



Edu

Chemical Reactions

Dr. Oxford Edu

Cambridge, Oxford, 의대출신 강사진들과의 1:1 맞춤
A-LEVEL/IB/영국대학 입시전문

Chemistry

Dr. Oxford Edu

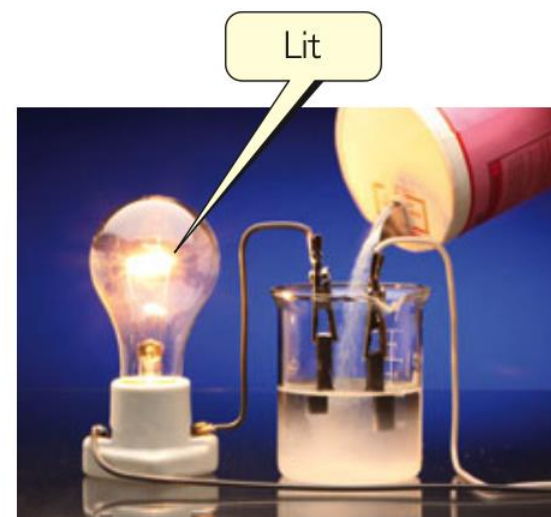




Pure water,
 $\text{H}_2\text{O}(l)$
does not conduct electricity



Sucrose solution,
 $\text{C}_{12}\text{H}_{22}\text{O}_{11}(aq)$
Nonelectrolyte
does not conduct electricity



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

A substance (such as NaCl) whose aqueous solutions contain ions is called an **electrolyte**. A substance (such as $\text{C}_{12}\text{H}_{22}\text{O}_{11}$) that does not form ions in solution is called a **nonelectrolyte**. The different classifications of NaCl and $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ arise largely because NaCl is ionic, whereas $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ is molecular.

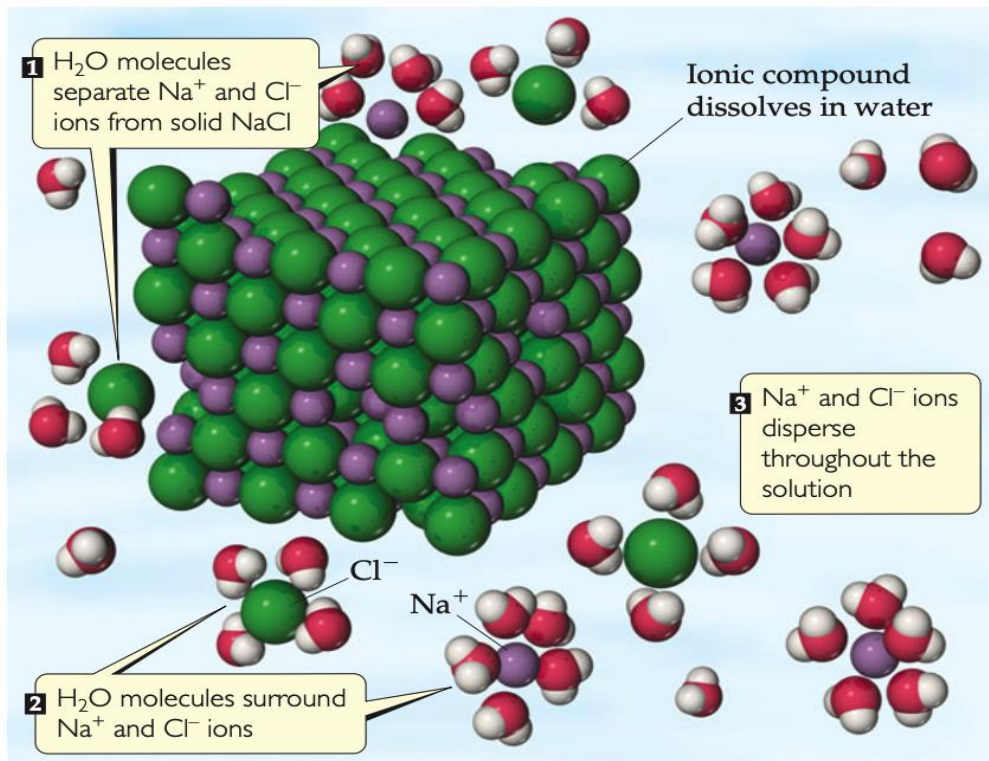
◀ **FIGURE 4.2**
Electrical
conductivities of
water and two
aqueous solutions.

Ionic Compounds in Water

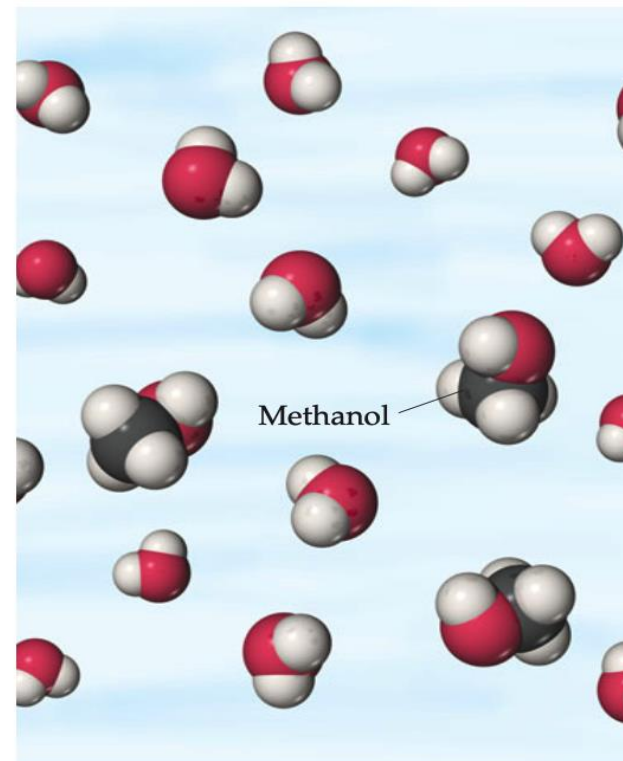
Recall from Figure 2.21 that solid NaCl consists of an orderly arrangement of Na^+ and Cl^- ions. When NaCl dissolves in water, each ion separates from the solid structure and disperses throughout the solution [▼ FIGURE 4.3(a)]. The ionic solid *dissociates* into its component ions as it dissolves.

GO FIGURE

Which solution, $\text{NaCl}(\text{aq})$ or $\text{CH}_3\text{OH}(\text{aq})$, conducts electricity?

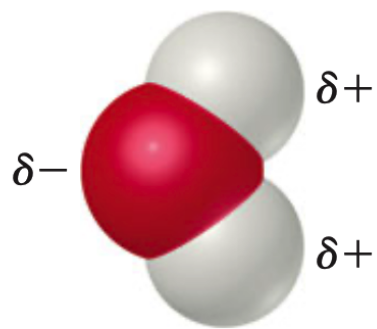


(a) Ionic compounds like sodium chloride, NaCl, form ions when they dissolve




(b) Molecular substances like methanol, CH_3OH , dissolve without forming ions

▲ **FIGURE 4.3** **Dissolution in water.** (a) When an ionic compound, such as sodium chloride, NaCl, dissolves in water, H_2O molecules separate, surround, and uniformly disperse the ions into the liquid. (b) Molecular substances that dissolve in water, such as methanol, CH_3OH , usually do so without forming ions. We can think of this as a simple mixing of two molecular species. In both (a) and (b) the water molecules have been moved apart so that the solute particles can be seen clearly.



Water is a very effective solvent for ionic compounds. Although H_2O is an electrically neutral molecule, the O atom is rich in electrons and has a partial negative charge, denoted by δ^- . Each H atom has a partial positive charge, denoted by δ^+ . Cations are attracted by the negative end of H_2O , and anions are attracted by the positive end.

As an ionic compound dissolves, the ions become surrounded by H_2O molecules, as shown in Figure 4.3(a). The ions are said to be *solvated*. In chemical equations, we denote solvated ions by writing them as $\text{Na}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$, where *aq* is an abbreviation for “aqueous.”  (Section 3.1) **Solvation** helps stabilize the ions in solution and prevents cations and anions from recombining. Furthermore, because the ions and their shells of surrounding water molecules are free to move about, the ions become dispersed uniformly throughout the solution.

We can usually predict the nature of the ions in a solution of an ionic compound from the chemical name of the substance. Sodium sulfate (Na_2SO_4), for example, dissociates into sodium ions (Na^+) and sulfate ions (SO_4^{2-}). You must remember the formulas and charges of common ions (Tables 2.4 and 2.5) to understand the forms in which ionic compounds exist in aqueous solution.

Strong and Weak Electrolytes

Electrolytes differ in the extent to which they conduct electricity. **Strong electrolytes** are those solutes that exist in solution completely or nearly completely as ions. Essentially all water-soluble ionic compounds (such as NaCl) and a few molecular compounds (such as HCl) are strong electrolytes. **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. For example, in a solution of acetic acid (CH_3COOH) most of the solute is present as $\text{CH}_3\text{COOH}(aq)$ molecules. Only a small fraction (about 1%) of the CH_3COOH has dissociated into $\text{H}^+(aq)$ and $\text{CH}_3\text{COO}^-(aq)$ ions.*

We must be careful not to confuse the extent to which an electrolyte dissolves (its solubility) with whether it is strong or weak. For example, CH_3COOH is extremely soluble in water but is a weak electrolyte. $\text{Ca}(\text{OH})_2$, on the other hand, is not very soluble in water, but the amount that does dissolve dissociates almost completely. Thus, $\text{Ca}(\text{OH})_2$ is a strong electrolyte.

When a weak electrolyte, such as acetic acid, ionizes in solution, we write the reaction in the form



SAMPLE EXERCISE 4.1 Relating Relative Numbers of Anions and Cations to Chemical Formulas

The accompanying diagram represents an aqueous solution of either MgCl_2 , KCl , or K_2SO_4 . Which solution does the drawing best represent?

SOLUTION

Analyze We are asked to associate the charged spheres in the diagram with ions present in a solution of an ionic substance.

Plan We examine each ionic substance given to determine the relative numbers and charges of its ions. We then correlate these ionic species with the ones shown in the diagram.

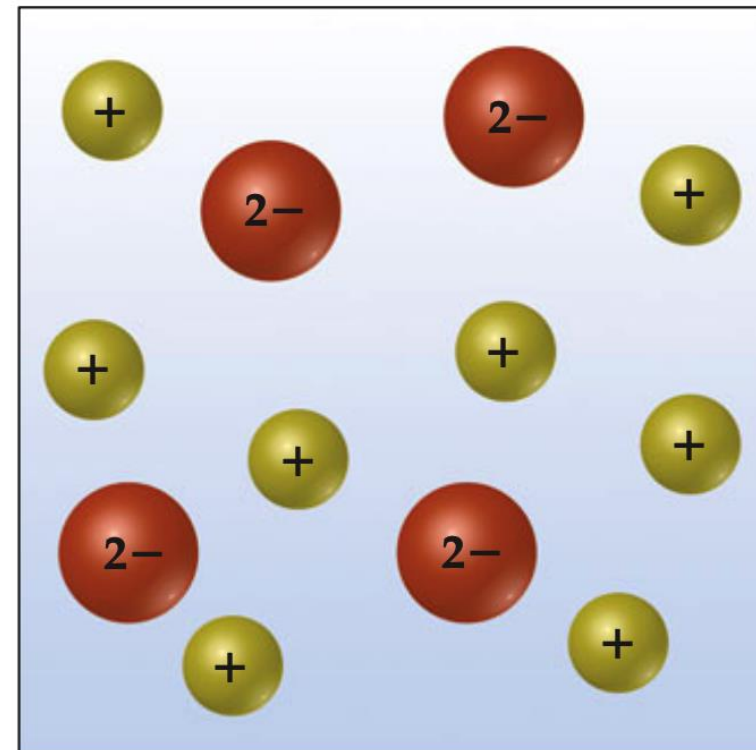
Solve The diagram shows twice as many cations as anions, consistent with the formulation K_2SO_4 .

Check Notice that the net charge in the diagram is zero, as it must be if it is to represent an ionic substance.

PRACTICE EXERCISE

If you were to draw diagrams representing aqueous solutions of (a) NiSO_4 , (b) $\text{Ca}(\text{NO}_3)_2$, (c) Na_3PO_4 , (d) $\text{Al}_2(\text{SO}_4)_3$, how many anions would you show if each diagram contained six cations?

Answers: (a) 6, (b) 12, (c) 2, (d) 9



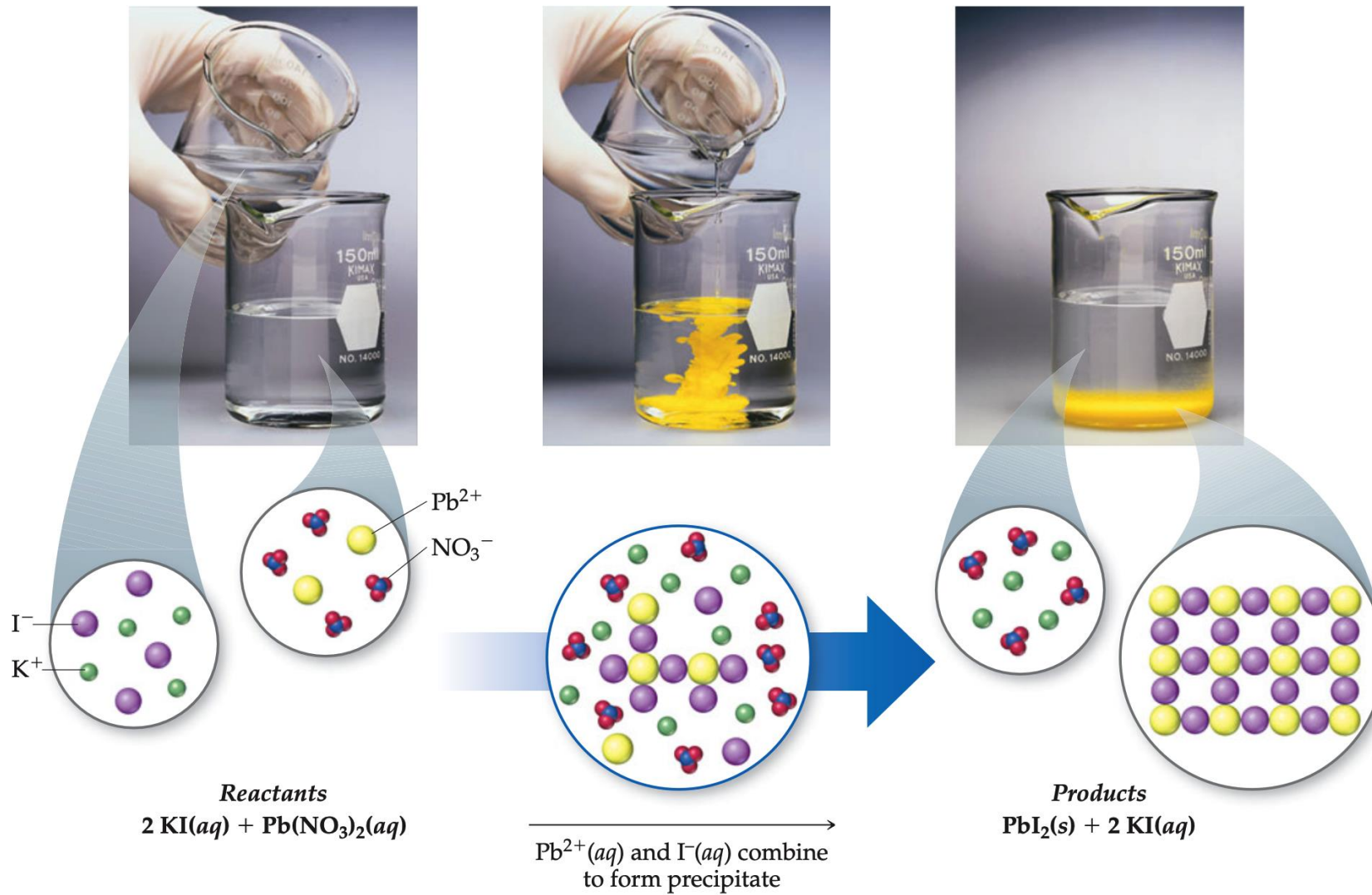
4.2 | PRECIPITATION REACTIONS

► **FIGURE 4.4** shows two clear solutions being mixed. One solution contains potassium iodide, KI, dissolved in water and the other contains lead nitrate, $\text{Pb}(\text{NO}_3)_2$, dissolved in water. The reaction between these two solutes produces a water-insoluble yellow solid. 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. In Figure 4.4 the precipitate is lead iodide (PbI_2), a compound that has a very low solubility in water:



The other product of this reaction, potassium nitrate (KNO_3), remains in solution.

Which ions remain in solution after PbI_2 precipitation is complete?




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. In our discussions, any substance with a solubility less than 0.01 mol/L will be referred to as *insoluble*. In those cases the attraction between the oppositely charged ions in the solid is too great for the water molecules to separate the ions to any significant extent; the substance remains largely undissolved.

Unfortunately, there are no rules based on simple physical properties such as ionic charge to guide us in predicting whether a particular ionic compound will be soluble. Experimental observations, however, have led to guidelines for predicting solubility for ionic compounds. For example, experiments show that all common ionic compounds that contain the nitrate anion, NO_3^- , are soluble in water. ► **TABLE 4.1** summarizes the solubility guidelines for common ionic compounds. The table is organized according to the anion in the compound, but it also reveals many important facts about cations. Note that *all common ionic compounds of the alkali metal ions (group 1A of the periodic table) and of the ammonium ion (NH_4^+) are soluble in water.*

Exchange (Metathesis) Reactions

Notice in Equation 4.5 that the reactant cations exchange anions— Mg^{2+} ends up with OH^- , and Na^+ ends up with NO_3^- . The chemical formulas of the products are based on the charges of the ions—two OH^- ions are needed to give a neutral compound with Mg^{2+} , and one NO_3^- ion is needed to give a neutral compound with Na^+ .  (Section 2.7) *The equation can be balanced only after the chemical formulas of the products have been determined.*

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** (meh-TATH-eh-sis, Greek for “to transpose”). Precipitation reactions conform to this pattern, as do many neutralization reactions between acids and bases, as we will see in Section 4.3.

To complete and balance the equation for a metathesis reaction, we follow these steps:

1. Use the chemical formulas of the reactants to determine which ions are present.
2. Write the chemical formulas of the products by combining the cation from one reactant with the anion of the other, using the ionic charges to determine the subscripts in the chemical formulas.
3. Check the water solubilities of the products. For a precipitation reaction to occur, at least one product must be insoluble in water.
4. Balance the equation.

SAMPLE EXERCISE 4.3 Predicting a Metathesis Reaction

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

SOLUTION

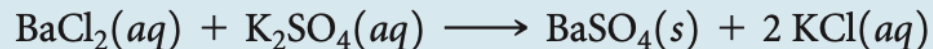
Analyze We are given two ionic reactants and asked to predict the insoluble product that they form.

Plan We need to write the ions present in the reactants and exchange the anions between the two cations. Once we have written the chemical formulas for these products, we can use Table 4.1 to determine which is insoluble in water. Knowing the products also allows us to write the equation for the reaction.

Solve

(a) 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 and will precipitate from solution. KCl is soluble.

(b) From part (a) we know the chemical formulas of the products, BaSO_4 and KCl . The balanced equation is



PRACTICE EXERCISE

(a) What compound precipitates when aqueous solutions of $\text{Fe}_2(\text{SO}_4)_3$ and LiOH are mixed? (b) Write a balanced equation for the reaction. (c) Will a precipitate form when solutions of $\text{Ba}(\text{NO}_3)_2$ and KOH are mixed?

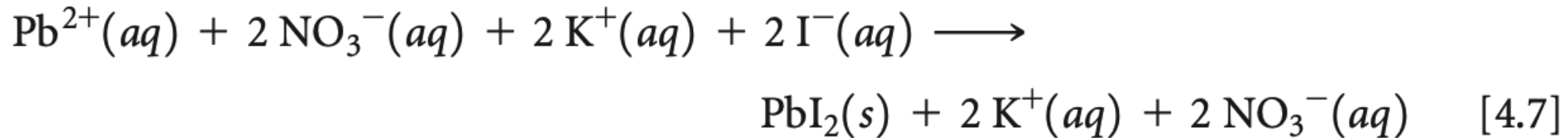
Answers: (a) $\text{Fe}(\text{OH})_3$, (b) $\text{Fe}_2(\text{SO}_4)_3(aq) + 6 \text{LiOH}(aq) \longrightarrow 2 \text{Fe}(\text{OH})_3(s) + 3 \text{Li}_2\text{SO}_4(aq)$, (c) no (both possible products, $\text{Ba}(\text{OH})_2$ and KNO_3 , are water soluble)

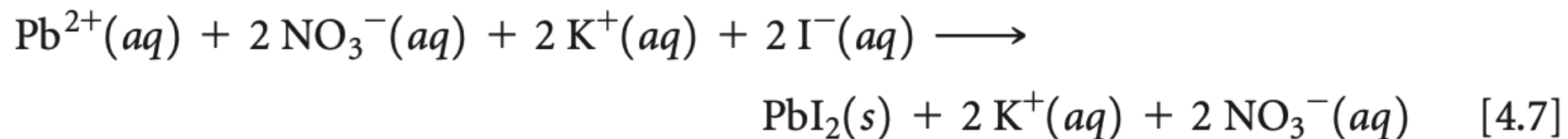
Ionic Equations

In writing equations for reactions in aqueous solution, it is often useful to indicate whether the dissolved substances are present predominantly as ions or as molecules. Let's reconsider the precipitation reaction between $\text{Pb}(\text{NO}_3)_2$ and 2 KI:



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. Because $\text{Pb}(\text{NO}_3)_2$, KI, and KNO_3 are all water-soluble ionic compounds and therefore strong electrolytes, we can write the equation in a form that indicates which species exist as ions in the solution:





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

Notice that $\text{K}^{+}(\text{aq})$ and $\text{NO}_3^{-}(\text{aq})$ appear on both sides of Equation 4.7. Ions that appear in identical forms on both sides of a complete ionic equation, called **spectator ions**, play no direct role in the reaction. When spectator ions are omitted from the equation (they cancel out like algebraic quantities), we are left with the **net ionic equation**, which is one that includes only the ions and molecules directly involved in the reaction:



Because charge is conserved in reactions, the sum of the ionic charges must be the same on both sides of a balanced net ionic equation. In this case the 2+ charge of the cation and the two 1- charges of the anions add to zero, the charge of the electrically neutral product. *If every ion in a complete ionic equation is a spectator, no reaction occurs.*

GIVE IT SOME THOUGHT

Which ions, if any, are spectator ions in the reaction $\text{AgNO}_3(aq) + \text{NaCl}(aq) \longrightarrow \text{AgCl}(s) + \text{NaNO}_3(aq)$?

Net ionic equations illustrate the similarities between various reactions involving electrolytes. For example, Equation 4.8 expresses the essential feature of the precipitation reaction between any strong electrolyte containing $\text{Pb}^{2+}(aq)$ and any strong electrolyte containing $\text{I}^{-}(aq)$: The ions combine to form a precipitate of PbI_2 . Thus, a net ionic equation demonstrates that more than one set of reactants can lead to the same net reaction. For example, aqueous solutions of KI and MgI_2 share many chemical similarities because both contain I^{-} ions. Either solution when mixed with a $\text{Pb}(\text{NO}_3)_2$ solution produces $\text{PbI}_2(s)$. The complete ionic equation, on the other hand, identifies the actual reactants that participate in a reaction.

The following steps summarize the procedure for writing net ionic equations:

1. Write a balanced molecular equation for the reaction.
2. Rewrite the equation to show the ions that form in solution when each soluble strong electrolyte dissociates into its ions. *Only strong electrolytes dissolved in aqueous solution are written in ionic form.*
3. Identify and cancel spectator ions.

4.3 ACIDS, BASES, AND NEUTRALIZATION REACTIONS

Many acids and bases are industrial and household substances (◀ **FIGURE 4.5**), and some are important components of biological fluids. Hydrochloric acid, for example, is an important industrial chemical and the main constituent of gastric juice in your stomach. Acids and bases are also common electrolytes.



▲ **FIGURE 4.5** Vinegar and lemon juice are common household acids. Ammonia and baking soda (sodium bicarbonate) are common household bases.

Acids

As noted in Section 2.8, **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*. Molecular models of three common acids are shown in ◀ **FIGURE 4.6**.

Protons in aqueous solution are solvated by water molecules, just as other cations are [Figure 4.3(a)]. In writing chemical equations involving protons in water, therefore, we write $\text{H}^+(\text{aq})$.

Molecules of different acids ionize to form different numbers of H^+ ions. Both HCl and HNO_3 are *monoprotic* acids, yielding one H^+ per molecule of acid. Sulfuric acid, H_2SO_4 , is a *diprotic* acid, one that yields two H^+ per molecule of acid. The ionization of H_2SO_4 and other diprotic acids occurs in two steps:

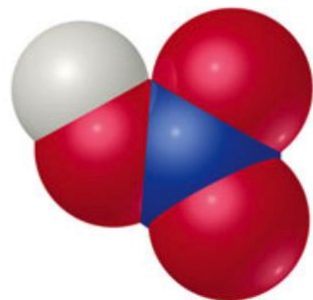


Although H_2SO_4 is a strong electrolyte, only the first ionization (Equation 4.9) is complete. Thus, aqueous solutions of sulfuric acid contain a mixture of $\text{H}^+(\text{aq})$, $\text{HSO}_4^-(\text{aq})$, and $\text{SO}_4^{2-}(\text{aq})$.

The molecule CH_3COOH (acetic acid) that we have mentioned frequently is the primary component in vinegar. Acetic acid has four hydrogens, as Figure 4.6 shows, but only one of them, the H in the COOH group, is ionized in water. The three other hydrogens are bound to carbon and do not break their C—H bonds in water.



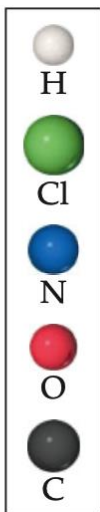
Hydrochloric acid, HCl



Nitric acid, HNO_3



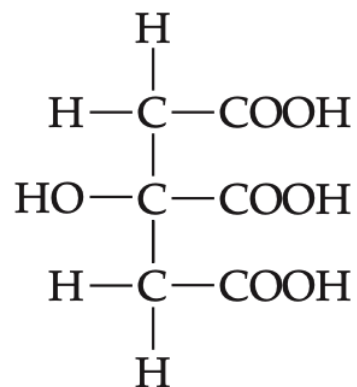
Acetic acid, CH_3COOH



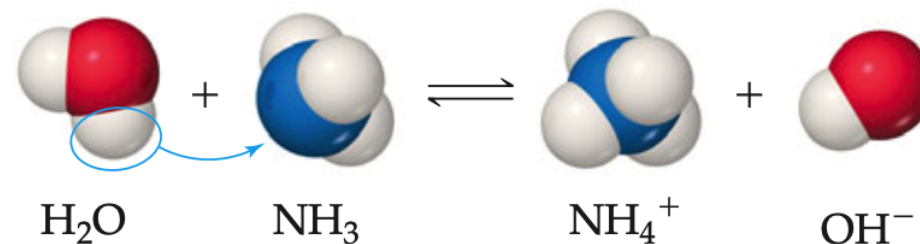
▲ **FIGURE 4.6** Molecular models of three common acids.

GIVE IT SOME THOUGHT

The structural formula of citric acid, a main component of citrus fruits, is



How many $\text{H}^+(\text{aq})$ can be generated by each citric acid molecule dissolved in water?

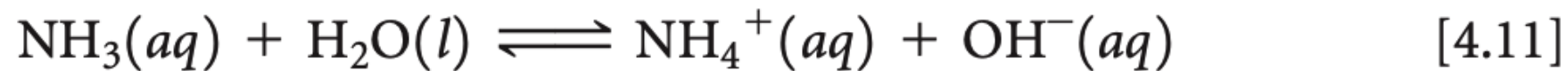


▲ FIGURE 4.7 Hydrogen ion transfer. An H_2O molecule acts as a proton donor (acid), and NH_3 acts as a proton acceptor (base). Only a fraction of the NH_3 molecules react with H_2O . Consequently, NH_3 is a weak electrolyte.

Bases

Bases are substances that accept (react with) H^+ ions. Bases produce hydroxide ions (OH^-) when they dissolve in water. Ionic hydroxide compounds, such as NaOH , KOH , and $\text{Ca}(\text{OH})_2$, are among the most common bases. When dissolved in water, they dissociate into ions, introducing OH^- ions into the solution.

Compounds that do not contain OH^- ions can also be bases. For example, ammonia (NH_3) is a common base. When added to water, it accepts an H^+ ion from a water molecule and thereby produces an OH^- ion (► **FIGURE 4.7**):



Ammonia is a weak electrolyte because only about 1% of the NH_3 forms NH_4^+ and OH^- ions.

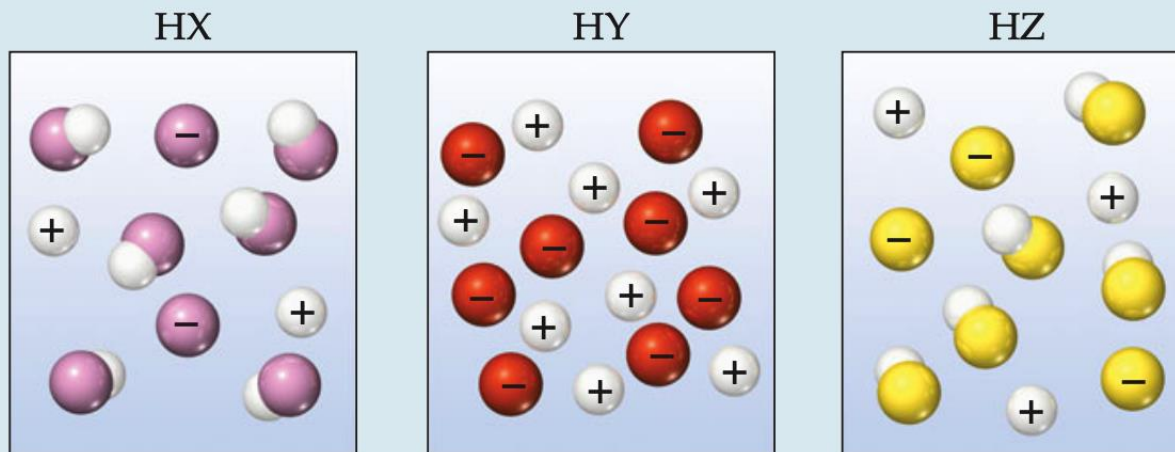
Strong and Weak Acids and Bases

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. The reactivity of an acid, however, can depend on the anion as well as on $\text{H}^+(\text{aq})$ concentration. For example, hydrofluoric acid (HF) is a weak acid (only partly ionized in aqueous solution), but it is very reactive and vigorously attacks many substances, including glass. This reactivity is due to the combined action of $\text{H}^+(\text{aq})$ and $\text{F}^-(\text{aq})$.

▼ **TABLE 4.2** lists the strong acids and bases we are most likely to encounter. You need to commit this information to memory in order to correctly identify strong electrolytes and write net ionic equations. The brevity of this list tells us that most acids are weak. (For H_2SO_4 , as we noted earlier, only the first proton completely ionizes.) The only common strong bases are the common soluble metal hydroxides. Most other metal hydroxides are insoluble in water. The most common weak base is NH_3 , which reacts with water to form OH^- ions (Equation 4.11).

SAMPLE EXERCISE 4.5 Comparing Acid Strengths

The following diagrams represent aqueous solutions of acids HX, HY, and HZ, with water molecules omitted for clarity. Rank the acids from strongest to weakest.



SOLUTION

Analyze We are asked to rank three acids from strongest to weakest, based on schematic drawings of their solutions.

Plan We can determine the relative numbers of uncharged molecular species in the diagrams. The strongest acid is the one with the most H⁺ ions and fewest undissociated molecules in solution. The weakest acid is the one with the largest number of undissociated molecules.

Solve The order is $\text{HY} > \text{HZ} > \text{HX}$. HY is a strong acid because it is totally ionized (no HY molecules in solution), whereas both HX and HZ are weak acids, whose solutions consist of a mixture of molecules and ions. Because HZ contains more H⁺ ions and fewer molecules than HX, it is a stronger acid.

PRACTICE EXERCISE

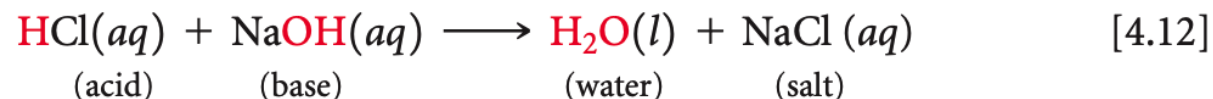
Imagine a diagram showing 10 Na⁺ ions and 10 OH⁻ ions. If this solution were mixed with the one pictured above for HY, what species would be present in a diagram that represents the combined solutions after any possible reaction?

Answer: The diagram would show 10 Na⁺ ions, 2 OH⁻ ions, 8 Y⁻ ions, and 8 H₂O molecules.

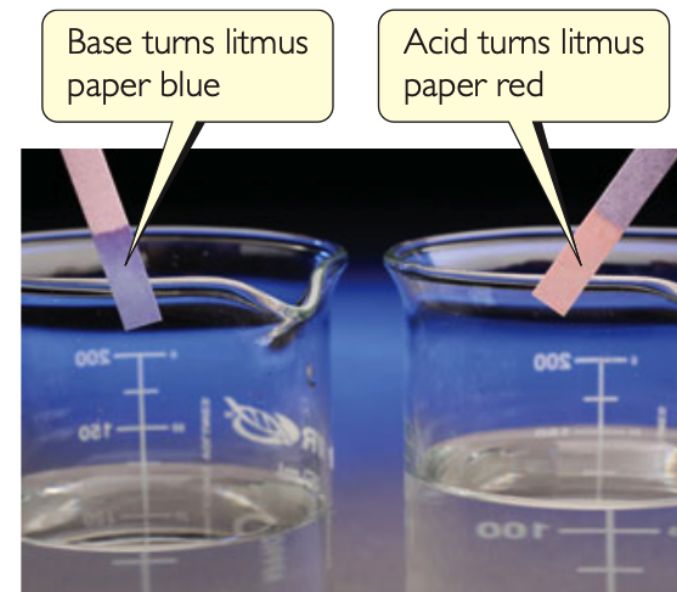
Neutralization Reactions and Salts

The properties of acidic solutions are quite different from those of basic solutions. Acids have a sour taste, whereas bases have a bitter taste.* Acids change the colors of certain dyes in a way that differs from the way bases affect the same dyes. This is the principle behind the indicator known as litmus paper (► **FIGURE 4.8**). In addition, acidic and basic solutions differ in chemical properties in several other important ways that we explore in this chapter and in later chapters.

When a solution of an acid and a solution of a base are mixed, a **neutralization reaction** occurs. The products of the reaction have none of the characteristic properties of either the acidic solution or the basic solution. For example, when hydrochloric acid is mixed with a solution of sodium hydroxide, the reaction is



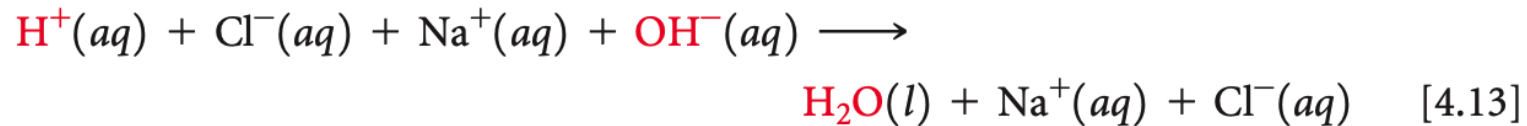
*Tasting chemical solutions is not a good practice. However, we have all had acids such as ascorbic acid (vitamin C), acetylsalicylic acid (aspirin), and citric acid (in citrus fruits) in our mouths, and we are familiar with their characteristic sour taste. Soaps, which are basic, have the characteristic bitter taste of bases.



▲ **FIGURE 4.8** Litmus paper. Litmus paper is coated with dyes that change color in response to exposure to either acids or bases.

Water and table salt, NaCl, are the products of the reaction. By analogy to this reaction, the term **salt** has come to mean any ionic compound whose cation comes from a base (for example, Na^+ from NaOH) and whose anion comes from an acid (for example, Cl^- from HCl). In general, *a neutralization reaction between an acid and a metal hydroxide produces water and a salt.*

Because HCl, NaOH, and NaCl are all water-soluble strong electrolytes, the complete ionic equation associated with Equation 4.12 is



Therefore, the net ionic equation is



Equation 4.14 summarizes the main feature of the neutralization reaction between any strong acid and any strong base: $\text{H}^+(aq)$ and $\text{OH}^-(aq)$ ions combine to form H_2O .

▼ **FIGURE 4.9** shows the neutralization reaction between hydrochloric acid and the water-insoluble base $\text{Mg}(\text{OH})_2$:

Molecular equation:

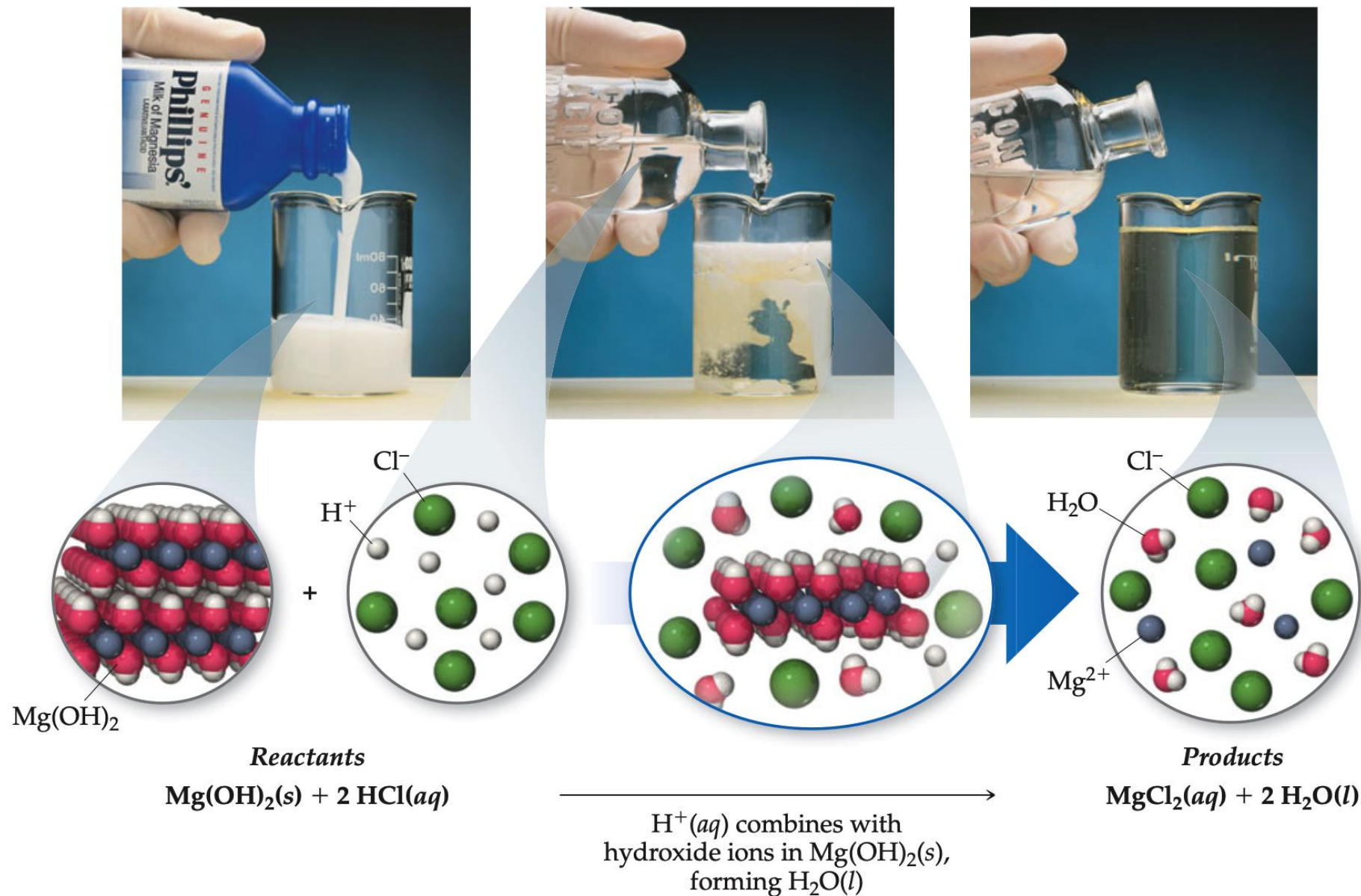


Net ionic equation:



Notice that the OH^- ions (this time in a solid reactant) and H^+ ions combine to form H_2O . Because the ions exchange partners, neutralization reactions between acids and metal hydroxides are metathesis reactions.

Adding just a few drops of hydrochloric acid would not be sufficient to dissolve all the $\text{Mg}(\text{OH})_2(\text{s})$. Why not?



▲ **FIGURE 4.9** Neutralization reaction between $\text{Mg}(\text{OH})_2(\text{s})$ and hydrochloric acid. Milk of magnesia is a suspension of water-insoluble magnesium hydroxide, $\text{Mg}(\text{OH})_2(\text{s})$, in water. When sufficient hydrochloric acid, $\text{HCl}(\text{aq})$, is added a reaction ensues that leads to an aqueous solution containing $\text{Mg}^{2+}(\text{aq})$ and $\text{Cl}^-(\text{aq})$ ions.

Neutralization Reactions with Gas Formation

Many bases besides OH^- react with H^+ to form molecular compounds. Two of these that you might encounter in the laboratory are the sulfide ion and the carbonate ion. Both of these anions react with acids to form gases that have low solubilities in water. Hydrogen sulfide (H_2S), the substance that gives rotten eggs their foul odor, forms when an acid such as $\text{HCl}(aq)$ reacts with a metal sulfide such as Na_2S :

Molecular equation:



Net ionic equation:



Carbonates and bicarbonates react with acids to form $\text{CO}_2(g)$. Reaction of CO_3^{2-} or HCO_3^- with an acid first gives carbonic acid (H_2CO_3). For example, when hydrochloric acid is added to sodium bicarbonate, the reaction is



Carbonic acid is unstable. If present in solution in sufficient concentrations, it decomposes to H_2O and CO_2 , which escapes from the solution as a gas:



The overall reaction is summarized by the equations

Molecular equation:

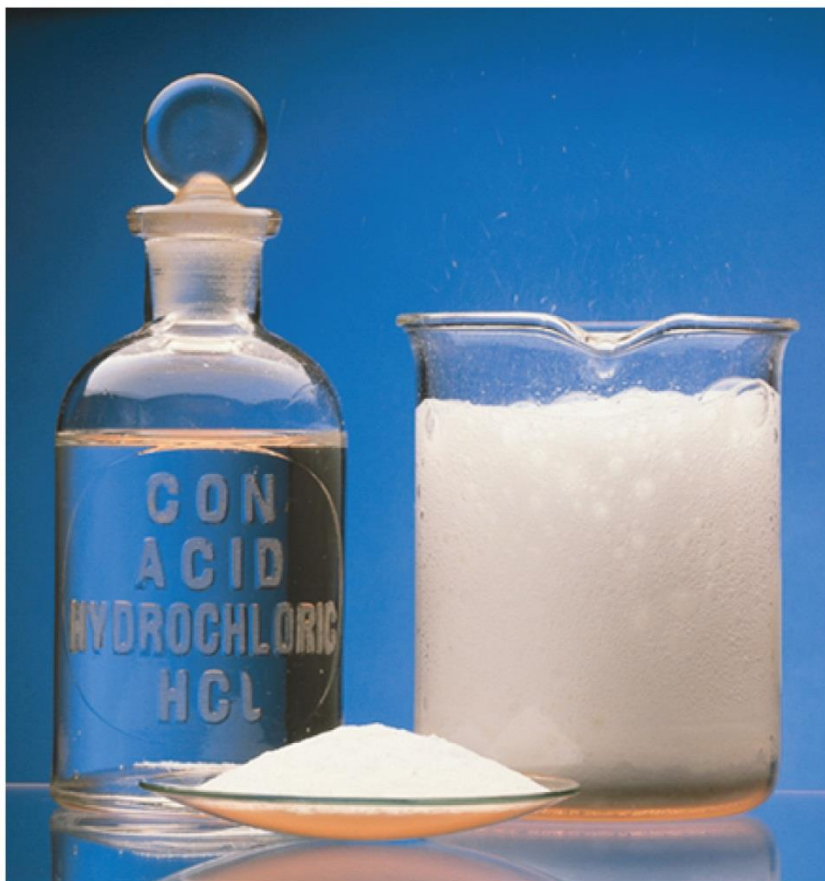


Net ionic equation:



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 the fizzing caused by $\text{CO}_2(g)$ formation stops. Sometimes sodium bicarbonate is used as an antacid to soothe an upset stomach. In that case the HCO_3^- reacts with stomach acid to form $\text{CO}_2(g)$.

Acids



- **Arrhenius** defined acids as substances that increase the concentration of H^+ when dissolved in water.
- **Brønsted and Lowry** defined them as proton donors.

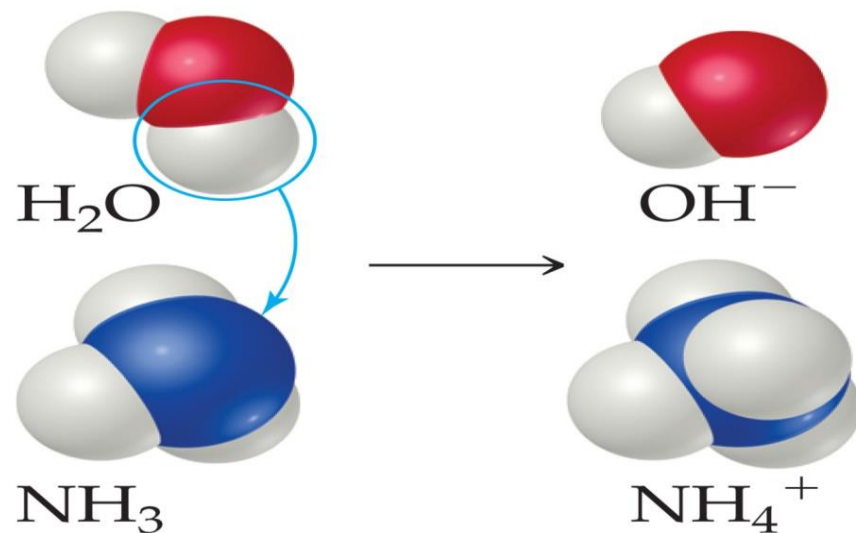
Bases

- **Arrhenius** defined bases as substances that increase the concentration of OH^- when dissolved in water.
- **Brønsted and Lowry** defined them as proton acceptors.



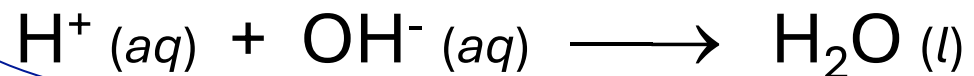
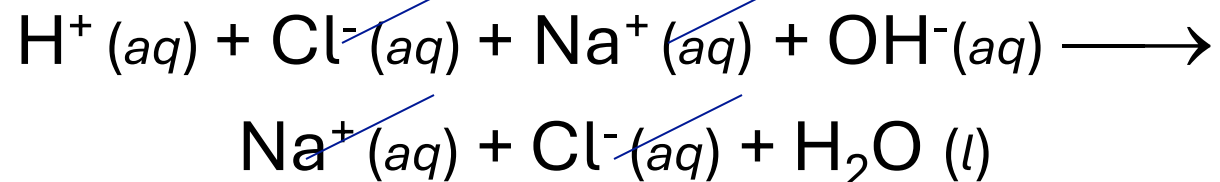
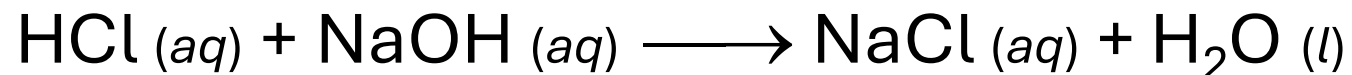
Acid-Base Reactions

In an acid-base reaction, the acid donates a proton (H^+) to the base.



Neutralization Reactions

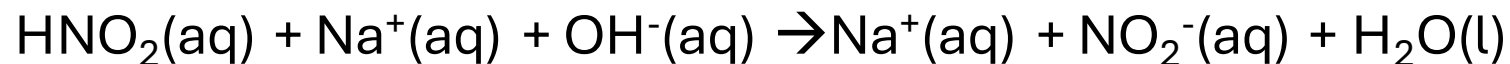
When a strong acid reacts with a strong base, the net ionic equation is...



Neutralization Reactions:

- What happens when the neutralization reaction involves a weak acid (not one of the seven strong acids that you memorized!)?
- A weak acid is a weak electrolyte and will not fully dissociate in water.

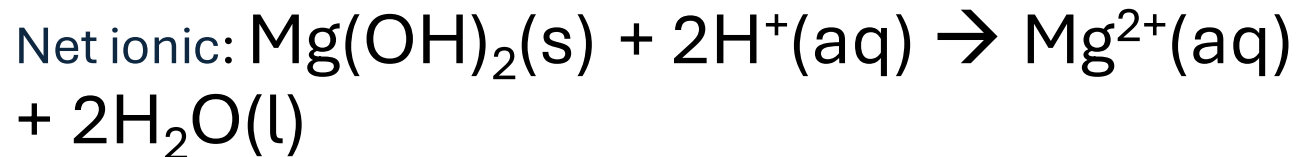
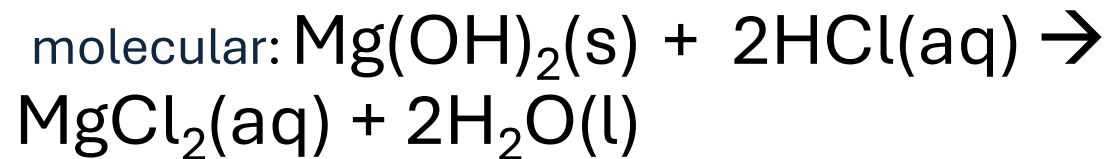
Ex:



Why is $\text{Na}^+(\text{aq})$ the only spectator ion?

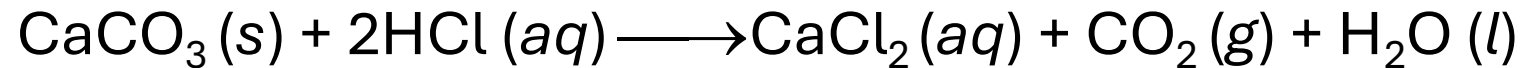
What about net ionic and insoluble salts?

- Write the molecular equation and net ionic equation for the reaction between magnesium hydroxide and hydrochloric acid.



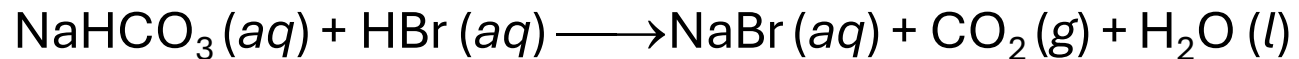
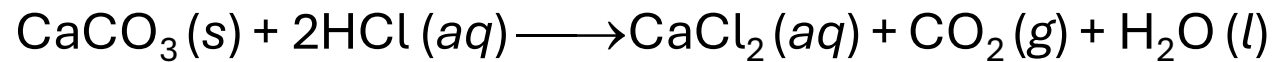
Gas-Forming Reactions

- Some double replacement reactions do not give the product expected.
- In this reaction, the expected product (H_2CO_3) decomposes to give a gaseous product (CO_2).



Gas-Forming Reactions

When a carbonate or bicarbonate reacts with an acid, the products are a salt, carbon dioxide, and water.



Gas-Forming Reactions

1. metal carbonates + acid \rightarrow metal salt + $\text{CO}_2(\text{g})$ + $\text{H}_2\text{O}(\text{l})$



2. Metal sulfide + acid \rightarrow metal salt + $\text{H}_2\text{S}(\text{g})$



3. Metal Sulfite + acid \rightarrow metal salt + $\text{SO}_2(\text{g})$ + $\text{H}_2\text{O}(\text{l})$

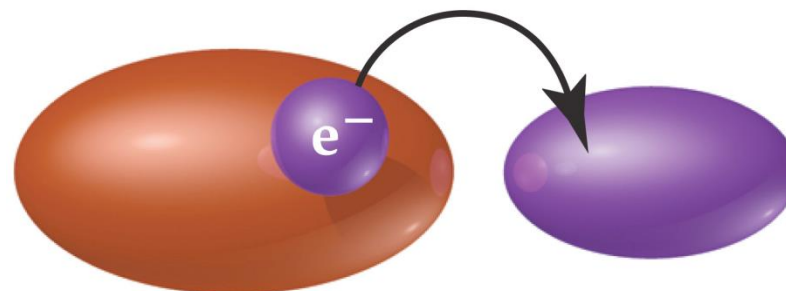


4. Ammonium salt + strong base \rightarrow metal salt + $\text{NH}_3(\text{g})$ + $\text{H}_2\text{O}(\text{l})$



Oxidation-Reduction Reactions

- An **oxidation** occurs when an atom or ion *loses* electrons.
- A **reduction** occurs when an atom or ion *gains* electrons.
- One cannot occur without the other.



Oxidation Numbers

To determine if an oxidation-reduction reaction has occurred, we assign an **oxidation number** to each element in a neutral compound or charged ion.

Oxidation numbers reflect the association (distribution) of electrons in a compound or molecule.

Guidelines have been established to help assign oxidation number

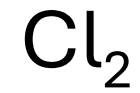
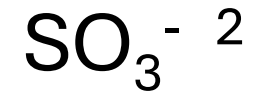
Guidelines for Assigning Oxidation Numbers

1. Elements in their elemental form have an oxidation number of 0 .
2. The oxidation number of a monatomic ion is the same as its charge .
3. Oxygen is assigned an oxidation state of -2 in its covalent compounds (ex. CO_2). An exception to this rule occurs with peroxides (O_2^{2-}).
4. Hydrogen is assigned +1 when found in covalent compounds with nonmetals. When forming metal hydrides, it is assigned -1.
5. Fluorine is always assigned an oxidation state of -1.

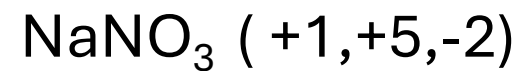
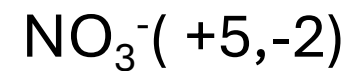
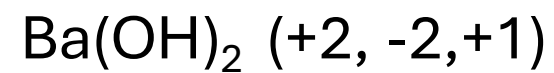
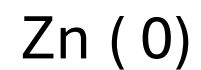
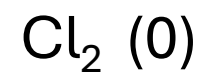
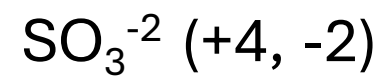
Oxidation Numbers cont.

6. The sum of the oxidation numbers in a neutral compound is 0.
7. The sum of the oxidation numbers in a polyatomic ion is the charge on the ion.

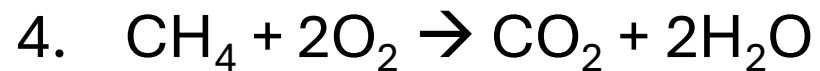
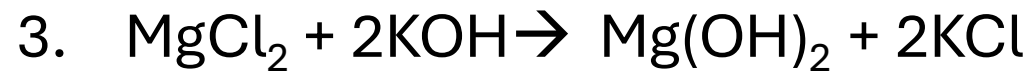
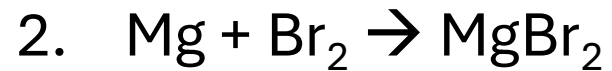
Assign Oxidation Numbers



Answers:

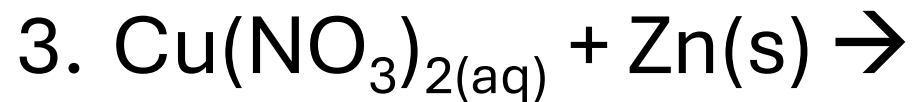
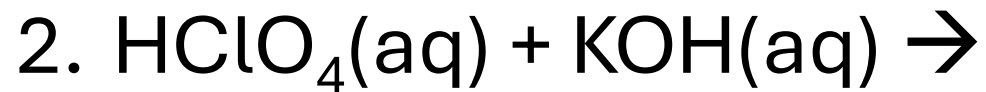
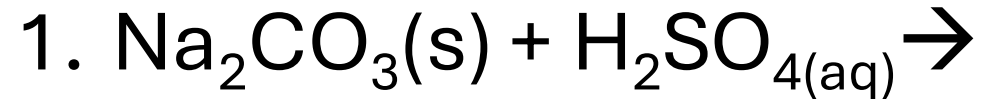


Write Oxidation Numbers for each element and determine if an oxidation-reduction has occurred.



Quick Check:

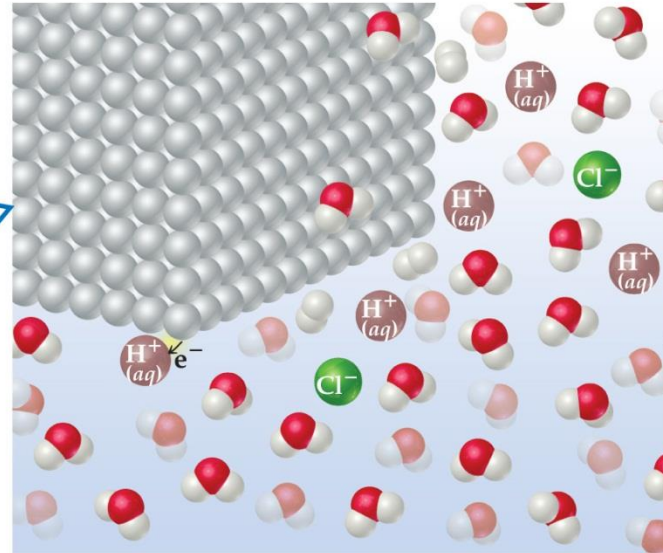
Write the net ionic equation



Answers:



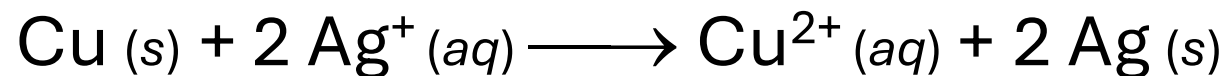
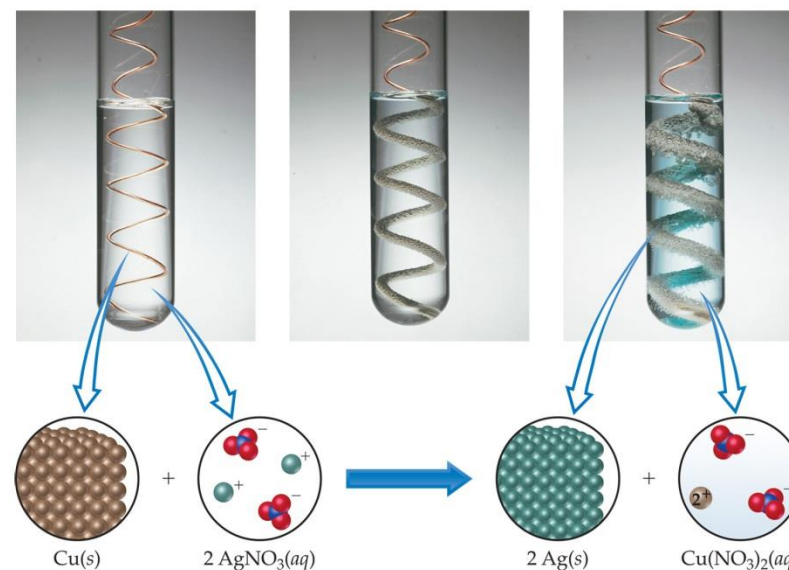
Singe Replacement (Displacement) Reactions



- In displacement reactions, ions oxidize an element.
- The ions, then, are reduced.

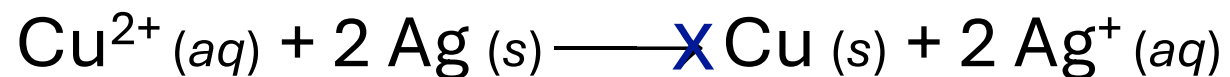
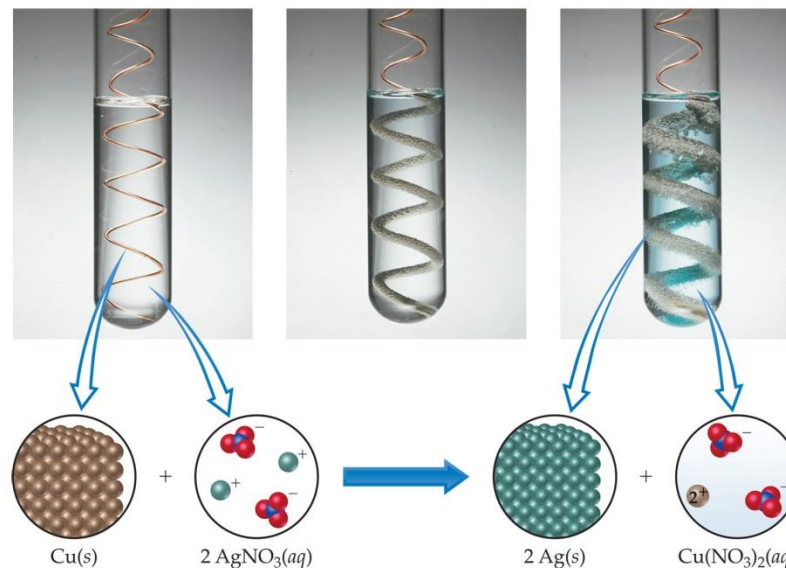
Displacement Reactions

In this reaction,
silver ions oxidize
copper metal.



Displacement Reactions

The reverse reaction, however, does not occur.



Metal reactivity & Activity Series

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	$\text{Au}(s) \longrightarrow \text{Au}^{3+}(aq) + 3e^-$



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Steps for balancing half reactions:

1. Recognize reaction as a redox reaction by assigning oxidation numbers.
2. Separate the process into half-reactions- (Leo Ger)
3. Balance atoms of elements for each half reaction.
4. Balance each half reaction for charge (e-).
5. Multiply each half reaction by an appropriate factor (balance electrons)
6. Add the half reactions to produce the overall balance equations. Simplify if needed.

Practice: half reactions

Balance the following net ionic equation:



Half Reaction: Acidic Solution

- Additional step:
 - Balance oxygen's by adding H₂O,
 - balance hydrogen's with H⁺ ions.

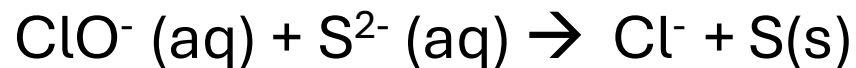
Try it!



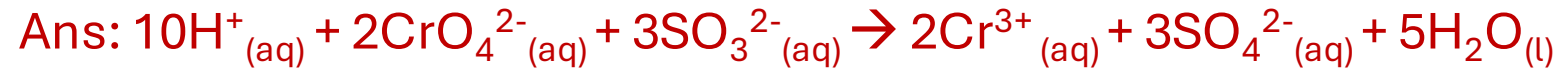
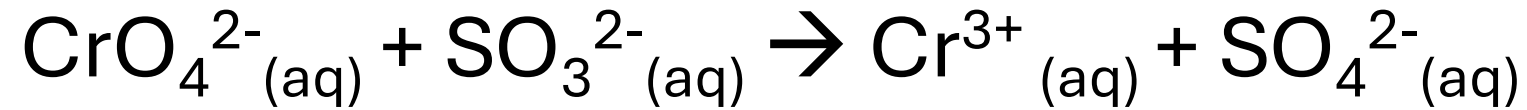
Half Reaction: Basic Solutions

- Additional step:
 - In the final step, for each H^+ in the equation, add an OH^- on both sides of the equation.
 - On one side combine H^+ , OH^- to H_2O
 - Simplify the each by reducing multiple H_2O

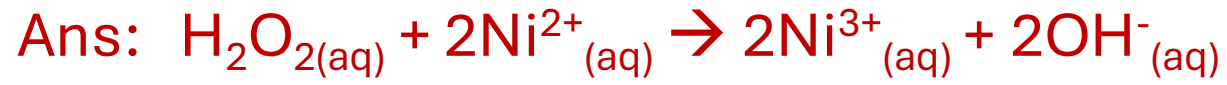
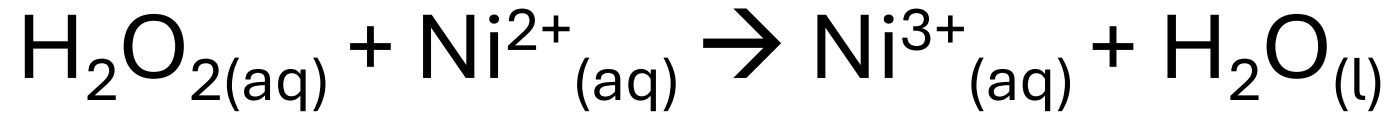
Try one:



Balance the following reaction in **acid** solution:



Balance the following reaction in **basic** solution



4.4 | OXIDATION-REDUCTION REACTIONS

In precipitation reactions, cations and anions come together to form an insoluble ionic compound. In neutralization reactions, H^+ ions and OH^- ions come together to form H_2O molecules. Now let's consider a third kind of reaction, one in which electrons are transferred from one reactant to another. Such reactions are called either **oxidation-reduction reactions** or **redox reactions**. In this chapter we concentrate on redox reactions where one of the reactants is a metal in its elemental form.

Oxidation and Reduction

One of the most familiar redox reactions is *corrosion* of a metal (▼ **FIGURE 4.11**). In some instances corrosion is limited to the surface of the metal, with the green coating that forms on copper roofs and statues being one such case. In other instances the corrosion goes deeper, eventually compromising the structural integrity of the metal. Iron rusting is an important example.

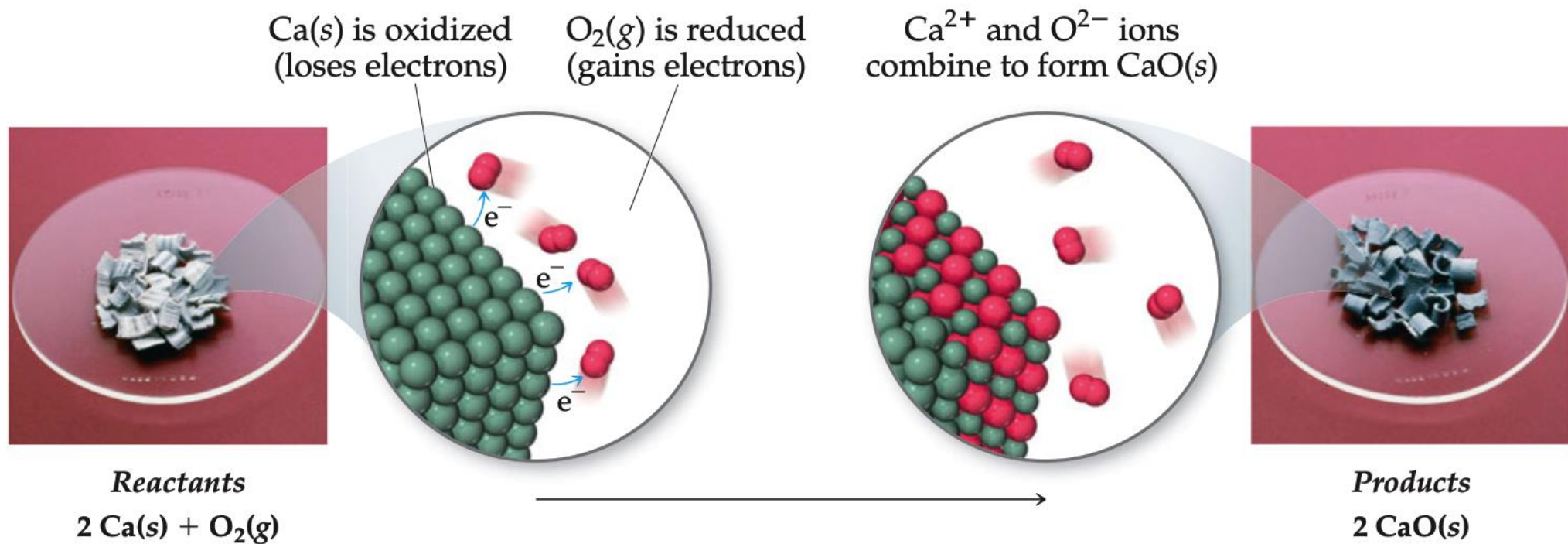
Corrosion is the conversion of a metal into a metal compound by a reaction between the metal and some substance in its environment. When a metal corrodes, each metal atom loses electrons and so forms a cation, which can combine with an anion to form an ionic compound. The green coating on the Statue of Liberty contains Cu^{2+} combined with carbonate and hydroxide anions, rust contains Fe^{3+} combined with oxide and hydroxide anions, and silver tarnish contains Ag^+ combined with sulfide anions.

When an atom, ion, or molecule becomes more positively charged (that is, when it loses electrons), we say that it has been oxidized. *Loss of electrons by a substance is called oxidation*. The term *oxidation* is used because the first reactions of this sort to be studied were reactions with oxygen. Many metals react directly with O_2 in air to form metal oxides. In these reactions the metal loses electrons to oxygen, forming an ionic compound of the metal ion and oxide ion. The familiar example of rusting involves the reaction between iron metal and oxygen in the presence of water. In this process Fe is *oxidized* (loses electrons) to form Fe^{3+} .

The reaction between iron and oxygen tends to be relatively slow, but other metals, such as the alkali and alkaline earth metals, react quickly upon exposure to air. ► **FIGURE 4.12** shows how the bright metallic surface of calcium tarnishes as CaO forms in the reaction



In this reaction Ca is oxidized to Ca^{2+} and neutral O_2 is transformed to O^{2-} ions. 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*. When one reactant loses electrons (that is, when it is *oxidized*), another reactant must gain them. In other words, oxidation of one substance must be accompanied by reduction of some other substance.



▲ **FIGURE 4.12** Oxidation of calcium metal by molecular oxygen. The oxidation involves transfer of electrons from the calcium metal to the O₂, leading to formation of CaO.

Oxidation Numbers

Before we can identify an oxidation-reduction reaction, we must have a bookkeeping system—a way of keeping track of electrons gained by the substance being reduced and electrons lost by the substance being oxidized. The concept of oxidation numbers (also called *oxidation states*) was devised as a way of doing this. Each atom in a neutral substance or ion is assigned an **oxidation number**. For monatomic ions the oxidation number is the same as the charge. For neutral molecules and polyatomic ions, the oxidation number of a given atom is a hypothetical charge. This charge is assigned by artificially dividing up the electrons among the atoms in the molecule or ion. We use the following rules for assigning oxidation numbers:

1. For an atom in its **elemental form**, the oxidation number is always zero. Thus, each H atom in the H_2 molecule has an oxidation number of 0 and each P atom in the P_4 molecule has an oxidation number of 0.
2. For any **monatomic ion** the oxidation number equals the ionic charge. Thus, K^+ has an oxidation number of +1, S^{2-} has an oxidation number of -2 , and so forth. In ionic compounds the alkali metal ions (group 1A) always have a 1+ charge and therefore an oxidation number of +1. The alkaline earth metals (group 2A) are always +2, and aluminum (group 3A) is always +3 in ionic compounds. (In writing oxidation numbers we will write the sign before the number to distinguish them from the actual electronic charges, which we write with the number first.)
3. **Nonmetals** usually have negative oxidation numbers, although they can sometimes be positive:
 - (a) 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 .
 - (b) The oxidation number of **hydrogen** is usually +1 when bonded to nonmetals and -1 when bonded to metals.
 - (c) 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, they have positive oxidation states.
4. **The sum of the oxidation numbers of all atoms in a neutral compound is zero. The sum of the oxidation numbers in a polyatomic ion equals the charge of the ion.** For example, in the hydronium ion H_3O^+ the oxidation number of each hydrogen is +1 and that of oxygen is -2 . Thus, the sum of the oxidation numbers is $3(+1) + (-2) = +1$, which equals the net charge of the ion. This rule is useful in obtaining the oxidation number of one atom in a compound or ion if you know the oxidation numbers of the other atoms, as illustrated in Sample Exercise 4.8.

SAMPLE EXERCISE 4.8 Determining Oxidation Numbers

Determine the oxidation number of sulfur in (a) H_2S , (b) S_8 , (c) SCl_2 , (d) Na_2SO_3 , (e) SO_4^{2-} .

SOLUTION

Analyze We are asked to determine the oxidation number of sulfur in two molecular species, in the elemental form, and in two substances containing ions.

Plan In each species the sum of oxidation numbers of all the atoms must equal the charge on the species. We will use the rules outlined previously to assign oxidation numbers.

Solve

(a) When bonded to a nonmetal, hydrogen has an oxidation number of +1 (rule 3b). Because the H_2S molecule is neutral, the sum of the oxidation numbers must equal zero (rule 4). Letting x equal the oxidation number of S, we have $2(+1) + x = 0$. Thus, S has an oxidation number of -2 .

(b) Because this is an elemental form of sulfur, the oxidation number of S is 0 (rule 1).

(c) Because this is a binary compound, we expect chlorine to have an oxidation number of -1 (rule 3c). The sum of the oxidation numbers must equal zero (rule 4). Letting x equal the oxidation number of S, we have $x + 2(-1) = 0$. Consequently, the oxidation number of S must be $+2$.

(d) Sodium, an alkali metal, always has an oxidation number of $+1$ in its compounds (rule 2). Oxygen has a common oxidation state of -2 (rule 3a). Letting x equal the oxidation number of S, we have $2(+1) + x + 3(-2) = 0$. Therefore, the oxidation number of S in this compound is $+4$.

(e) The oxidation state of O is -2 (rule 3a). The sum of the oxidation numbers equals -2 , the net charge of the SO_4^{2-} ion (rule 4). Thus, we have $x + 4(-2) = -2$. From this relation we conclude that the oxidation number of S in this ion is $+6$.

Comment These examples illustrate that the oxidation number of a given element depends on the compound in which it occurs. The oxidation numbers of sulfur, as seen in these examples, range from -2 to $+6$.

PRACTICE EXERCISE

What is the oxidation state of the boldfaced element in (a) P_2O_5 , (b) NaH , (c) $\text{Cr}_2\text{O}_7^{2-}$, (d) SnBr_4 , (e) BaO_2 ?

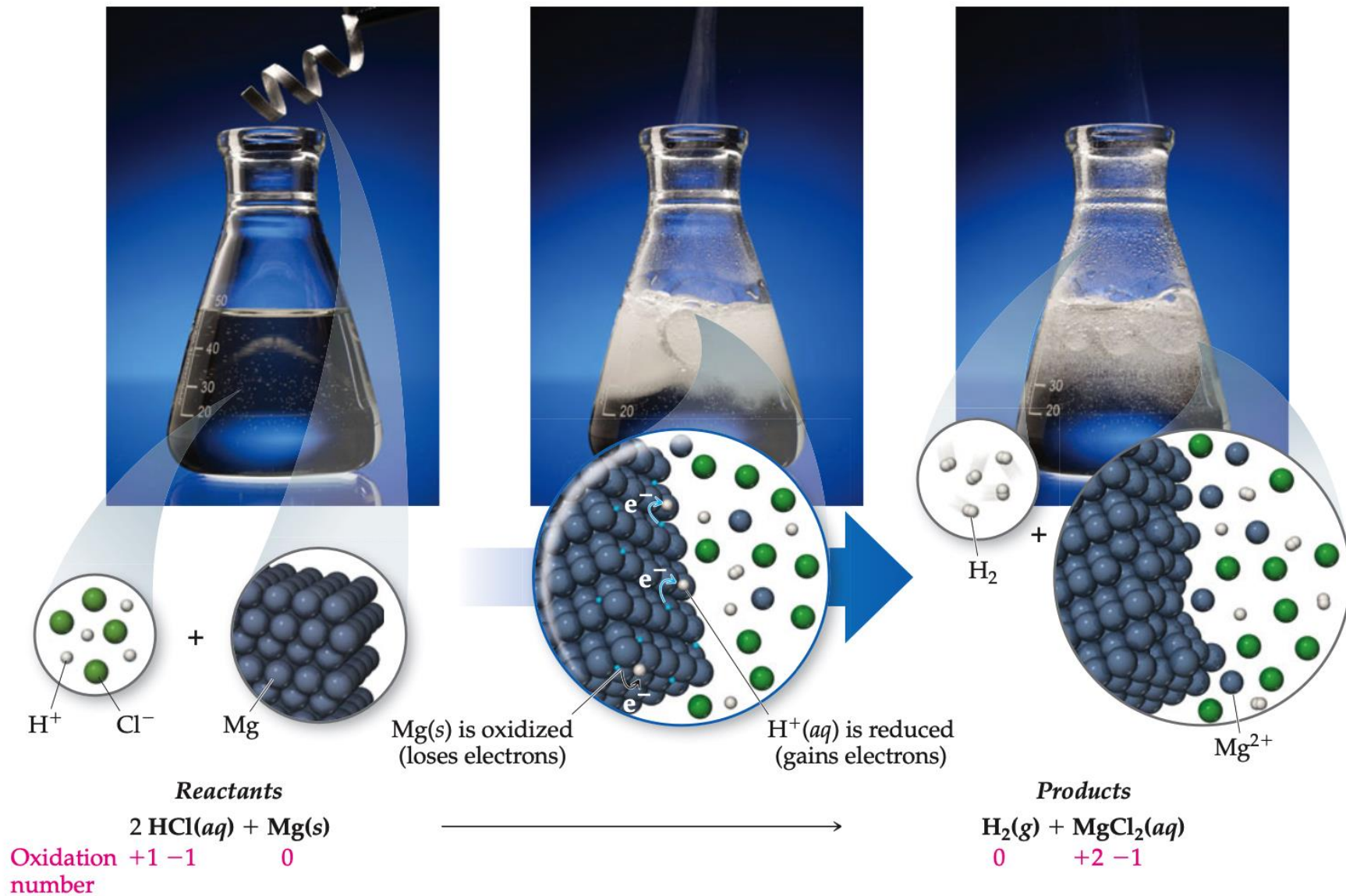
Answers: (a) $+5$, (b) -1 , (c) $+6$, (d) $+4$, (e) -1

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

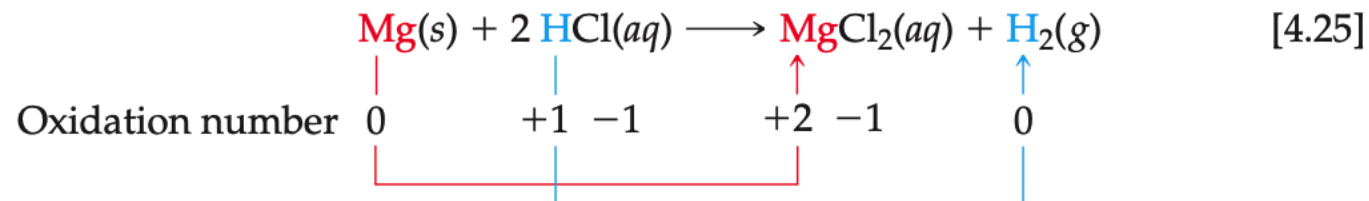


These reactions are called **displacement reactions** because the ion in solution is *displaced* (replaced) through oxidation of an element.

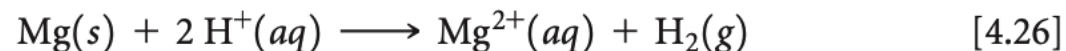


▲ FIGURE 4.13 Reaction of magnesium metal with hydrochloric acid. The metal is readily oxidized by the acid, producing hydrogen gas, $\text{H}_2(g)$, and $\text{MgCl}_2(aq)$.

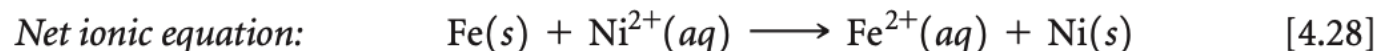
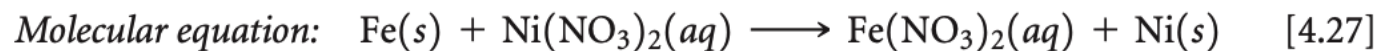
Many metals undergo displacement reactions with acids, producing salts and hydrogen gas. For example, magnesium metal reacts with hydrochloric acid to form magnesium chloride and hydrogen gas (▲ **FIGURE 4.13**):



The oxidation number of Mg changes from 0 to +2, an increase that indicates the atom has lost electrons and has therefore been oxidized. The oxidation number of H⁺ in the acid decreases from +1 to 0, indicating that this ion has gained electrons and has therefore been reduced. Chlorine has an oxidation number of −1 both before and after the reaction, indicating that it is neither oxidized nor reduced. In fact the Cl[−] ions are spectator ions, dropping out of the net ionic equation:



Metals can also be oxidized by aqueous solutions of various salts. Iron metal, for example, is oxidized to Fe²⁺ by aqueous solutions of Ni²⁺ such as Ni(NO₃)₂(aq):



The oxidation of Fe to Fe²⁺ in this reaction is accompanied by the reduction of Ni²⁺ to Ni. Remember: *Whenever one substance is oxidized, another substance must be reduced.*

SAMPLE EXERCISE 4.9 Writing Equations for Oxidation-Reduction Reactions

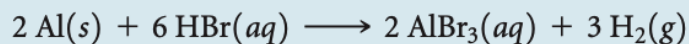
Write the balanced molecular and net ionic equations for the reaction of aluminum with hydrobromic acid.

SOLUTION

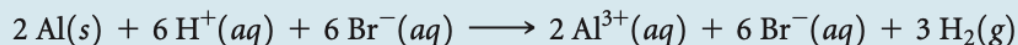
Analyze We must write two equations—molecular and net ionic—for the redox reaction between a metal and an acid.

Plan Metals react with acids to form salts and H₂ gas. To write the balanced equations, we must write the chemical formulas for the two reactants and then determine the formula of the salt, which is composed of the cation formed by the metal and the anion of the acid.

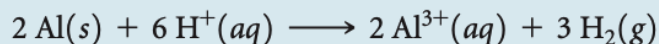
Solve The reactants are Al and HBr. The cation formed by Al is Al³⁺, and the anion from hydrobromic acid is Br⁻. Thus, the salt formed in the reaction is AlBr₃. Writing the reactants and products and then balancing the equation gives the molecular equation:



Both HBr and AlBr₃ are soluble strong electrolytes. Thus, the complete ionic equation is



Because Br⁻ is a spectator ion, the net ionic equation is



Comment The substance oxidized is the aluminum metal because its oxidation state changes from 0 in the metal to +3 in the cation, thereby increasing in oxidation number. The H⁺ is reduced because its oxidation state changes from +1 in the acid to 0 in H₂.

PRACTICE EXERCISE

(a) Write the balanced molecular and net ionic equations for the reaction between magnesium and cobalt(II) sulfate. (b) What is oxidized and what is reduced in the reaction?

Answers: (a) $\text{Mg}(s) + \text{CoSO}_4(aq) \longrightarrow \text{MgSO}_4(aq) + \text{Co}(s)$;
 $\text{Mg}(s) + \text{Co}^{2+}(aq) \longrightarrow \text{Mg}^{2+}(aq) + \text{Co}(s)$, (b) Mg is oxidized and Co²⁺ is reduced.

The Activity Series

Can we predict whether a certain metal will be oxidized either by an acid or by a particular salt? This question is of practical importance as well as chemical interest. According to Equation 4.27, for example, it would be unwise to store a solution of nickel nitrate in an iron container because the solution would dissolve the container. When a metal is oxidized, it forms various compounds. Extensive oxidation can lead to the failure of metal machinery parts or the deterioration of metal structures.

Different metals vary in the ease with which they are oxidized. Zn is oxidized by aqueous solutions of Cu^{2+} , for example, but Ag is not. Zn, therefore, loses electrons more readily than Ag; that is, Zn is easier to oxidize than Ag.

A list of metals arranged in order of decreasing ease of oxidation, such as ► **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*. 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.

The activity series can be used to predict the outcome of reactions between metals and either metal salts or acids. *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:

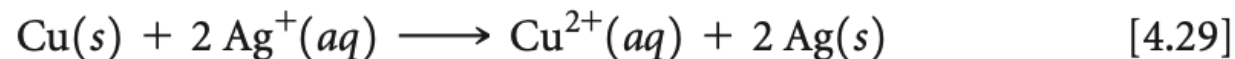
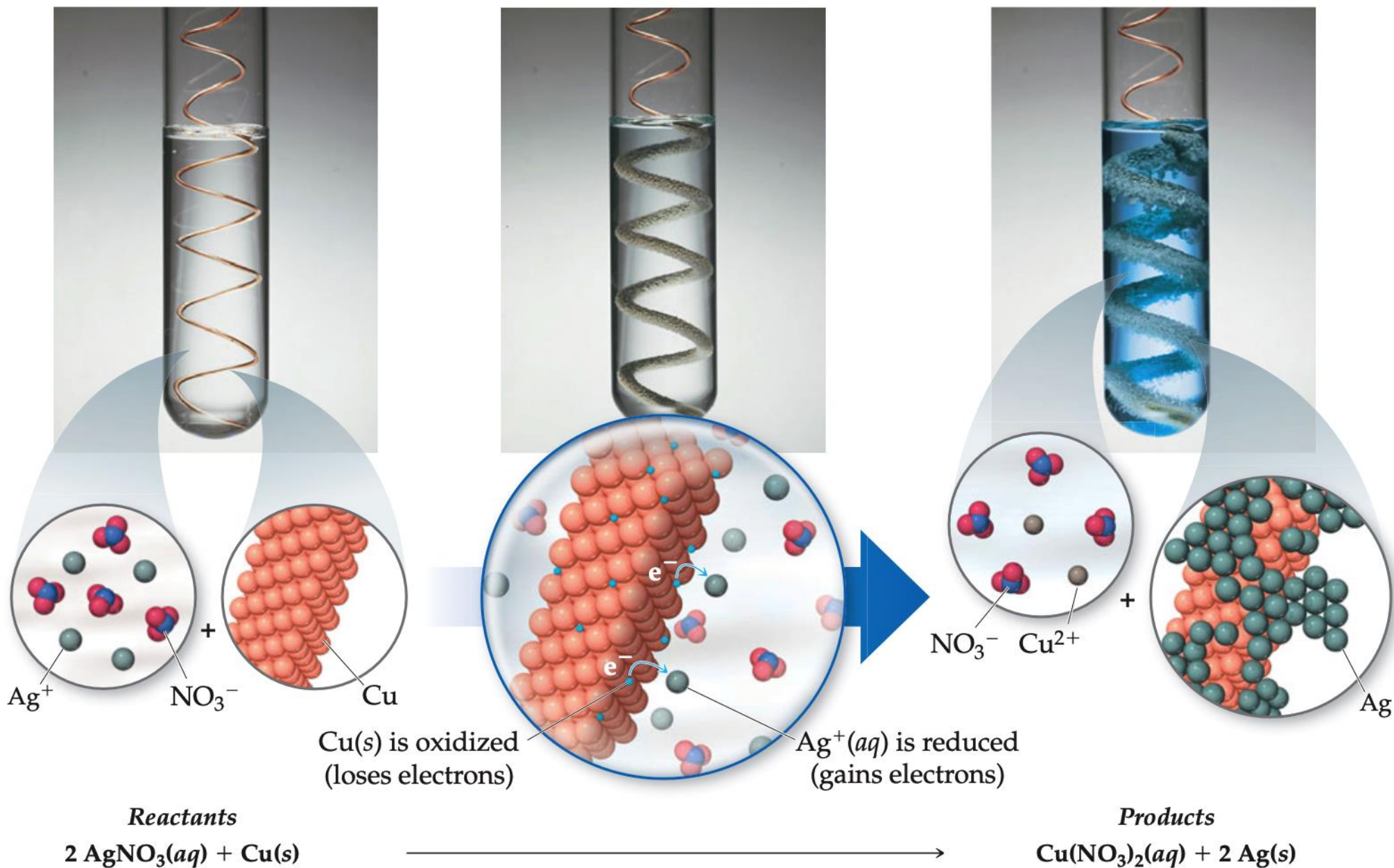


TABLE 4.5 • Activity Series of Metals in Aqueous Solution

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	$\text{Au}(s) \longrightarrow \text{Au}^{3+}(aq) + 3e^-$





SAMPLE EXERCISE 4.10**Determining When an Oxidation-Reduction Reaction Can Occur**

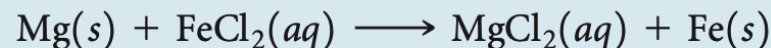
Will an aqueous solution of iron(II) chloride oxidize magnesium metal? If so, write the balanced molecular and net ionic equations for the reaction.

SOLUTION

Analyze We are given two substances—an aqueous salt, FeCl_2 , and a metal, Mg —and asked if they react with each other.

Plan A reaction occurs if the reactant that is a metal in its elemental form (Mg) is located above the reactant that is a metal in its oxidized form (Fe^{2+}) in Table 4.5. If the reaction occurs, the Fe^{2+} ion in FeCl_2 is reduced to Fe , and the Mg is oxidized to Mg^{2+} .

Solve Because Mg is above Fe in the table, the reaction occurs. To write the formula for the salt produced in the reaction, we must remember the charges on common ions. Magnesium is always present in compounds as Mg^{2+} ; the chloride ion is Cl^- . The magnesium salt formed in the reaction is MgCl_2 , meaning the balanced molecular equation is



Both FeCl_2 and MgCl_2 are soluble strong electrolytes and can be written in ionic form, which shows us that Cl^- is a spectator ion in the reaction. The net ionic equation is



The net ionic equation shows that Mg is oxidized and Fe^{2+} is reduced in this reaction.

Check Note that the net ionic equation is balanced with respect to both charge and mass.

PRACTICE EXERCISE

Which of the following metals will be oxidized by $\text{Pb}(\text{NO}_3)_2$: Zn , Cu , Fe ?

Answer: Zn and Fe