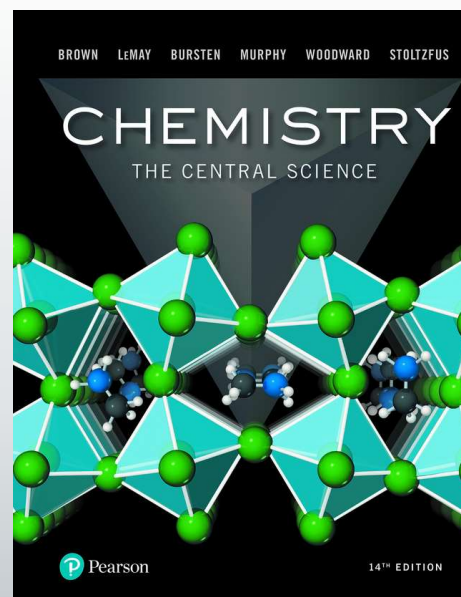


Chapter 4

Reactions in Aqueous Solution

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4.1 General Properties of Aqueous Solutions

- ❖ The substance present in the greatest quantity in a solution is usually called the **solvent**, and the other substances are called **solutes**; they are said to be dissolved in the solvent.
- ❖ A solution in which water is the dissolving medium is called an **aqueous solution**.

Electrolytes and Nonelectrolytes

- ❖ A substance whose aqueous solutions contain ions is called an **electrolyte**.
- ❖ A substance that does not form ions in solutions is called an **nonelectrolyte**.

4.1 General Properties of Aqueous Solutions

Pure water does not conduct electricity.



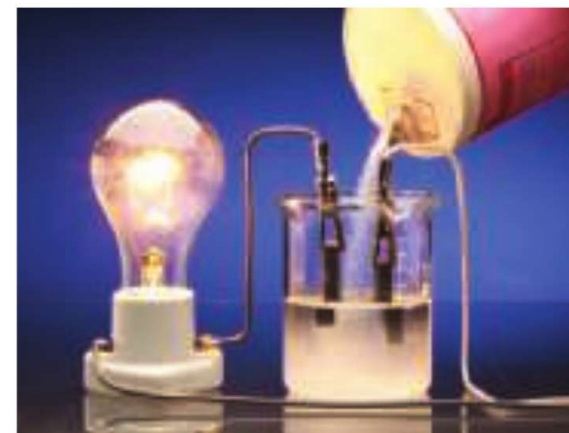
Pure water,
 $\text{H}_2\text{O}(l)$

A **nonelectrolyte solution** does not conduct electricity.



Sucrose solution,
 $\text{C}_{12}\text{H}_{22}\text{O}_{11}(aq)$

An **electrolyte solution** conducts electricity.



Sodium chloride solution,
 $\text{NaCl}(aq)$

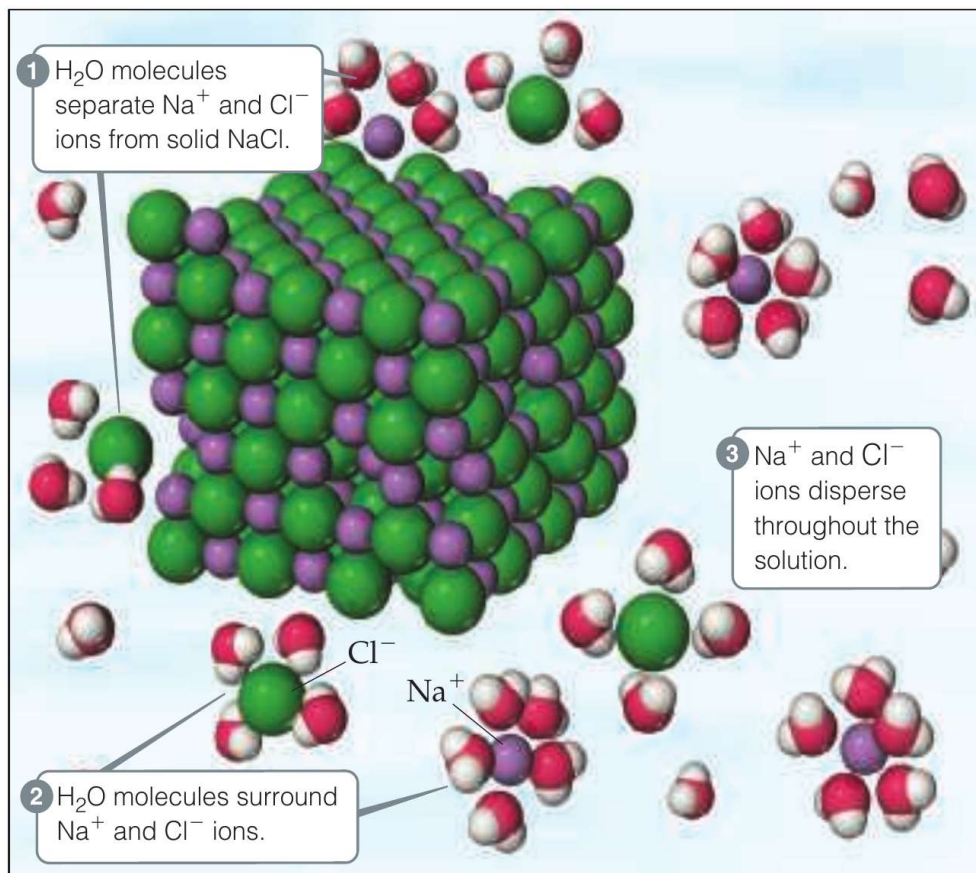
▲ **Figure 4.2** Completion of an electrical circuit with an electrolyte turns on the light.

4.1 General Properties of Aqueous Solutions

How Compounds Dissolve in Water

- ❖ When NaCl dissolves in water, each ion separates from the solid structure and disperses throughout the solution.
- ❖ Although H₂O is an electrically neutral molecule, the O atom is rich in electrons and has a partial negative charge (δ^-), while each H atom has a partial positive charge (δ^+).
- ❖ Cations are attracted by the negative end of H₂O, and anions are attracted by the positive end.
- ❖ The ions are said to be solvated.

4.1 General Properties of Aqueous Solutions



(a) Ionic compounds like sodium chloride, NaCl , form ions when they dissolve.

4.1 General Properties of Aqueous Solutions

Strong and Weak electrolytes

- ❖ **Strong electrolytes** are those solutes that exist in solution completely or nearly completely as ions.
- ❖ **Weak electrolytes** are those solutes that exist in solution mostly in the form of neutral molecules with only a small fraction in the form of ions.
- ❖ When a weak electrolyte, such as acetic acid, ionizes in solution, we write the reaction in the form



- ❖ In contrast, a single reaction arrow is used for reactions that largely go forward, such as the ionization of strong electrolytes.

4.2 Precipitation Reactions

- ❖ Reactions that result in the formation of an insoluble product are called **precipitation reactions**.
- ❖ A **precipitate** is an insoluble solid formed by a reaction in solution.



4.2 Precipitation Reactions

Solubility Guidelines for Ionic Compounds

- ❖ The **solubility** of a substance at a given temperature is the amount of the substance that can be dissolved in a given quantity of solvent at the given temperature.
- ❖ Any substance with a solubility less than 0.01 mol/L will be considered **insoluble**.
- ❖ Note that all common ionic compounds of the **alkali metal** ions (group 1A of the periodic table) and of the ammonium ions (NH_4^+) are soluble in water.

4.2 Precipitation Reactions

TABLE 4.1 Solubility Guidelines for Common Ionic Compounds in Water

Soluble Ionic Compounds		Important Exceptions
Compounds containing	NO_3^-	None
	CH_3COO^-	None
	Cl^-	Compounds of Ag^+ , Hg_2^{2+} , and Pb^{2+}
	Br^-	Compounds of Ag^+ , Hg_2^{2+} , and Pb^{2+}
	I^-	Compounds of Ag^+ , Hg_2^{2+} , and Pb^{2+}
	SO_4^{2-}	Compounds of Sr^{2+} , Ba^{2+} , Hg_2^{2+} , and Pb^{2+}
Insoluble Ionic Compounds		Important Exceptions
Compounds containing	S^{2-}	Compounds of NH_4^+ , the alkali metal cations, Ca^{2+} , Sr^{2+} , and Ba^{2+}
	CO_3^{2-}	Compounds of NH_4^+ and the alkali metal cations
	PO_4^{3-}	Compounds of NH_4^+ and the alkali metal cations
	OH^-	Compounds of NH_4^+ , the alkali metal cations, Ca^{2+} , Sr^{2+} , and Ba^{2+}

Sample Exercise 4.2

Classify these ionic compounds as soluble or insoluble in water:

a. sodium carbonate, Na_2CO_3

- According to Table 4.1, most carbonates are insoluble, but carbonates of the alkali metal cations are an exception to this rule and are soluble.
- Thus, Na_2CO_3 is soluble in water.

b. lead sulfate, PbSO_4

- Table 4.1 indicates that although most sulfates are water soluble, the sulfate of Pb^{2+} is an exception.
- Thus, PbSO_4 is insoluble in water.

4.2 Precipitation Reactions

Exchange (Metathesis) Reactions

- ❖ Reactions in which cations and anions appear to exchange partners conform to the general equation



- ❖ Such reactions are called either **exchange reactions** or **metathesis reactions**.



Sample Exercise 4.3

- Predict the identity of the precipitate that forms when aqueous solutions of BaCl_2 and K_2SO_4 are mixed.
- Write the balanced chemical equation for the reaction.

- The reactants contain Ba^{2+} , Cl^- , K^+ , and SO_4^{2-} ions.

Exchanging the anions gives us BaSO_4 and KCl .

According to Table 4.1, most compounds of SO_4^{2-} are soluble but those of Ba^{2+} are not.

Thus, BaSO_4 is insoluble, whereas KCl is soluble.

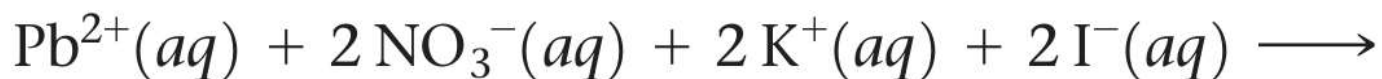
- $$\text{BaCl}_2(aq) + \text{K}_2\text{SO}_4(aq) \longrightarrow \text{BaSO}_4(s) + 2 \text{KCl}(aq)$$

4.2 Precipitation Reactions

Ionic equations and Spectator Ions



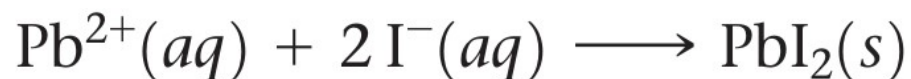
- ❖ An equation written in this fashion, showing the complete chemical formulas of reactants and products, is called a **molecular equation** because it shows chemical formulas without indicating ionic character.



- ❖ An equation written in this form, with all soluble strong electrolytes shown as ions, is called a **complete ionic equation**.

4.2 Precipitation Reactions

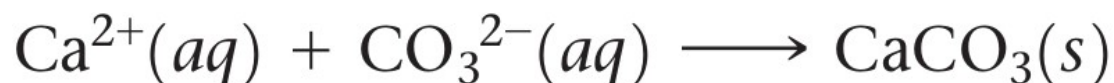
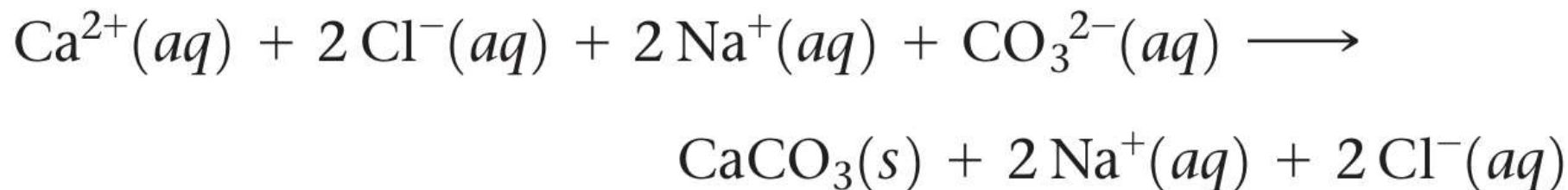
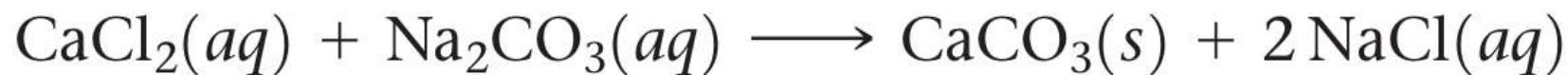
- ❖ Ions that appear in identical forms on both sides of a complete ionic equation, called **spectator ions**, play no direct role in the reaction.
- ❖ Once we cancel the spectator ions, we are left with the **net ionic equation**, which is one that includes only the ions and molecules directly involved in the reaction:



- ❖ If every ion in a complete ionic equation is a spectator, no reaction occurs.

Sample Exercise 4.4

Write the net ionic equation for the precipitation reaction that occurs when aqueous solutions of calcium chloride and sodium carbonate are mixed.

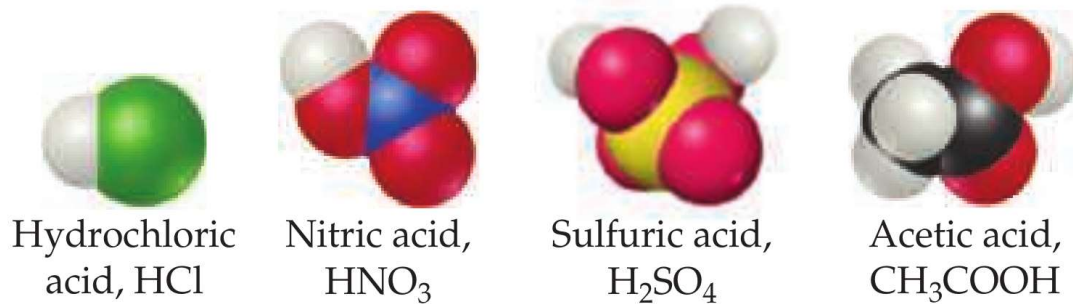


4.3 Acids, Bases, and Neutralization Reactions

Acids

- ❖ **Acids** are substances that ionize in aqueous solution to form hydrogen ions $\text{H}^+(\text{aq})$.
- ❖ Because a hydrogen atom consists of a proton and an electron, H^+ is simply a proton.
- ❖ Thus, acids are often called **proton donors**.

► **Figure 4.6** Molecular models of four common acids.



4.3 Acids, Bases, and Neutralization Reactions

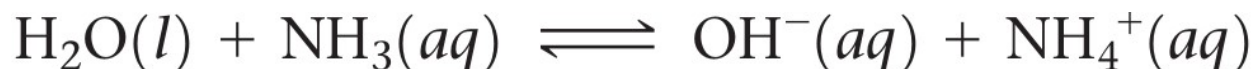
- ❖ Both HCl and HNO₃ are monoprotic acids, yielding one H⁺ per molecule of acid.
- ❖ Sulfuric acid, H₂SO₄, is a diprotic acid, one that yields two H⁺ per molecule of acid.
- ❖ The ionization of H₂SO₄ and other diprotic acids occurs in two steps:



4.3 Acids, Bases, and Neutralization Reactions

Bases

- ❖ **Bases** are substances that accept (react with) H^+ ions.
- ❖ Bases produce hydroxide ions (OH^-) when they dissolve in water.
- ❖ Compounds that do not contain OH^- ions can also be bases; for example, ammonia (NH_3) is a common base.



4.3 Acids, Bases, and Neutralization Reactions

TABLE 4.2 Common Strong Acids and Bases

Strong Acids	Strong Bases
Hydrochloric acid, HCl	Group 1A metal hydroxides
Hydrobromic acid, HBr	[LiOH, NaOH, KOH, RbOH, CsOH]
Hydroiodic acid, HI	Heavy group 2A metal hydroxides
Chloric acid, HClO ₃	[Ca(OH) ₂ , Sr(OH) ₂ , Ba(OH) ₂]
Perchloric acid, HClO ₄	
Nitric acid, HNO ₃	
Sulfuric acid (first proton), H ₂ SO ₄	

4.3 Acids, Bases, and Neutralization Reactions

Strong and Weak Acids and Bases

- ❖ Acids and bases that are strong electrolytes (completely ionized in solution) are **strong acids** and **strong bases**.
- ❖ Those that are weak electrolytes (partly ionized) are **weak acids** and **weak bases**.
- ❖ When reactivity depends only on $\text{H}^+(\text{aq})$ concentration, strong acids are more reactive than weak acids.

4.3 Acids, Bases, and Neutralization Reactions

Identifying Strong and Weak electrolytes

- ❖ If we remember the common strong acids and bases (Table 4.2) and also remember that NH_3 is a weak base, we can make reasonable predictions about the electrolytic strength of a great number of water-soluble substances.
- ❖ We first ask whether the substance is ionic or molecular.

TABLE 4.3 Summary of the Electrolytic Behavior of Common Soluble Ionic and Molecular Compounds

	Strong Electrolyte	Weak Electrolyte	Nonelectrolyte
Ionic	All	None	None
Molecular	Strong acids (see Table 4.2)	Weak acids, weak bases	All other compounds

Sample Exercise 4.6

Classify these dissolved substances as a strong electrolyte, weak electrolyte, or nonelectrolyte: CaCl_2 , HNO_3 , $\text{C}_2\text{H}_5\text{OH}$ (ethanol), HCOOH (formic acid), KOH .

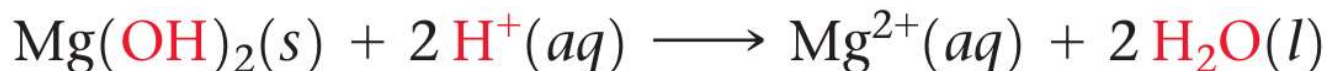
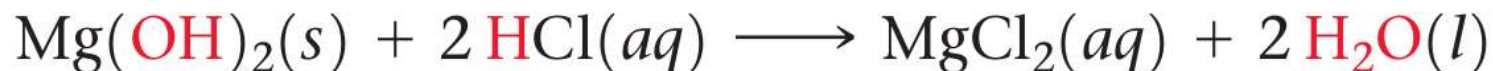
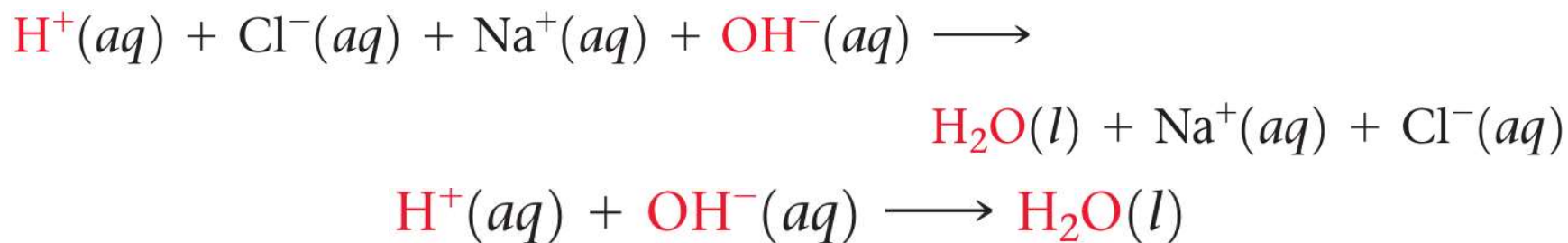
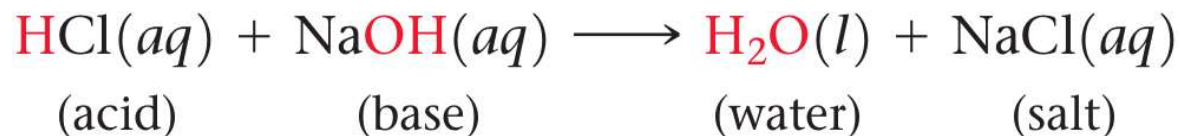
- CaCl_2 \Rightarrow ionic compound, strong electrolyte
- HNO_3 \Rightarrow strong acid, strong electrolyte
- $\text{C}_2\text{H}_5\text{OH}$ (ethanol) \Rightarrow molecular compound, nonelectrolyte
- HCOOH (formic acid) \Rightarrow weak acid, weak electrolyte
- KOH \Rightarrow ionic compound, strong electrolyte

4.3 Acids, Bases, and Neutralization Reactions

Neutralization Reactions and Salts

- ❖ Acids have a sour taste, whereas bases have a bitter taste.
- ❖ When a solution of an acid and a solution of a base are mixed, a **neutralization reaction** occurs.
- ❖ In general, a neutralization reaction between an acid and a metal hydroxide produces water and a salt.
- ❖ The term **salt** has come to mean any ionic compound whose cation comes from a base and whose anion comes from an acid.

4.3 Acids, Bases, and Neutralization Reactions

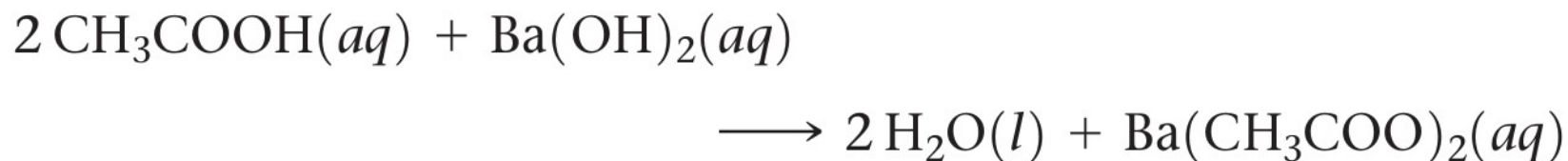


- ❖ Because the ions exchange partners, neutralization reactions between acids and metal hydroxides are metathesis reactions.

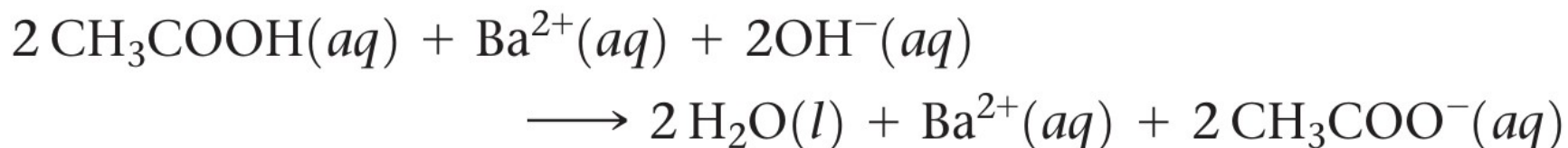
Sample Exercise 4.7

For the reaction between aqueous solutions of acetic acid (CH_3COOH) and barium hydroxide ($\text{Ba}(\text{OH})_2$), write

a. The balanced molecular equation



b. The complete ionic equation



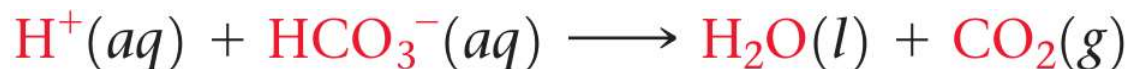
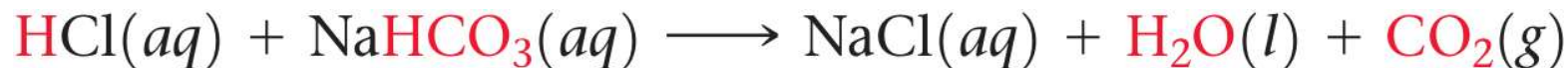
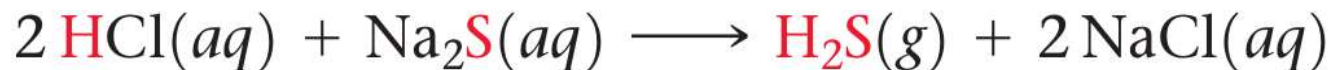
c. The net ionic equation



4.3 Acids, Bases, and Neutralization Reactions

Neutralization Reactions with Gas Formation

- ❖ The sulfide ion and the carbonate ion react with acids to form gases that have low solubilities in water.



4.3 Acids, Bases, and Neutralization Reactions

- ❖ Both $\text{NaHCO}_3(s)$ and $\text{Na}_2\text{CO}_3(s)$ are used as neutralizers in acid spills; either salt is added until fizzing caused by $\text{CO}_2(g)$ formation stops.
- ❖ Sometimes sodium bicarbonate is used as an antacid to soothe an upset stomach.

4.4 Oxidation-Reduction Reactions

- ❖ The reactions in which electrons are transferred from one reactant to another are called either **oxidation-reduction reactions** or **redox reactions**.

Oxidation and Reduction

- ❖ One of the most familiar redox reactions is **corrosion** of a metal.
- ❖ **Corrosion** is the conversion of a metal into a metal compound, by a reaction between the metal and some substance in its environment.
- ❖ When an atom, ion, or molecule becomes more positively charged (i.e., when it loses electrons), we say that it has been **oxidized**.
- ❖ Loss of electrons by a substance is called **oxidation**.

4.4 Oxidation-Reduction Reactions



(a)



(b)



(c)

▲ **Figure 4.11** Familiar corrosion products. (a) A green coating forms when copper is oxidized. (b) Rust forms when iron corrodes. (c) A black tarnish forms as silver corrodes.

4.4 Oxidation-Reduction Reactions

- ❖ When an atom, ion, or molecule becomes more negatively charged (gains electrons), we say that it is **reduced**.
- ❖ The gain of electrons by a substance is called **reduction**.

Oxidation Numbers

- ❖ Each atom in a neutral substance or ion is assigned an **oxidation number** (also known as an **oxidation state**).
- ❖ We use the following rules for assigning oxidation numbers:

4.4 Oxidation-Reduction Reactions

1. For an atom in its **elemental form**, the oxidation number is always zero.
2. For any **monatomic ion**, the oxidation number equals the ionic charge.
3. Nonmetals usually have negative oxidation numbers, although they can sometimes be positive:
 - The oxidation number of oxygen is usually -2 in both ionic and molecular compounds.
 - The major exception is in compounds called peroxides, which contain the O_2^{2-} ion, giving each oxygen an oxidation number of -1 .

4.4 Oxidation-Reduction Reactions

- The oxidation number of hydrogen is usually +1 when bonded to nonmetals and -1 when bonded to metals.
 - The oxidation number of fluorine is -1 in all compounds.
 - The other halogens have an oxidation number of -1 in most binary compounds.
 - When combined with oxygen, as in oxyanions, however, other halogens have positive oxidation states.
4. The sum of the oxidation numbers of all atoms in a neutral compound is zero.
 5. The sum of the oxidation numbers in a polyatomic ion equals the charge of the ion.

Sample Exercise 4.8

Determine the oxidation number of sulfur in

a. H_2S

- When bonded to a nonmetal, hydrogen has an oxidation number of +1.
- Because the H_2S molecule is neutral, the sum of the oxidation numbers must equal zero; thus, S has an oxidation number of -2.

b. S_8

- Because S_8 is an elemental form of sulfur, the oxidation number of S is 0.

Sample Exercise 4.8

c. SCl_2

- Because SCl_2 is a binary compound, we expect chlorine to have an oxidation number of -1 .
- The sum of the oxidation numbers must equal zero; consequently, the oxidation number of S must be $+2$.

d. Na_2SO_3

- Sodium, an alkali metal, always has an oxidation number of $+1$.
- Oxygen commonly has an oxidation state of -2 .
- Letting x equal the oxidation number of S, we have $2(+1) + x + 3(-2) = 0$; therefore, the oxidation number of S is $+4$.

Sample Exercise 4.8

e. SO_4^{2-}

- The oxidation state of O is -2 .
- The sum of oxidation numbers equals -2 .
- Thus, we have $x + 4(-2) = -2$; therefore, the oxidation number of S is $+6$.

4.4 Oxidation-Reduction Reactions

Oxidation of Metals by Acids and Salts

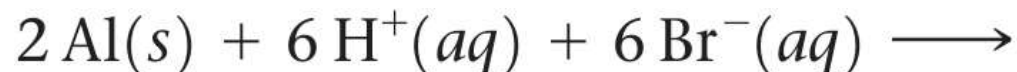
- ❖ The reaction between a metal and either an acid or a metal salt conforms to the general pattern:



- ❖ These reactions are called **displacement reactions** because the ion in solution is displaced through oxidation of an element.

Sample Exercise 4.9

Write the balanced molecular and net ionic equations for the reaction of aluminum with hydrobromic acid.



4.4 Oxidation-Reduction Reactions

The Activity Series

- ❖ A list of metals arranged in order of decreasing ease of oxidation, such as in Table 4.5, is called an **activity series**.
- ❖ The metals at the top of the table, such as the alkali metals and the alkaline earth metals, are most easily oxidized; that is, they react most readily to form compounds.
- ❖ They are called the active metals.

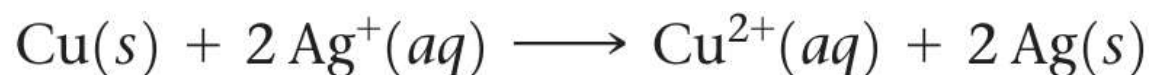
TABLE 4.5 Activity Series of Metals in Aqueous Solution

Metal	Oxidation Reaction
Lithium	$\text{Li}(s) \longrightarrow \text{Li}^+(aq) + e^-$
Potassium	$\text{K}(s) \longrightarrow \text{K}^+(aq) + e^-$
Barium	$\text{Ba}(s) \longrightarrow \text{Ba}^{2+}(aq) + 2e^-$
Calcium	$\text{Ca}(s) \longrightarrow \text{Ca}^{2+}(aq) + 2e^-$
Sodium	$\text{Na}(s) \longrightarrow \text{Na}^+(aq) + e^-$
Magnesium	$\text{Mg}(s) \longrightarrow \text{Mg}^{2+}(aq) + 2e^-$
Aluminum	$\text{Al}(s) \longrightarrow \text{Al}^{3+}(aq) + 3e^-$
Manganese	$\text{Mn}(s) \longrightarrow \text{Mn}^{2+}(aq) + 2e^-$
Zinc	$\text{Zn}(s) \longrightarrow \text{Zn}^{2+}(aq) + 2e^-$
Chromium	$\text{Cr}(s) \longrightarrow \text{Cr}^{3+}(aq) + 3e^-$
Iron	$\text{Fe}(s) \longrightarrow \text{Fe}^{2+}(aq) + 2e^-$
Cobalt	$\text{Co}(s) \longrightarrow \text{Co}^{2+}(aq) + 2e^-$
Nickel	$\text{Ni}(s) \longrightarrow \text{Ni}^{2+}(aq) + 2e^-$
Tin	$\text{Sn}(s) \longrightarrow \text{Sn}^{2+}(aq) + 2e^-$
Lead	$\text{Pb}(s) \longrightarrow \text{Pb}^{2+}(aq) + 2e^-$
Hydrogen	$\text{H}_2(g) \longrightarrow 2\text{H}^+(aq) + 2e^-$
Copper	$\text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq) + 2e^-$
Silver	$\text{Ag}(s) \longrightarrow \text{Ag}^+(aq) + e^-$
Mercury	$\text{Hg}(l) \longrightarrow \text{Hg}^{2+}(aq) + 2e^-$
Platinum	$\text{Pt}(s) \longrightarrow \text{Pt}^{2+}(aq) + 2e^-$
Gold	$\text{Au}(s) \longrightarrow \text{Au}^{3+}(aq) + 3e^-$

Ease of oxidation increases

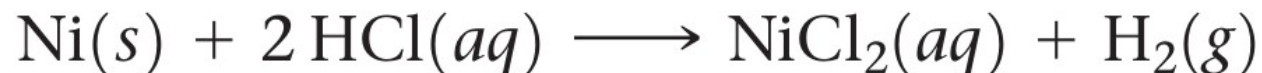
4.4 Oxidation-Reduction Reactions

- ❖ The metals at the bottom of the activity series, such as the transition elements from groups 8B and 1B, are very stable and form compounds less readily.
- ❖ These metals, which are used to make coins and jewelry, are called noble metals because of their low reactivity.
- ❖ Any metal on the list can be oxidized by the ions of elements below it.
- ❖ For example, copper is above silver in the series. Thus, copper metal is oxidized by silver ions:



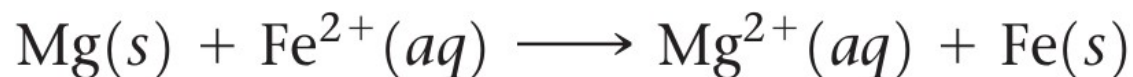
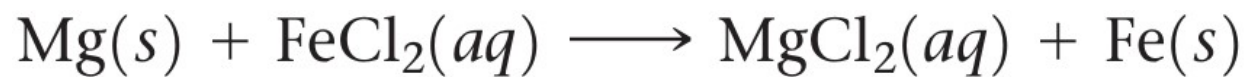
4.4 Oxidation-Reduction Reactions

- ❖ Only metals above hydrogen in the activity series are able to react with acids to form H_2 .
- ❖ **Example:** Ni reacts with $\text{HCl}(aq)$ to form H_2 :



Sample Exercise 4.10

Will an aqueous solution of iron(II) chloride oxidize magnesium metal? If so, write the balanced molecular and net ionic equations for the reaction.



4.5 Concentrations of Solutions

- ❖ **Concentration** designates the amount of solute dissolved in a given quantity of solvent or quantity of solution.
- ❖ The greater the amount of solute dissolved in a certain amount of solvent, the more concentrated the resulting solution.

Molarity

- ❖ **Molarity (M)** expresses the concentration of a solution as the number of moles (n) of solute in a liter of solution (V_L):

$$M = \frac{n}{V_L}$$

$$n = \frac{m}{MM}$$

Sample Exercise 4.11

Calculate the molarity of a solution made by dissolving 23.4 g of sodium sulfate (Na_2SO_4) in enough water to form 125 mL of solution.

$$n = \frac{m}{MM} = \frac{23.4}{142.04} = 0.1647 \text{ mol}$$

$$M = \frac{n}{V_L} = \frac{0.1647}{125 \times 10^{-3}} = 1.32 \text{ M}$$

4.5 Concentrations of Solutions

Expressing the Concentration of an Electrolyte

- ❖ When an ionic compound dissolves, the relative concentrations of the ions in the solution depend on the chemical formula of the compound.
- ❖ **Example:** a 1.0 M solution of Na_2SO_4 is 2.0 M in Na^+ ions and 1.0 M in SO_4^{2-} ions.

Interconverting Molarity, Moles, and Volume

Sample Exercise 4.12

What is the molar concentration of each ion present in a 0.025 M aqueous solution of calcium nitrate?

$$M \text{ Ca}^{2+} = 0.025 \frac{\text{mol Ca(NO}_3)_2}{\text{L}} \left(\frac{1 \text{ mol Ca}^{2+}}{1 \text{ mol Ca(NO}_3)_2} \right) = 0.025 \text{ M}$$

$$M \text{ NO}_3^- = 0.025 \frac{\text{mol Ca(NO}_3)_2}{\text{L}} \left(\frac{2 \text{ mol NO}_3^-}{1 \text{ mol Ca(NO}_3)_2} \right) = 0.050 \text{ M}$$

Sample Exercise 4.13

How many grams of Na_2SO_4 are required to make 0.350 L of 0.500 M Na_2SO_4 ?

$$M = \frac{n}{V_L}$$

$$n = MV_L = (0.500)(0.350) = 0.175 \text{ mol}$$

$$n = \frac{m}{MM}$$

$$m = (n)(MM) = (0.175)(142.04) = 24.9 \text{ g}$$

4.5 Concentrations of Solutions

Dilution

- ❖ Aqueous solutions of lower concentrations can be obtained by adding water, a process called **dilution**.
- ❖ The main point to remember is that when solvent is added to a solution, the number of moles of solute remains unchanged:

moles solute in conc soln (n_c) = moles solute in dilute soln (n_d)

$$M_c V_c = M_d V_d$$

Sample Exercise 4.14

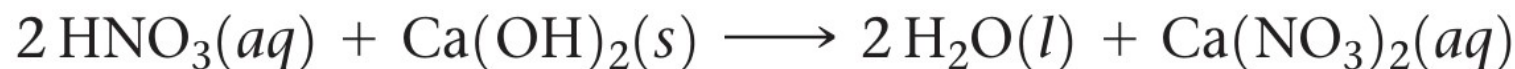
How many milliliters of 3.0 M H_2SO_4 are needed to make 450 mL of 0.10 M H_2SO_4 ?

$$M_c V_c = M_d V_d$$

$$V_c = \frac{M_d V_d}{M_c} = \frac{(0.10)(450)}{3.0} = 15 \text{ mL}$$

Sample Exercise 4.15

How many grams of Ca(OH)_2 are needed to neutralize 25.0 mL of 0.100 M HNO_3 ?



$$M = \frac{n}{V_L}$$

$$n \text{ HNO}_3 = (M)(V_L) = (0.100)(25.0 \times 10^{-3}) = 0.00250 \text{ mol}$$

$$n \text{ Ca(OH)}_2 = 0.00250 \text{ mol HNO}_3 \left(\frac{1 \text{ mol Ca(OH)}_2}{2 \text{ mol HNO}_3} \right) = 0.00125 \text{ mol}$$

Sample Exercise 4.15

$$n = \frac{m}{MM}$$

$$m = (n)(MM) = (0.00125)(74.10) = 0.0926 \text{ g}$$