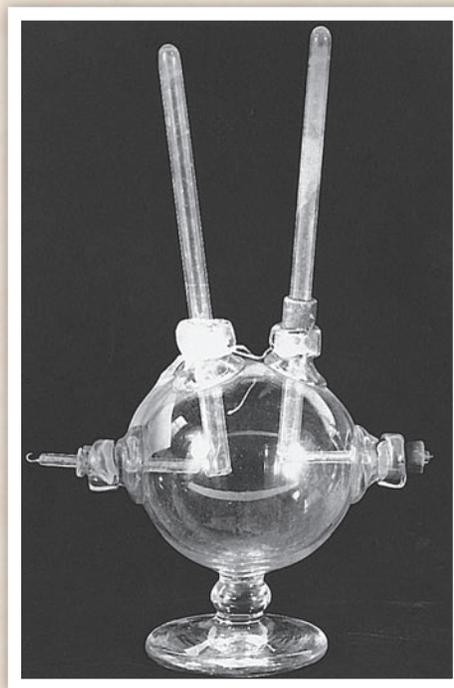
Although the battery's poles were, in fact, later shown to play a part in the current, Faraday had established the active role of the electrolytic solution in electrolysis. And in realizing that electricity affected the chemical nature of the solution, he anticipated the ideas of oxidation and reduction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

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

Electrolytic processes are used every day for such things as depositing a thin layer of a valuable metal (like gold or silver) over a metal of lower quality (such as iron or brass), extracting pure metals from impure ones, and refining them. These processes are known as *electroplating*, *electrorefining*, and *electrometallurgy*.

Still valid, these principles put electrolysis on a quantitative footing, leading to our current understanding of the phenomenon. They 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.



Michael Faraday used this instrument in his studies of electrolysis.

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*.

Questions

1. To which scientist does this feature give the most credit for the initial understanding of the basic nature of electrolysis? Briefly summarize his contributions in this area.
2. How are amounts of hydrogen and oxygen gas made from the electrolytic decomposition of water related to the chemical formula of water?

SECTION 2

Main Ideas

- ▶ Lowering vapor pressure depends on nonelectrolyte solute concentration.
- ▶ A solution with a nonelectrolyte solute will have a lower freezing point than the pure solvent.
- ▶ A solution with a nonelectrolyte solute will have a higher boiling point than the pure solvent.
- ▶ Osmotic pressure is determined by the concentration of dissolved solute particles.
- ▶ The total molality of all dissolved particles determines changes in colligative properties.

Colligative Properties of Solutions

Key Terms

colligative properties	freezing-point depression, Δt_f	semipermeable membrane
nonvolatile substance	molal boiling-point constant, K_b	osmosis
molal freezing-point constant, K_f	boiling-point elevation, Δt_b	osmotic pressure

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.** The magnitude of the colligative properties depends on the molal concentration, m .

MAIN IDEA

Lowering vapor pressure depends on nonelectrolyte solute concentration.

The boiling point and freezing point of a solution differ from those of the pure solvent. The graph in **Figure 2.1** shows that a nonvolatile solute raises

FIGURE 2.1

Vapor-Pressure Lowering Vapor pressure as a function of temperature is shown for a pure solvent and for a solution of a nonvolatile solute in that solvent. 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

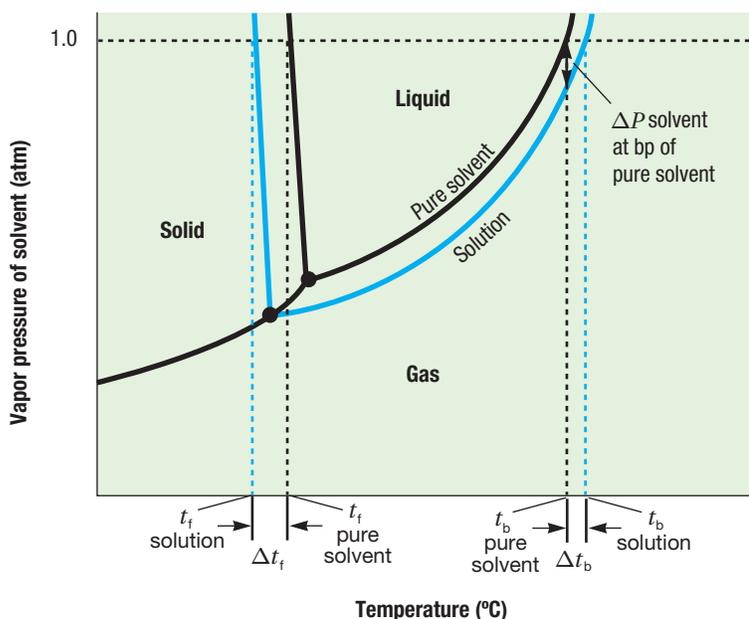
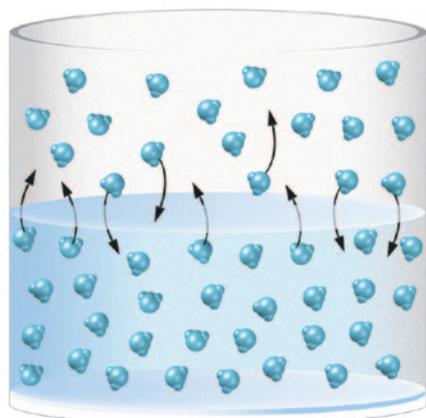
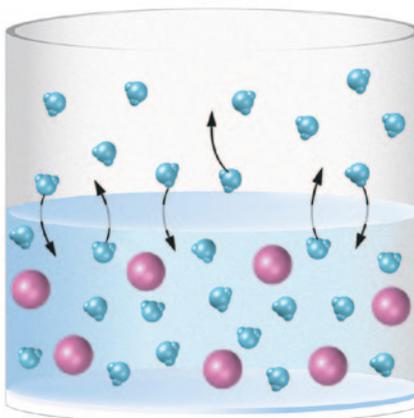


FIGURE 2.2

Vapor-Pressure Lowering: Pure Solvent vs. Solution



Pure water



Aqueous solution of nonvolatile solute

Used to represent $C_{12}H_{22}O_{11}$, sucroseUsed to represent H_2O , water

CRITICAL THINKING

Compare Compare and contrast the two images, and explain how they relate to vapor-pressure lowering.

the boiling point and lowers the freezing point. **A nonvolatile substance is one that has little tendency to become a gas under existing conditions.**

To understand why a nonvolatile solute changes the boiling point and freezing point, you must consider equilibrium vapor pressure. Vapor pressure is the pressure caused by molecules in the gas phase that are in equilibrium with the liquid 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 2.2**. As the number of solute particles increases in a given volume of solution, the proportion of solvent (water) molecules decreases. Fewer water molecules will be available to escape from the liquid. As a result, the tendency of water molecules to leave the solution and enter the vapor phase decreases. Thus, the vapor pressure of the solution is less than the vapor pressure of pure water.

Nonelectrolyte solutions of the same molality have the same concentration of particles. Nonelectrolyte solutes with the same molarity in the same solvent lower the vapor pressure the same amount. For example, a 1 *m* aqueous solution of the nonelectrolyte glucose, $C_6H_{12}O_6$, lowers the vapor pressure of water by 5.5×10^{-4} atm at 25°C. A 1 *m* solution of sucrose, $C_{12}H_{22}O_{11}$, another nonelectrolyte, also lowers the vapor pressure by 5.5×10^{-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 2.1**. 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.

▶ MAIN IDEA

A solution with a nonelectrolyte solute will have a lower freezing point than the pure solvent.

The freezing point of a 1 *m* solution of any nonelectrolyte solute in water is found by experiment to be 1.86°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°C instead of 0.00°C. When 2 mol of a nonelectrolyte solute is dissolved in 1 kg of water, the freezing point of the solution is −3.72°C. This is 2 × (−1.86°C). In fact, for any concentration of a nonelectrolyte solute in water, the decrease in freezing point can be estimated by using the value of −1.86°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 **Figure 2.3**. These values are most accurate for dilute solutions at 1 atmosphere of pressure. The table 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 1 kg water is 1.86°C lower than the normal freezing point of water. **The freezing-point depression, Δt_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.

Freezing-Point Depression

$$\Delta t_f = K_f m$$

K_f is expressed as °C/*m*, *m* is expressed in mol solute/kg solvent (molality), and Δt_f is expressed in °C. Sample Problems C and D show how this relationship can be used to determine the freezing-point depression and molal concentration of a solution.

✔ CHECK FOR UNDERSTANDING

Interpret In your own words, describe the process by which ice cream is made at home and explain how the process relates to freezing-point depression.

FIGURE 2.3

MOLAL FREEZING-POINT AND BOILING-POINT CONSTANTS

Solvent	Normal f.p. (°C)	Molal f.p. constant, K_f (°C/ <i>m</i>)	Normal b.p. (°C)	Molal b.p. constant, K_b (°C/ <i>m</i>)
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



Calculating Freezing-Point Depression

Sample Problem C What is the freezing-point depression of a solution of 210.0 g of glycerol, $C_3H_8O_3$, in 350 g of water? What is the actual freezing point of the solution?

1 ANALYZE

Given: solute mass and chemical formula = 210.0 g of glycerol, $C_3H_8O_3$
solvent mass and identity = 350 g water

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

2 PLAN

Look up the molal freezing-point constant, K_f , for water in **Figure 2.3**. 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 SOLVE

$$210.0 \text{ g } C_3H_8O_3 \times \frac{1 \text{ mol } C_3H_8O_3}{92.11 \text{ g } C_3H_8O_3} = 2.279 \text{ mol } C_3H_8O_3$$

$$\frac{2.279 \text{ mol } C_3H_8O_3}{350. \text{ g water}} \times \frac{1000 \text{ g water}}{\text{kg water}} = \frac{6.511 \text{ mol } C_3H_8O_3}{\text{kg water}} = 6.511 \text{ } m$$

a. $\Delta t_f = 6.511 \text{ } m \times (-1.86^\circ\text{C}/m) = -12.1^\circ\text{C}$

b. f.p. solution = $0.000^\circ\text{C} + (-12.1^\circ\text{C}) = -12.1^\circ\text{C}$



Calculating Molal Concentration

Sample Problem D A water solution containing an unknown quantity of a nonelectrolyte solute is found to have a freezing point of -0.23°C . What is the molal concentration of the solution?

1 ANALYZE

Given: freezing point of solution = -0.23°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 **Figure 2.3**. The Δt_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.

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

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

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

Calculating Molal Concentration (continued)

3 SOLVE

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

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

4 CHECK YOUR WORK

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

Practice

Answers in Appendix E

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?
2. In a laboratory experiment, the freezing point of an aqueous solution of glucose is found to be -0.325°C . What is the molal concentration of this solution?
3. What is the freezing point of a solution of 60.0 g of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, dissolved in 80.0 g of water?
4. The freezing point of an aqueous solution that contains a nonelectrolyte is -9.0°C .
 - a. What is the freezing-point depression of the solution?
 - b. What is the molal concentration of the solution?

MAIN IDEA

A solution with a nonelectrolyte solute will have a higher boiling point than the pure solvent.

As discussed previously, 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. In other words, if the vapor pressure is lowered, the boiling point is raised. If the vapor pressure is increased, the boiling point decreases. The vapor pressure of a solution containing a nonvolatile solute is lower than the vapor pressure of the pure solvent. This means that more energy as 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°C . Thus, the molal boiling-point constant for water is $0.51^\circ\text{C}/m$.

For different solvents, the molal boiling-point constants have different values. Some other values for K_b are included in **Figure 2.3**. Like the freezing-point constants, these values are most accurate for dilute solutions.

The **boiling-point elevation, Δt_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.

$$\text{Boiling-Point Elevation } \Delta t_b = K_b m$$

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

Calculating Boiling-Point Elevation

Sample Problem E What is the boiling-point elevation of a solution containing 34.3 g of the nonelectrolyte compound glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, dissolved in 107 g of water?

1 ANALYZE

Given: solute mass = 34.3 g
solute molar mass = 180.16 g/mol
solvent mass and identity = 107 g of water

Unknown: boiling-point elevation

2 PLAN

Find the molal boiling-point constant, K_b , for water in **Figure 2.3**. To use the equation for boiling-point elevation, $\Delta t_b = K_b m$, you need to determine the molality of the solution.

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

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

$$\Delta t_b = K_b m$$

3 SOLVE

$$34.3 \text{ g of solute} \times \frac{1 \text{ mol solute}}{180.16 \text{ g of solute}} = 0.190 \text{ mol of solute}$$

$$\frac{0.190 \text{ mol of solute}}{107 \text{ g water}} \times \frac{1000 \text{ g water}}{1 \text{ kg water}} = 1.776 \frac{\text{mol solute}}{\text{kg water}} = 1.776 m$$

$$\Delta t_b = 0.51^{\circ}\text{C}/m \times 1.775 m = 0.905^{\circ}\text{C}$$

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?
2. Determine the boiling point of a solution of 72.4 g of glycerol dissolved in 122.5 g of water.
3. If the boiling-point elevation of an aqueous solution containing a nonvolatile electrolyte is 1.02°C , what is the molality of the solution?
4. The boiling point of an aqueous solution containing a nonvolatile electrolyte is 100.75°C .
 - a. What is the boiling-point elevation?
 - b. What is the molality of the solution?

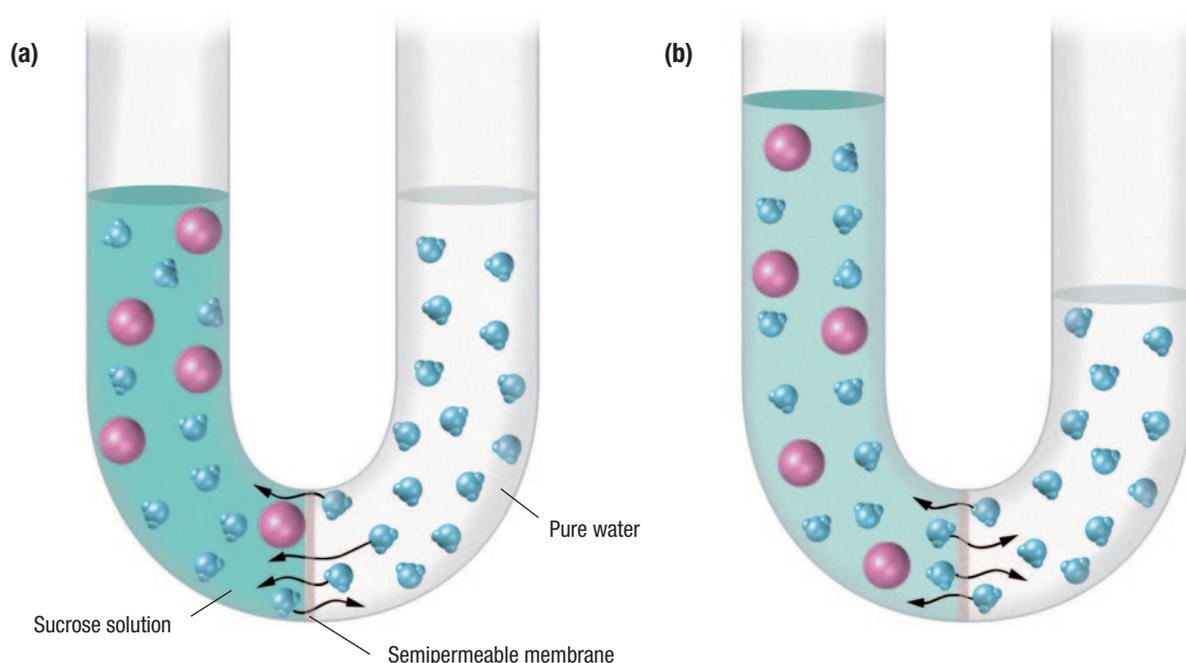


FIGURE 2.4

Osmotic Pressure (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.

MAIN IDEA

Osmotic pressure is determined by the concentration of dissolved solute particles.

Figure 2.4 illustrates another colligative property. In the figure, an aqueous sucrose solution is separated from pure water by a semipermeable membrane. **A semipermeable membrane allows the passage of some particles while blocking the passage 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 to 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 side. 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 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.

▶ MAIN IDEA

The total molality of all dissolved particles determines changes in 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, CaCl₂, 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. Sugar is a nonelectrolyte. 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. 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 2.5** 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.

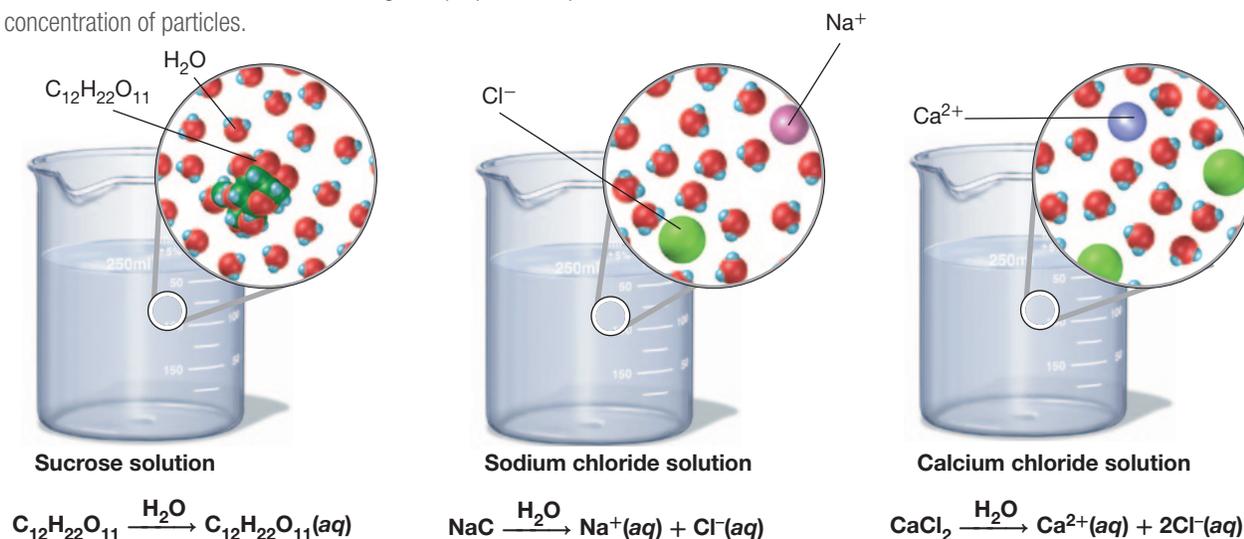
WHY IT MATTERS

Water Purification by Reverse Osmosis **S.T.E.M.**

The process of reverse osmosis is used to purify water because it removes many contaminants at relatively low cost. The osmosis process can be reversed by applying a pressure greater than the osmotic pressure to an aqueous solution. This causes the water, but not the dissolved solutes, to flow from the solution through the semipermeable membrane. The largest municipal desalination plant in the United States is in Sarasota, Florida. It treats salt water by reverse osmosis to produce more than 12 million gallons of fresh water per day. Other applications include the desalination of sea water on ocean-going vessels and wastewater purification.

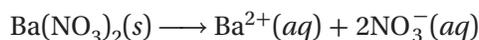
FIGURE 2.5

Colligative Properties 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. The changes in colligative properties caused by electrolytes will be proportional to the total molality of all dissolved particles, not to 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.

Freezing-Point Depression of Electrolytes

Sample Problem F 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?

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.

$$\frac{\text{mass of solute (g)}}{\text{mass of solvent (kg)}} \times \frac{1 \text{ mass solute}}{\text{molar mass solute (g)}} = \text{molality of solution} \left(\frac{\text{mol}}{\text{kg}} \right)$$
$$\text{molality of solution} \left(\frac{\text{mol}}{\text{kg}} \right) \times \text{molality conversion} \left(\frac{\text{mol ions}}{\text{mol}} \right) \times K_f \left(\frac{^\circ\text{C} \cdot \text{kg H}_2\text{O}}{\text{mol ions}} \right)$$
$$= \text{expected freezing-point depression (}^\circ\text{C)}$$

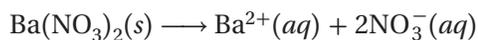
This problem is similar to Sample Problem E, except that the solute is ionic rather than a nonionizing molecular solute. The number of particles in solution will therefore equal the number of ions of the solute.

3 SOLVE

$$\frac{62.5 \text{ g } \text{Ba}(\text{NO}_3)_2}{1.00 \text{ kg H}_2\text{O}} \times \frac{1 \text{ mol } \text{Ba}(\text{NO}_3)_2}{261.35 \text{ g } \text{Ba}(\text{NO}_3)_2} = \frac{0.239 \text{ mol } \text{Ba}(\text{NO}_3)_2}{\text{kg H}_2\text{O}}$$

Continued

Freezing-Point Depression of Electrolytes (continued)



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 CHECK YOUR WORK

The units cancel properly to give the desired answer in °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

Answers in Appendix E

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?
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?
3. The freezing point of an aqueous sodium chloride solution is -0.20°C . What is the molality of the solution?

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 **Figure 2.6**. 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.

FIGURE 2.6

MOLAL FREEZING-POINT DEPRESSIONS FOR AQUEOUS SOLUTIONS OF IONIC SOLUTES

Solute	Concentration (m)	Δt_f , observed (°C)	Δt_f , nonelectrolyte solution (°C)	$\frac{\Delta t_f, \text{observed}}{\Delta t_f, \text{nonelectrolyte solution}} (^\circ\text{C})$
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 ₄	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 ₂	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 2.7

Freezing-Point Depression

The salts applied to icy roads lower the freezing point of water and melt the ice.



Look at the values given for KCl solutions in **Figure 2.6**, on the previous page. 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 nonelectrolyte solution (see **Figure 2.7**).

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. 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. 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 MgSO_4 have charges of 2^+ and 2^- . Ions formed by KCl have charges of 1^+ and 1^- . Note in **Figure 2.6** that MgSO_4 in a solution does not depress the freezing point as much as the same concentration of KCl.



SECTION 2 FORMATIVE ASSESSMENT

▶ Reviewing Main Ideas

- What colligative properties are displayed by each of the following situations?
 - Antifreeze is added to a car's cooling system to prevent freezing when the air temperature is below 0°C .
 - Ice melts on sidewalks after salt has been spread on them.
- Two moles of a nonelectrolyte 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? Suggest a possible identity of the solvent.
- 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?

- Calculate the expected freezing-point depression of a 0.200 *m* KNO_3 solution.
 - Will the value you calculated match the actual freezing-point depression for this solution? Why or why not?

✓ Critical Thinking

- INFERRING RELATIONSHIPS** The freezing-point depressions of aqueous solutions A, B, and C are -2.3°C , -1.2°C , and -4.1°C , respectively. Predict the order of the boiling-point elevations of these solutions, from lowest to highest. Explain your ranking.

The presence of a nonvolatile solute causes the freezing point of a solution to be lower and the boiling point to be higher than those of the pure solvent. The freezing-point depression, Δt_f , is the amount that the freezing point is lowered. It is calculated by using the formula $\Delta t_f = K_f m$. The boiling-point elevation, Δt_b , is the amount that the boiling point is elevated. It is found by using the equation $\Delta t_b = K_b m$. To determine Δt_f or Δt_b ,

you need to know its *molal* concentration, m (moles of solute per kilogram of solvent). You also need to know the molal freezing-point constant, K_f , or the molal boiling-point constant, K_b . The values for K_f and K_b depend on the solvent and are given in **Figure 2.3**. When these equations are used for electrolytes, the molality represents the total number of moles of ions in solution.

Problem-Solving TIPS

- Make sure that you find the molal concentration, not the molar concentration.
- For electrolytes, calculate the total number of moles of ions in solution.

Sample Problem

What is the theoretical boiling point of a solution of 247 g of potassium chloride, KCl, dissolved in 2.90 kg of water? Potassium chloride is a strong electrolyte.

First, determine the molality of the KCl that dissolved.

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

$$247 \text{ g KCl} \times \frac{1 \text{ mol KCl}}{74.55 \text{ g KCl}} = 3.31 \text{ mol KCl}$$

$$\text{molality KCl}(m) = \frac{\text{mol solute particles}}{\text{mass of solvent (kg)}} = \frac{3.31 \text{ mol KCl}}{2.90 \text{ kg H}_2\text{O}} = 1.14 \text{ } m \text{ KCl}$$

Because KCl is an electrolyte, the total moles of ions in solution must now be determined. The equation $\text{KCl}(s) \rightarrow \text{K}^+(aq) + \text{Cl}^-(aq)$ shows that 1 mol KCl will yield 2 mol of ions.

To find the total molality of particles in solution, multiply the molality of the solute by the moles of ions produced by the dissociation: $2 \times 1.14 \text{ } m \text{ KCl} = 2.28 \text{ } m$.

Next, use the equation $\Delta t_b = K_b m$, where K_b for water is $0.51^\circ\text{C}/m$ and the value for m is 2.28.

$$\Delta t_b = (0.51^\circ\text{C}/m)(2.28 \text{ } m) = 1.16^\circ\text{C}$$

The new boiling point is equal to the sum of the boiling point of the solvent and Δt_b .

$$\text{boiling point of solution} = 100^\circ\text{C} + 1.16^\circ\text{C} = 101.16^\circ\text{C}$$

Practice

1. What is the freezing point of a solution containing 28.0 g of the strong electrolyte calcium chloride, CaCl_2 , dissolved in 295 g of water?
2. What is the boiling point of a solution composed of 850 g of ethylene glycol, $\text{C}_2\text{H}_6\text{O}_2$, mixed with 1100 g of water?

CHAPTER 13 Summary

BIG IDEA Ionic compounds dissociate in aqueous solutions. Colligative properties of a solution depend only on the number of solute particles present.

SECTION 1 Compounds in Aqueous Solutions

KEY TERMS

- 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 molecular compounds is called ionization. Acids are molecular compounds that form ions in aqueous solutions. In an acid, a polar covalently bonded H atom is ionized in aqueous solutions.
- An H_3O^+ 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.

dissociation
net ionic equation
spectator ions
ionization
hydronium ion
strong electrolyte
weak electrolyte

SECTION 2 Colligative Properties of Solutions

KEY TERMS

- 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 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 nonelectrolytes do.
- Except in very dilute solutions, the values of colligative properties of electrolyte solutions are less than expected because of the attraction between ions in solution.

colligative properties
nonvolatile substance
molal freezing-point constant, K_f
freezing-point depression, Δt_f
molal boiling-point constant, K_b
boiling-point elevation, Δt_b
semipermeable membrane
osmosis
osmotic pressure



SECTION 1

Compounds in Aqueous Solutions

REVIEWING MAIN IDEAS

- How many moles of ions are contained in 1 L of a 1 M solution of KCl? of $\text{Mg}(\text{NO}_3)_2$?
- Use **Figure 1.3** to predict whether each of the following compounds is considered soluble or insoluble:
 - KCl
 - NaNO_3
 - AgCl
 - BaSO_4
 - $\text{Ca}_3(\text{PO}_4)_2$
 - $\text{Pb}(\text{ClO}_3)_2$
 - $(\text{NH}_4)_2\text{S}$
 - PbCl_2 (in cold water)
 - FeS
 - $\text{Al}_2(\text{SO}_4)_3$
- What is a net ionic equation?
- What is ionization?
 - Distinguish between ionization and dissociation.
- Define and distinguish between strong electrolytes and weak electrolytes.
 - Give two examples of each type.
- What determines the strength of a solute as an electrolyte?
- Distinguish between the use of the terms *strong* and *weak* and the use of the terms *dilute* and *concentrated* when describing electrolyte solutions.

PRACTICE PROBLEMS

- Write the equation for the dissolution of each of the following ionic compounds in water. (Hint: See Sample Problem A.)

a. KI	c. MgCl_2
b. NaNO_3	d. Na_2SO_4
- 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.

- 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.
 - 0.50 mol strontium nitrate
 - 0.50 mol sodium phosphate
- Using **Figure 1.3**, 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 B.)
 - mercury(II) chloride (*aq*) + potassium sulfide (*aq*) \longrightarrow
 - sodium carbonate (*aq*) + calcium chloride (*aq*) \longrightarrow
 - copper(II) chloride (*aq*) + ammonium phosphate (*aq*) \longrightarrow
- Identify the spectator ions in the reaction between KCl and AgNO_3 in an aqueous solution.
- Copper(II) chloride and lead(II) nitrate react in aqueous solutions by double displacement. 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?

SECTION 2

Colligative Properties of Solutions

REVIEWING MAIN IDEAS

- How does the presence of a nonvolatile solute affect each of the following properties of the solvent in which the solute is dissolved?
 - vapor pressure
 - freezing point
 - boiling point
 - osmotic pressure
- Using **Figure 2.1** as a guide, make a graph of vapor pressure versus temperature that shows the comparison of pure water, a solution with x concentration of solute, and a solution with $2x$ concentration of solute. What is the relationship between Δt_f for the x solution and Δt_f for the $2x$ solution?

- 16. 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, is there movement of water molecules across the membrane?
- 17. 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?
- 18.** 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?

PRACTICE PROBLEMS

- 19.** Determine the freezing-point depression of H_2O in each of the following solutions. (Hint: See Sample Problem C.)
- a.** 1.50 *m* solution of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (sucrose) in H_2O
- b.** 171 g of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ in 1.00 kg H_2O
- c.** 77.0 g of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ in 400. g H_2O
- 20.** Given the following freezing-point depressions, determine the molality of each solution of an unknown nonelectrolyte in water. (Hint: See Sample Problem D.)
- a.** -0.930°C
- b.** -3.72°C
- c.** -8.37°C
- 21.** A solution contains 20.0 g of $\text{C}_6\text{H}_{12}\text{O}_6$ (glucose) in 250. g of water.
- a.** What is the freezing-point depression of the solvent?
- b.** What is the freezing point of the solution?
- 22.** 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°C ?
- 23.** Pure benzene, C_6H_6 , freezes at 5.45°C . A solution containing 7.24 g $\text{C}_2\text{Cl}_4\text{H}_2$ in 115 g of benzene (specific gravity = 0.879) freezes at 3.55°C . Based on these data, what is the molal freezing-point constant for benzene?
- 24.** If 1.500 g of a solute that has 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?
- 25.** Determine the boiling-point elevation of H_2O in each of the following solutions. (Hint: See Sample Problem E.)
- a.** 2.5 *m* solution of $\text{C}_6\text{H}_{12}\text{O}_6$ (glucose) in H_2O
- b.** 3.20 g $\text{C}_6\text{H}_{12}\text{O}_6$ in 1.00 kg H_2O
- c.** 20.0 g $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (sucrose) in 500. g H_2O
- 26.** Given the following boiling points, determine the molality of each water solution.
- a.** 100.25°C
- b.** 101.53°C
- c.** 102.805°C
- 27.** Given 1.00 *m* aqueous solutions of each of the following electrolytic substances, determine the expected change in the freezing point of the solvent. (Hint: See Sample Problem F.)
- a.** KI
- b.** CaCl_2
- c.** $\text{Ba}(\text{NO}_3)_2$
- 28.** What is the expected change in the freezing point of water for a 0.015 *m* aqueous solution of AlCl_3 ?
- 29.** What is the expected freezing point of a solution containing 85.0 g NaCl dissolved in 450. g of water?
- 30.** Determine the expected boiling point of a solution made by dissolving 25.0 g of barium chloride in 0.150 kg of water.
- 31.** The change in the boiling point of water for an aqueous solution of potassium iodide is 0.65°C . Determine the molal concentration of potassium iodide.
- 32.** The freezing point of an aqueous solution of barium nitrate is -2.65°C . Determine the molal concentration of barium nitrate.
- 33.** Calculate the expected freezing point of a solution containing 1.00 kg H_2O and 0.250 mol NaCl.
- 34.** Experimental data for a 1.00 *m* MgI_2 aqueous solution indicate an actual change in the freezing point of water of -4.78°C . Find the expected change in the freezing point of water. Suggest a possible reason for the discrepancy between the experimental and expected values.

Mixed Review

REVIEWING MAIN IDEAS

35. 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
 - CaCl₂
 - K₃PO₄
 - C₆H₁₂O₆ (glucose)
36. What is the molal concentration of an aqueous calcium chloride solution that freezes at -2.43°C ?
37. a. Write the balanced formula equation that shows the possible products of a double-displacement reaction between calcium nitrate and sodium chloride.
b. Using **Figure 1.3**, determine whether there is a precipitate.
c. Does this reaction occur?
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.
- 0.275 mol of potassium sulfide
 - 0.15 mol of 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, AgNO₃, in 2.00 kg of water.
41. Nitrous acid, HNO₂, is a weak electrolyte. Nitric acid, HNO₃, 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 equation.
42. Find the boiling point of an aqueous solution containing a nonelectrolyte that freezes at -6.51°C .
43. Write a balanced equation for the dissolution of sodium carbonate, Na₂CO₃, 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 **Figure 1.3**, 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, Al(NO₃)₃, in 8.50 kg of water.

CRITICAL THINKING

46. Applying Models

- You are conducting a freezing-point determination in the laboratory by using an aqueous solution of KNO₃. The observed freezing point of the solution is -1.15°C . Using a pure water sample, you recorded the freezing point of the pure solvent on the same thermometer as 0.25°C . Determine the molal concentration of KNO₃. Assume that there are no forces of attraction between ions.
- 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 0.415 g KNO₃. Determine the actual molal concentration of KNO₃ and the percentage difference between the concentration observed in the freezing-point determination and the actual concentration of KNO₃. Assume that the solution's density is 1.00 g/mL.

47. **Analyzing Information** The observed freezing-point depression for electrolyte solutions is sometimes not as much as 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:

$$\pi = MRT$$

π = 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?

USING THE HANDBOOK

49. Common reactions for Group 13 elements are found in the *Elements Handbook* (Appendix A). Review this material, and answer the following:
- Write net ionic equations for each of the example reactions listed under "Common Reactions" for Group 13.
 - 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* (Appendix A). Review this material, and answer the following:
- Write net ionic equations for each of the example reactions listed under "Common Reactions" for Group 14.
 - Which reactions did not change when written in net ionic form? Why?

RESEARCH AND 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 has 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.

Standards-Based Assessment

Record your answers on a separate piece of paper.

MULTIPLE CHOICE

- Identify which of the following substances would be soluble in water in all cases.
 - lead(II) iodide
 - sodium nitrate
 - silver carbonate
 - barium sulfate
- Identify the reaction in which a precipitate occurs.
 - $\text{NaOH} + \text{HCl} \rightarrow$
 - $\text{NaNO}_3 + \text{KI} \rightarrow$
 - $\text{MgBr}_2 + \text{AgNO}_3 \rightarrow$
 - None of the above form precipitates.
- Identify the precipitate in the following reaction:
 $\text{Ca(OH)}_2(\text{aq}) + \text{FeCl}_3(\text{aq}) \rightarrow$
 - Ca(OH)_2
 - FeCl_3
 - Fe(OH)_3
 - CaCl_2
- Which of the following must not be split up when writing net ionic equations?
 - molecular substances, liquids, and solids
 - solids, liquids, and ionic substances
 - ionic substances, soluble substances, and gases
 - soluble substances, molecular substances, and solids
- Which of the following is not incorporated into a net ionic equation?
 - solids
 - liquids
 - spectator ions
 - precipitates

- Which of the following statements accurately describes precipitates and precipitation reactions?
 - Dissolve* means the same thing as *dissociate*.
 - Ionize* means the same thing as *dissociate*.
 - A substance can dissolve without dissociating.
 - Electrolytes form whenever solids are added to water.
- Which of the following is the best representation of the precipitation reaction that occurs when aqueous solutions of sodium carbonate and calcium chloride are mixed?
 - $\text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow 2\text{NaCl}(\text{s})$
 - $\text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{CaCO}_3(\text{s})$
 - $2\text{Na}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) + \text{Ca}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{CaCO}_3(\text{s}) + 2\text{NaCl}(\text{s})$
 - No precipitation reaction occurs.

GRIDDED RESPONSE

- An aqueous solution of an unknown quantity of a nonelectrolyte solute is found to have a freezing point of -0.58°C . What is the molar concentration of the solution?



Test Tip

Before choosing an answer to a question, try to answer the question without looking at the answer choices on the test.