

CHAPTER 19

Oxidation-Reduction Reactions

BIG IDEA

In oxidation-reduction reactions, atoms and ions change oxidation states, either by losing electrons (oxidizing) or gaining electrons (reducing).



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SECTION 1

Oxidation and Reduction

SECTION 2

Balancing Redox Equations

SECTION 3

Oxidizing and Reducing Agents

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- Oxidation-Reduction Reactions
- Reduction of Manganese in Permanganate Ion



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Equations and Reactions

Oxidation and Reduction

Key Terms

oxidation	reduced	redox reaction
oxidized	oxidation-reduction reaction	half-reaction
reduction		

MAIN IDEA

Atoms can change their oxidation states.

Chemists classify reactions according to different criteria. You have learned of a few already. For example, a precipitation reaction can be any reaction that takes place in solution in which one of the products is insoluble. An acid-base reaction commonly refers to an acid reacting with a base to produce water and a salt, a neutralization. What distinguishes an oxidation-reduction reaction is that it involves a transfer of electrons, a change in an atom's oxidation state. You previously learned the rules for assigning oxidation states, summarized below in **Figure 1.1**.

FIGURE 1.1

RULES FOR ASSIGNING OXIDATION NUMBERS

Rule	Example
1. The oxidation number of any pure element is 0.	The oxidation number of Na(s) is 0.
2. The oxidation number of a monatomic ion equals the charge on the ion.	The oxidation number of Cl ⁻ is -1.
3. The more-electronegative element in a binary compound is assigned the number equal to the charge it would have if it were an ion.	The oxidation number of O in NO is -2.
4. The oxidation number of fluorine in a compound is always -1.	The oxidation number of F in LiF is -1.
5. Oxygen has an oxidation number of -2 unless it is combined with F, in which case it is +1 or +2, or it is in a peroxide, in which case it is -1.	The oxidation number of O in NO ₂ is -2.
6. Hydrogen's oxidation state in most of its compounds is +1 unless it is combined with a metal, in which case it is -1.	The oxidation number of H in LiH is -1.
7. In compounds, Group 1 and 2 elements and aluminum have oxidation numbers of +1, +2, and +3, respectively.	The oxidation number of Ca in CaCO ₃ is +2.
8. The sum of the oxidation numbers of all atoms in a neutral compound is 0.	The oxidation number of C in CaCO ₃ is +4.
9. The sum of the oxidation numbers of all atoms in a polyatomic ion equals the charge of the ion.	The oxidation number of P in H ₂ PO ₄ ⁻ is +5.

Main Ideas

- ▶ Atoms can change their oxidation states.
- ▶ Oxidation occurs when valence electrons are lost.
- ▶ Reduction occurs when valence electrons are gained.
- ▶ Oxidation and reduction are paired reactions.

FIGURE 1.2

Oxidation States of Chromium Compounds Chromium provides a very visual example of oxidation numbers. Different oxidation states of chromium have dramatically different colors. Solutions with the same oxidation state show less dramatic differences.

CRITICAL THINKING

Relate Examine the tables of ions and their oxidation numbers, **Figures 1.1 and 1.3**, in the chapter “Chemical Formulas and Chemical Compounds.” Compare the elements that have multiple ions or oxidation states with the placement of those elements on the periodic table. What relationship is there between the ability to form multiple ions and where those elements are generally found on the periodic table?

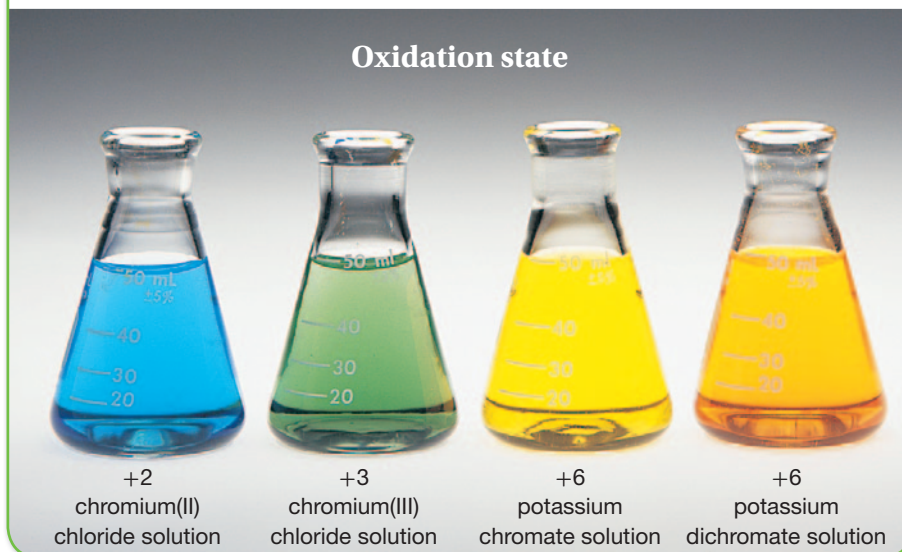
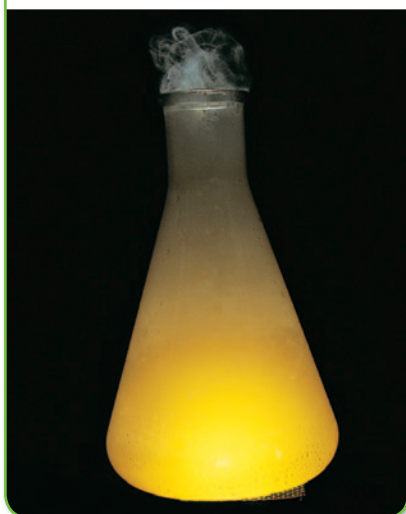


FIGURE 1.3

Oxidation in NaCl Synthesis

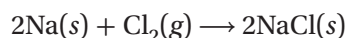
Sodium and chlorine react violently to form NaCl. The synthesis of NaCl from its elements illustrates the oxidation-reduction process.



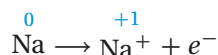
MAIN IDEA

Oxidation occurs when valence electrons are lost.

Processes in which the atoms or ions of an element experience an increase in oxidation state are **oxidation processes**. The combustion of metallic sodium in an atmosphere of chlorine gas is shown in **Figure 1.3**. The sodium ions and chloride ions produced during this strongly exothermic reaction form a cubic crystal lattice in which sodium cations form ionic bonds to chloride anions. The chemical equation for this reaction is written as follows.



The formation of sodium ions illustrates an oxidation process because each sodium atom loses an electron to become a sodium ion. The oxidation state is represented by placing an oxidation number above the symbol of the atom and the ion.

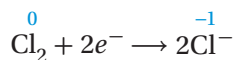


The oxidation state of sodium has changed from 0 to the +1 state of the ion (Rules 1 and 7, **Figure 1.1**). **A species whose oxidation number increases is oxidized.** The sodium atom is *oxidized* to a sodium ion.

▶ MAIN IDEA

Reduction occurs when valence electrons are gained.

Processes in which the oxidation state of an element decreases are **reduction processes**. Consider the behavior of chlorine in its reaction with sodium. Each chlorine atom accepts an electron and becomes a chloride ion. The oxidation state of chlorine decreases from 0 to -1 for the chloride ion (Rules 1 and 2, Figure 1.1).



A species that undergoes a decrease in oxidation state is **reduced**. The chlorine atom is reduced to the chloride ion.

▶ MAIN IDEA

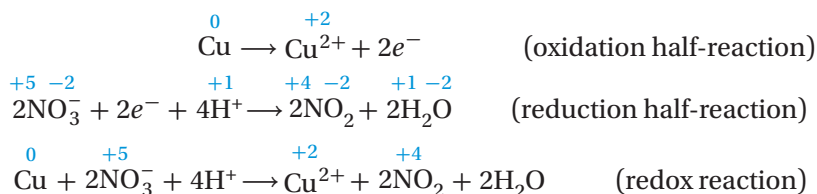
Oxidation and reduction are paired reactions.

Electrons are released in oxidation and acquired in reduction. Therefore, for oxidation to occur during a chemical reaction, reduction must also occur. Furthermore, the number of electrons produced in oxidation must equal the number of electrons acquired in reduction. Recall that electrons are negatively charged and that for charge to be conserved, the number of electrons lost must equal the number of electrons gained. Mass is conserved in any chemical reaction. Therefore, like mass, the electrons exchanged during oxidation and reduction are conserved.

But why do we say a substance is *reduced* when it *gains* electrons? Remember that when electrons are gained, their negative electrical charge will cause the overall oxidation number to drop, that is, be reduced.

A transfer of electrons causes changes in the oxidation states of one or more elements. **Any chemical process in which elements undergo changes in oxidation number is an oxidation-reduction reaction. This name is often shortened to redox reaction.** An example of a redox reaction can be seen in Figure 1.4, in which copper is being oxidized and NO_3^- from nitric acid is being reduced. **The part of the reaction involving oxidation or reduction alone can be written as a half-reaction.** The overall equation for a redox reaction is the sum of two half-reactions. Because the number of electrons involved is the same for oxidation and reduction, they cancel each other out and do not appear in the overall chemical equation.

Equations for the reaction between nitric acid and copper illustrate the relationship between half-reactions and the overall redox reaction.



Notice that electrons lost in oxidation appear on the product side of the oxidation half-reaction. Electrons are gained in reduction and appear as reactants in the reduction half-reaction.

FIGURE 1.4

Oxidation of Copper Copper is oxidized and nitrogen dioxide is produced when this penny is placed in a concentrated nitric acid solution.



WHY IT MATTERS

Photochromic Lenses **S.T.E.M.**

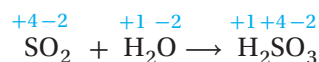
Photochromic eyeglasses darken when exposed to ultraviolet light and become transparent again in the absence of ultraviolet light. This process is the result of oxidation-reduction reactions. Silver chloride and copper(I) chloride are embedded in the lenses. The chloride ions absorb photons, and the silver chloride dissociates and forms chlorine atoms and silver atoms. The elemental silver darkens the lenses. Note that the chlorine ions are oxidized and the silver atoms are reduced. Then, the copper(I) ions reduce the chlorine atoms and form copper(II) ions. In the reverse process, the copper(II) ions oxidize the silver atoms back to the transparent silver ions.

Distinguishing Redox Reactions

Combining the half-reactions gives a full picture of what occurs. Metallic copper reacts in nitric acid, and in so doing, one copper atom is oxidized from Cu to Cu^{2+} as two nitrogen atoms are reduced from a +5 oxidation state to a +4 oxidation state. Both atoms and electrons are conserved. This balanced chemical equation shows this.

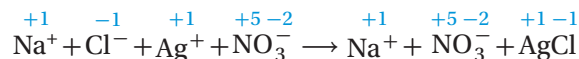


Remember that redox reactions are only those involving atoms that change oxidation states. If none of the atoms in a reaction change oxidation state, the reaction is *not* a redox reaction. For example, sulfur dioxide gas, SO_2 , dissolves in water to form an acidic solution containing a low concentration of sulfurous acid, H_2SO_3 .



No atoms change oxidation states, so this is *not* a redox reaction.

When a solution of sodium chloride is added to a solution of silver nitrate, an ion-exchange reaction occurs, and white silver chloride precipitates.

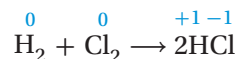


The oxidation state of each monatomic ion remains unchanged. Again, this reaction is *not* an oxidation-reduction reaction.

Redox Reactions and Covalent Bonds

The synthesis of NaCl from its elements involves ionic bonding. Substances with covalent bonds also undergo redox reactions. An oxidation number, unlike an ionic charge, has no physical meaning. That is, the oxidation number assigned to a particular atom is based on its electronegativity relative to the other atoms to which it is bonded in a given molecule; it is not based on any real charge on the atom. For example, an ionic charge of 1^- results from the complete gain of one electron by an atom or other neutral species, whereas an oxidation state of -1 means an increased attraction for a bonding electron. A change in oxidation number does not require a change in actual charge.

When hydrogen burns in chlorine, a covalent bond forms from the sharing of two electrons. The two bonding electrons in the HCl molecule are not shared equally. Rather, the pair of electrons is more strongly attracted to the chlorine atom because of its higher electronegativity.

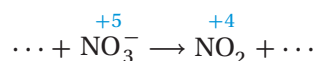


As specified by Rule 3 in **Figure 1.1**, chlorine in HCl is assigned an oxidation number of -1 . Thus, the oxidation number for the chlorine atoms changes from 0, its oxidation number in the elemental state, to -1 ; chlorine atoms are reduced. As specified by Rule 1, the oxidation number of each hydrogen atom in the hydrogen molecule is 0. As specified by Rule 6, the oxidation state of the hydrogen atom in the HCl molecule is $+1$; the hydrogen atom is oxidized.

Thinking of Oxidation States

When you think of atoms changing oxidation states, don't think that either atom has totally lost or totally gained any electrons. In the case of the formation of hydrogen chloride, for example, hydrogen simply has donated a share of its bonding electron to the chlorine; it has not completely transferred that electron. The assignment of oxidation numbers allows an approximation of the electron distribution of a molecule. An element can have different oxidation numbers in different compounds. This difference in oxidation numbers can reveal the difference in electron distribution of the compounds.

Reactants and products in redox reactions are not limited to monatomic ions and uncombined elements. Elements in molecular compounds or polyatomic ions can also be oxidized and reduced if they have more than one nonzero oxidation state. An example of this is provided in the reaction between the copper penny and nitric acid in which the nitrate ion, NO_3^- , is converted to nitrogen dioxide, NO_2 . Nitrogen is reduced in this reaction. Usually, we refer to the oxidation or reduction of the entire molecule or ion. Instead of saying that the nitrogen atom is reduced, we say the nitrate ion is reduced to nitrogen dioxide.



SECTION 1 FORMATIVE ASSESSMENT

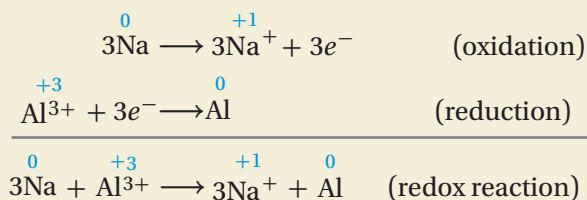
▶ Reviewing Main Ideas

1. What differentiates an oxidation-reduction reaction from other types of reactions, such as precipitation reactions or acid-base reactions?
2. Label each of the following half-reactions as either an oxidation or a reduction half-reaction:
 - a. $\overset{0}{\text{Br}_2} + 2e^- \rightarrow 2\overset{-1}{\text{Br}^-}$
 - b. $\overset{0}{\text{Na}} \rightarrow \overset{+1}{\text{Na}^+} + e^-$
 - c. $2\overset{-1}{\text{Cl}^-} \rightarrow \overset{0}{\text{Cl}_2} + 2e^-$
 - d. $\overset{0}{\text{Cl}_2} + 2e^- \rightarrow 2\overset{-1}{\text{Cl}^-}$
 - e. $\overset{+1}{\text{Na}^+} + e^- \rightarrow \overset{0}{\text{Na}}$
 - f. $\overset{0}{\text{Fe}} \rightarrow \overset{+2}{\text{Fe}^{2+}} + 2e^-$
 - g. $\overset{+2}{\text{Cu}^{2+}} + 2e^- \rightarrow \overset{0}{\text{Cu}}$
 - h. $\overset{+3}{\text{Fe}^{3+}} + e^- \rightarrow \overset{+2}{\text{Fe}^{2+}}$
3. Which of the following equations represent redox reactions?
 - a. $2\text{KNO}_3(s) \rightarrow 2\text{KNO}_2(s) + \text{O}_2(g)$
 - b. $\text{H}_2(g) + \text{CuO}(s) \rightarrow \text{Cu}(s) + \text{H}_2\text{O}(l)$
 - c. $\text{NaOH}(aq) + \text{HCl}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$
 - d. $\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{HCl}(g)$
 - e. $\text{SO}_3(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{SO}_4(aq)$

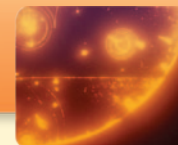
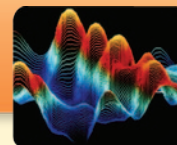
4. For each redox equation identified in the previous question, determine which element is oxidized and which is reduced.

✔ Critical Thinking

5. **ANALYZING INFORMATION** Use the following equations for the redox reaction between Al^{3+} and Na to answer the questions below.



- a. Explain how this reaction illustrates that charge is conserved in a redox reaction.
- b. Explain how this reaction illustrates that mass is conserved in a redox reaction.
- c. Explain why electrons do not appear as reactants or products in the combined equation.

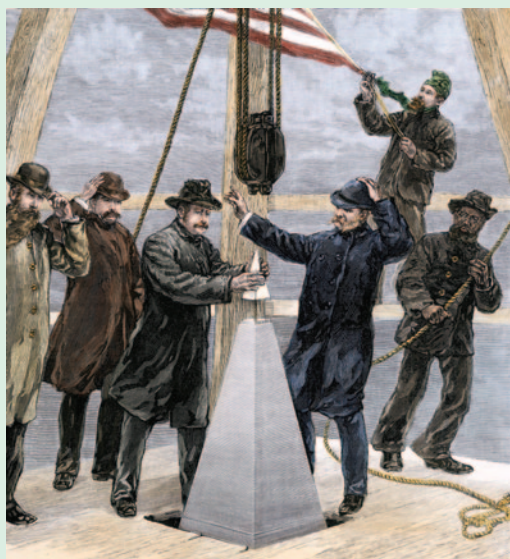


Production of Aluminum

S.T.E.M.

Aluminum, the third most abundant element after oxygen and silicon, is the most abundant metallic element in Earth's crust. However, aluminum always occurs combined with other elements, usually oxygen, silicon, and iron. You have to work very hard to produce pure aluminum metal.

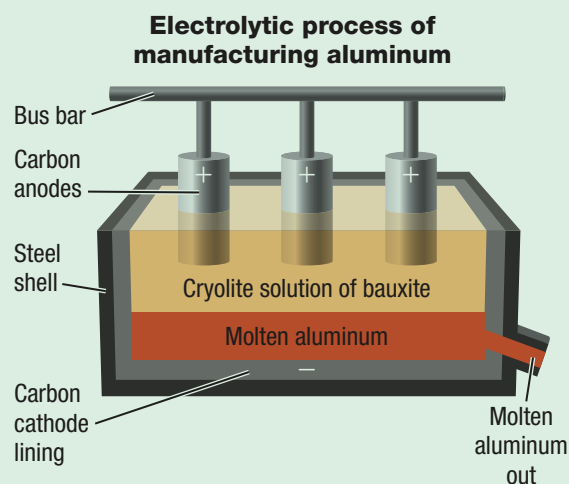
Aluminum, Al, was first discovered in 1825, and for more than 60 years was considered a very expensive rarity. Because aluminum was considered rare but was extremely resistant to corrosion, it was selected as the material for the lightning arrester atop the Washington Monument in Washington, D.C. A pyramid 23 cm tall, weighing 2.83 kg, was cast. At the time, it was the largest single piece of aluminum ever cast and was placed on the monument amid great ceremony on December 6, 1884.



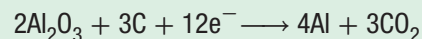
In 1886, American Charles Hall and Frenchman Paul Héroult independently invented the chemical process for producing pure aluminum from its ore. What is now called the Hall-Héroult process is still used for aluminum production.

Aluminum ore—the relatively common mineral, bauxite—is a mixture of aluminum oxide (alumina), silica (sand), and iron oxides. Alumina is first separated from the impurities.

Next, the Hall-Héroult process converts alumina to molten aluminum metal: in a large pot lined with carbon, alumina is dissolved in a bath of a molten cryolite, Na_3AlF_6 , at a temperature of about 1000°C



An electric current, 4–6 volts, 100,000–230,000 amperes, is passed through the molten cryolite, decomposing the dissolved alumina to aluminum and oxygen. The aluminum sinks to the bottom of the reaction vessel, and the oxygen reacts with the carbon lining, forming carbon dioxide, which bubbles off into the air. The overall reaction is:



The Hall-Héroult process has made aluminum products affordable even though aluminum used to be more expensive than gold!

Questions

1. Many industries use redox reactions to make products such as aluminum, steel, and lead storage batteries for cars and trucks. Explain why it has been so important to scale the Hall-Héroult process up to quantities of many tons per electrolytic cell for modern uses.
2. Identify which material is oxidized and which is reduced by the electric current in the Hall-Héroult process.

Balancing Redox Equations

Main Idea

Oxidation and reduction reactions are balanced separately and then added together.

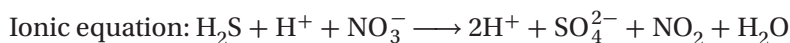
Equations for simple redox reactions can be balanced by inspection. Most redox equations, however, require more systematic methods. The equation-balancing process requires the use of oxidation numbers. In a balanced equation, both charge and mass are conserved. Although oxidation and reduction half-reactions occur together, their reaction equations are balanced separately and then combined to give the balanced redox-reaction equation.

MAIN IDEA

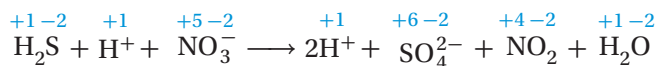
Oxidation and reduction reactions are balanced separately and then added together.

The *half-reaction method*, or ion-electron method, for balancing redox equations consists of seven steps. Oxidation numbers are assigned to all atoms and polyatomic ions to determine which species are part of the redox process. The oxidation and reduction equations are balanced separately for mass and charge. They are then added together to produce a complete balanced equation. These seven steps are applied to balance the reaction of hydrogen sulfide and nitric acid. Sulfuric acid, nitrogen dioxide, and water are the products of the reaction.

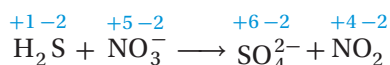
- 1. Write the formula equation if it is not given in the problem. Then write the ionic equation.**



- 2. Assign oxidation numbers. Delete substances containing only elements that do not change oxidation state.**

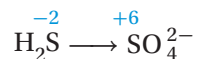


The sulfur changes oxidation state from -2 to $+6$. The nitrogen changes oxidation state from $+5$ to $+4$. The other substances are deleted.

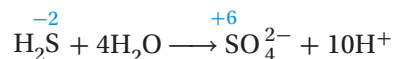


The remaining species are used in step 3.

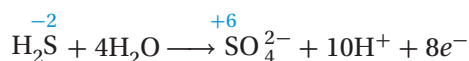
3. **Write the half-reaction for oxidation.** In this example, the sulfur is being oxidized.



- **Balance the atoms.** To balance the oxygen in this half-reaction, 4 water, H_2O , molecules must be added to the left side. This gives 10 extra hydrogen atoms on that side of the equation. Therefore, 10 hydrogen ions are added to the right side. In basic solution, OH^- ions and water may be used to balance atoms.

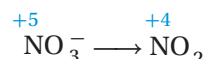


- **Balance the charge.** Electrons are added to the side having the greater positive net charge. The left side of the equation has no net charge; the right side has a net charge of 8+. For the charges to balance, each side must have the same net charge. Therefore, 8 electrons are added to the product side so that it has no charge and balances with the reactant side of the equation. Notice that the oxidation of sulfur from a state of -2 to $+6$ indicates a loss of 8 electrons.

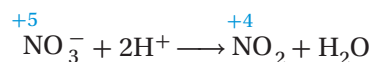


The oxidation half-reaction is now balanced.

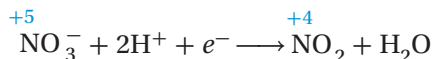
4. **Write the half-reaction for reduction.** In this example, nitrogen is being reduced from a $+5$ state to a $+4$ state.



- **Balance the atoms.** One water, H_2O , molecule must be added to the product side of the reaction to balance the oxygen atoms. Therefore, two hydrogen ions must be added to the reactant side to balance the hydrogen atoms.



- **Balance the charge.** Electrons are added to the side having the greater positive net charge. The left side of the equation has a net charge of 1+. Therefore, 1 electron must be added to this side to balance the charge.

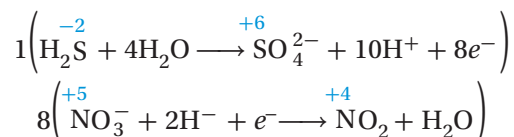


The reduction half-reaction is now balanced.

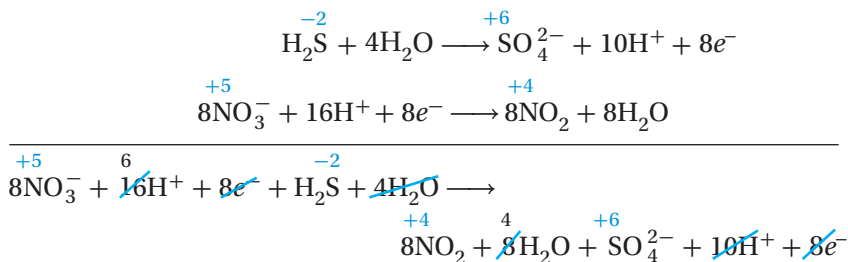
5. **Conserve charge by adjusting the coefficients in front of the electrons so that the number lost in oxidation equals the number gained in reduction.** Write the ratio of the number of electrons lost to the number of electrons gained.

$$\frac{e^- \text{ lost in oxidation}}{e^- \text{ gained in reduction}} = \frac{8}{1}$$

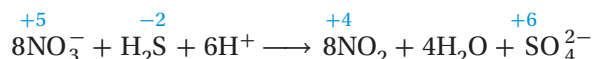
This ratio is already in its lowest terms. If it were not, it would need to be reduced. Multiply the oxidation half-reaction by 1 (it remains unchanged) and the reduction half-reaction by 8. The number of electrons lost now equals the number of electrons gained.



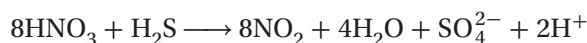
6. **Combine the half-reactions, and cancel out anything common to both sides of the equation.**



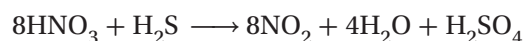
Each side of the above equation has 10H^+ , $8e^-$, and $4\text{H}_2\text{O}$. These cancel each other out and do not appear in the balanced equation.



7. **Combine ions to form the compounds shown in the original formula equation. Check to ensure that all other ions balance.** The NO_3^- ion appeared as nitric acid in the original equation. There are only 6 hydrogen ions to pair with the 8 nitrate ions. Therefore, 2 hydrogen ions must be added to complete this formula. If 2 hydrogen ions are added to the left side of the equation, 2 hydrogen ions must also be added to the right side of the equation.



The sulfate ion appeared as sulfuric acid in the original equation. The hydrogen ions added to the right side are used to complete the formula for sulfuric acid.



A final check must be made to ensure that all elements are correctly balanced.

FIGURE 2.1

Redox Titration As a KMnO_4 solution is titrated into an acidic solution of FeSO_4 , deep purple MnO_4^- ions are reduced to colorless Mn^{2+} ions. When all Fe^{2+} ions are oxidized, MnO_4^- ions are no longer reduced to colorless Mn^{2+} ions. Thus, the first faint appearance of the MnO_4^- color indicates the end point of the titration.





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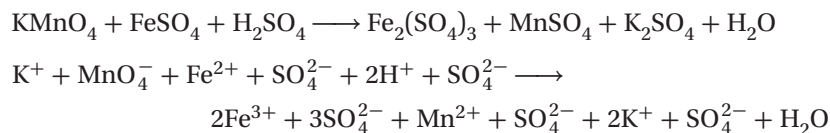
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Balancing Equations for Redox Reactions

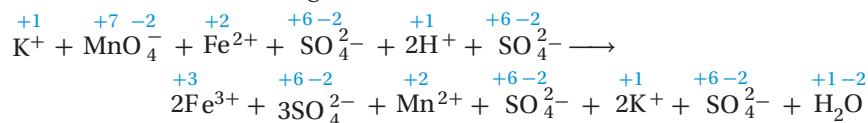
Sample Problem A Write a balanced equation for the reaction shown in Figure 2.1 (on the previous page). A deep purple solution of potassium permanganate is titrated with a colorless solution of iron(II) sulfate and sulfuric acid. The products are iron(III) sulfate, manganese(II) sulfate, potassium sulfate, and water—all of which are colorless.

SOLVE

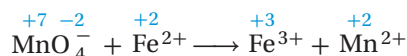
- Write the formula equation if it is not given in the problem. Then write the ionic equation.



- Assign oxidation numbers to each element and ion. Delete substances containing an element that does not change oxidation state.



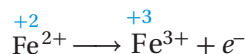
Only ions or molecules whose oxidation numbers change are retained.



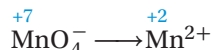
- Write the half-reaction for oxidation. The iron shows the increase in oxidation number. Therefore, it is oxidized.



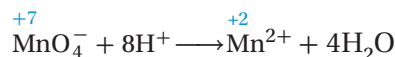
- Balance the mass. The mass is already balanced.
- Balance the charge.



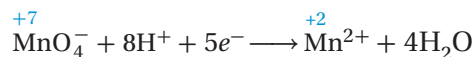
- Write the half-reaction for reduction. Manganese shows a change in oxidation number from +7 to +2. It is reduced.



- Balance the mass. Water and hydrogen ions must be added to balance the oxygen atoms in the permanganate ion.

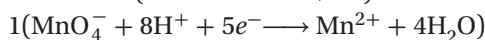
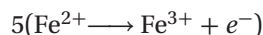


- Balance the charge.



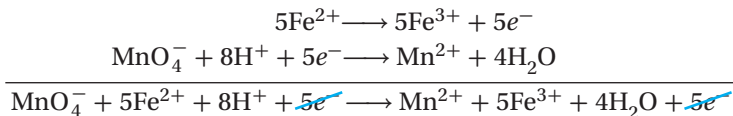
- Adjust the coefficients to conserve charge.

$$\frac{e^- \text{ lost in oxidation}}{e^- \text{ gained in reduction}} = \frac{1}{5}$$

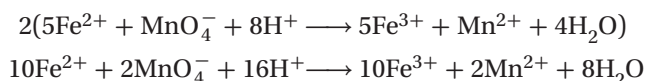


Balancing Equations for Redox Reactions (continued)

6. Combine the half-reactions, and cancel.



7. Combine ions to form compounds from the original equation. The iron(III) product appears in the original equation as $\text{Fe}_2(\text{SO}_4)_3$. Every iron(III) sulfate molecule requires two iron ions. Therefore, the entire equation must be multiplied by 2 to provide an even number of iron ions.



The iron(II), iron(III), manganese(II), and 2 hydrogen ions in the original equation are paired with sulfate ions. Iron(II) sulfate requires 10 sulfate ions, and sulfuric acid requires 8 sulfate ions. To balance the equation, 18 sulfate ions must be added to each side. On the product side, 15 of these ions form iron(III) sulfate, and 2 of them form manganese(II) sulfate. That leaves 1 sulfate ion unaccounted for. The permanganate ion requires the addition of 2 potassium ions to each side. These 2 potassium ions form potassium sulfate on the product side of the reaction.



Final inspection shows that atoms and charges are balanced.

Practice

Answers in Appendix E

- Copper reacts with hot, concentrated sulfuric acid to form copper(II) sulfate, sulfur dioxide, and water. Write and balance the equation for this reaction.
- Write and balance the equation for the reaction between nitric acid and potassium iodide. The products are potassium nitrate, iodine, nitrogen monoxide, and water.



SECTION 2 FORMATIVE ASSESSMENT

▶ Reviewing Main Ideas

- What two quantities are conserved in redox equations?
- Why do we add H^{+} and H_2O to some half-reactions and OH^{-} and H_2O to others?
- Balance the following redox reaction:
 $\text{Na}_2\text{SnO}_2 + \text{Bi}(\text{OH})_3 \longrightarrow \text{Bi} + \text{Na}_2\text{SnO}_3 + \text{H}_2\text{O}$

✔ Critical Thinking

- RELATING IDEAS** When heated, elemental phosphorus, P_4 , produces phosphine, PH_3 , and phosphoric acid, H_3PO_4 . How many grams of phosphine are produced if 56 g P_4 have reacted?

SECTION 3

Main Ideas

- ▶ The more active an element is, the better it acts as an oxidizer or reducer.
- ▶ Some substances can be oxidizers and reducers in the same reaction.

Oxidizing and Reducing Agents

Key Terms

reducing agent
oxidizing agent
disproportionation

A **reducing agent** is a substance that has the potential to cause another substance to be reduced. Reducing agents lose electrons; they attain a more positive oxidation state during an oxidation-reduction reaction. Therefore, the reducing agent is the oxidized substance.

An **oxidizing agent** is a substance that has the potential to cause another substance to be oxidized. Oxidizing agents gain electrons and attain a more negative oxidation state during an oxidation-reduction reaction. The oxidizing agent is the reduced substance. **Figure 3.1** helps clarify the terms describing the oxidation-reduction process.

▶ MAIN IDEA

The more active an element is, the better it acts as an oxidizer or reducer.

✓ CHECK FOR UNDERSTANDING

Describe In your own words, describe the relationship between the relative strength of oxidizing and reducing agents and their placement on the activity series table (given in the chapter “Chemical Equations and Reactions”).

Different substances can be compared and rated by their relative potential as reducing and oxidizing agents. For example, the order of the elements in the activity series, seen in the chapter on chemical equations and reactions, is related to each element’s tendency to lose electrons. Elements in this series lose electrons to the positively charged ions of any element below them in the series. The more active an element is, the greater its tendency to lose electrons and the better a reducing agent it is. The greater the distance is between two elements in the list, the more likely it is that a redox reaction will take place between them. These elements and some other familiar substances are arranged in **Figure 3.2** according to their activity as oxidizing and reducing agents.

FIGURE 3.1

OXIDATION-REDUCTION TERMINOLOGY

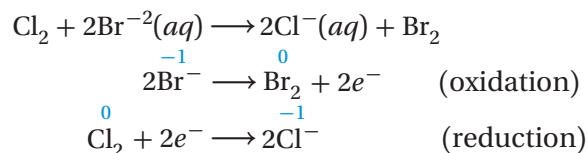
Term	Change in oxidation number	Change in electron population
Oxidation	increases	loss of electrons
Reduction	decreases	gain of electrons
Oxidizing agent	decreases	gains electrons
Reducing agent	increases	loses electrons

The fluorine atom is the most highly electronegative atom. It is also the most active oxidizing agent. Because of its strong attraction for its own electrons, the fluoride ion is the weakest reducing agent. The negative ion of a strong oxidizing agent is a weak reducing agent.

The positive ion of a strong reducing agent is a weak oxidizing agent. As shown in **Figure 3.2**, Li atoms are strong reducing agents because Li is a very active metal. When Li atoms oxidize, they produce Li^+ ions, which are unlikely to reacquire electrons, so Li^+ ions are weak oxidizing agents.

The left column of each pair also shows the relative abilities of these metals to displace other metals from compounds. Zinc, for example, is above copper, so zinc is a more active reducing agent. It displaces copper ions from solutions of copper compounds, as shown in **Figure 3.3**. A copper(II) ion, however, is a more active oxidizing agent than a zinc ion.

Nonmetals and some important ions also are included in the series in **Figure 3.2**. Any reducing agent is oxidized by the oxidizing agents below it. Observe that F_2 displaces Cl^- , Br^- , and I^- ions from their solutions. Cl_2 displaces Br^- and I^- ions, and Br_2 displaces I^- ions. The equation for the displacement of Br^- by Cl_2 is as follows.



In every redox reaction, there is one reducing agent and one oxidizing agent. In the preceding example, Br^- is the reducing agent, and Cl_2 is the oxidizing agent.

FIGURE 3.3

Reduction of Copper by Zinc

Zinc displaces copper ions from a copper(II) sulfate solution. Metallic copper precipitates.



CRITICAL THINKING

Analyze Examine **Figure 3.2** closely. Various oxidation states of iron (Fe) appear in both the top and bottom half and left and right columns of the table. What pattern becomes apparent when you compare the oxidation numbers in each case and iron's function as an oxidizing or reducing agent?

FIGURE 3.2

RELATIVE STRENGTH OF OXIDIZING AND REDUCING AGENTS

Reducing agents	Oxidizing agents
Li	Li^+
K	K^+
Ca	Ca^{2+}
Na	Na^+
Mg	Mg^{2+}
Al	Al^{3+}
Zn	Zn^{2+}
Cr	Cr^{3+}
Fe	Fe^{2+}
Ni	Ni^{2+}
Sn	Sn^{2+}
Pb	Pb^{2+}
H_2	H_3O^+
H_2S	S
Cu	Cu^{2+}
I^-	I_2
MnO_4^{2-}	MnO_4^-
Fe^{2+}	Fe^{3+}
Hg	Hg_2^{2+}
Ag	Ag^+
NO_2^-	NO_3^-
Br^-	Br_2
Mn^{2+}	MnO_2
SO_2	H_2SO_4 (conc.)
Cr^{3+}	$\text{Cr}_2\text{O}_7^{2-}$
Cl^-	Cl_2
Mn^{2+}	MnO_4^-
F^-	F_2

Increasing strength (upward arrow on left, downward arrow on right)

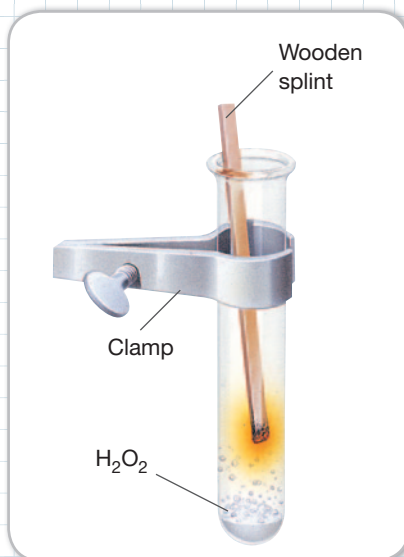
PROCEDURE

Record your results in a data table.

- Put 10 mL of hydrogen peroxide in a test tube. Add a small amount of manganese dioxide (equal to the size of about half a pea). What is the result?
- Insert a glowing wooden splint into the test tube (see diagram). What is the result? If oxygen is produced, a glowing wooden splint inserted into the test tube will glow brighter.
- Fill the 250 mL beaker halfway with the copper(II) chloride solution.
- Cut aluminum foil into 2 cm × 12 cm strips.
- Add the aluminum strips to the copper(II) chloride solution. Use a glass rod to stir the mixture, and observe for 12 to 15 minutes. What is the result?

DISCUSSION

- Write balanced equations showing what happened in each of the reactions.
- Write a conclusion for the two experiments.

**MATERIALS**

- aluminum foil
- beaker, 250 mL
- 1 M copper(II) chloride solution, CuCl_2
- 3% hydrogen peroxide
- manganese dioxide
- metric ruler
- scissors
- test-tube clamp
- test tube, 16 × 150 mm
- wooden splint

SAFETY

Wear safety goggles and an apron.

MAIN IDEA

Some substances can be oxidizers and reducers in the same reaction.

Some substances can be both reduced and oxidized easily. For example, peroxide ions, O_2^{2-} , have a relatively unstable covalent bond between the two oxygen atoms. The electron-dot formula is written as follows.



Each oxygen atom has an oxidation number of -1 . The peroxide ion structure represents an intermediate oxidation state between O_2 and O^{2-} . Therefore, the peroxide ion is highly reactive.

Hydrogen peroxide, H_2O_2 , is a covalent compound. It decomposes into water and molecular oxygen, as shown in the equation below.

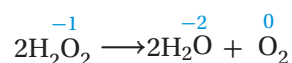


FIGURE 3.4

Disproportionation in Nature A bombardier beetle can repel large predators such as frogs with a chemical defense mechanism that uses the disproportionation of hydrogen peroxide.



Notice that in this reaction, hydrogen peroxide is both oxidized and reduced. Oxygen atoms that become part of gaseous oxygen molecules are oxidized. The oxidation number of these oxygen atoms increases from -1 to 0 . Oxygen atoms that become part of water are reduced. The oxidation number of these oxygen atoms decreases from -1 to -2 .

A process in which a substance acts as both an oxidizing agent and a reducing agent is called disproportionation. A substance that undergoes disproportionation is both *self-oxidizing* and *self-reducing*.

The bombardier beetle defends itself by spraying its enemies with an unpleasant hot chemical mixture, as shown in **Figure 3.4**. The catalyzed disproportionation of hydrogen peroxide produces hot oxygen gas. This gas gives the insect an ability to eject irritating chemicals from its abdomen with explosive force.



SECTION 3 FORMATIVE ASSESSMENT

▶ Reviewing Main Ideas

1. Describe the oxidation and reduction strengths of alkali metals and halogens.
2. Look at the photo. The test tube on the left shows a copper coil placed in a solution of zinc(II) sulfate. The test tube on the right shows a zinc coil placed in a solution of copper(II) sulfate. Both solutions have a similar concentration. Explain why a reaction happens in one test tube and not the other. What is the product of the reaction?
3. Would Cl_2 be reduced by I^- ? Explain.
4. In each pair, which is the stronger oxidizing agent: Cu^{2+} or Al^{3+} , I_2 or S , F_2 or Li^+ ?
5. What is meant by *disproportionation*?

✔ Critical Thinking

6. **ORGANIZING IDEAS** In general, where in the periodic table are the elements found that in elemental form are the strongest oxidizing agents? Explain.



A redox equation must conserve both mass and charge. So to balance a redox equation, you must balance both atoms and charge (electrons). The problem-solving tips and sample

below show how to balance an equation for a redox reaction in *basic* solution.

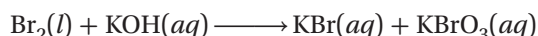
Problem-Solving TIPS

To balance redox equations for reactions in *basic* solution:

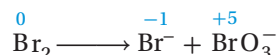
- Add OH^- and H_2O to balance oxygen and hydrogen in the redox half-reactions.
- Add OH^- ions to the side of the equation that needs oxygen atoms. Make sure you add enough OH^- ions so that the number of oxygen atoms added is twice the number needed.
- Then, add enough H_2O molecules to the other side of the equation to balance the hydrogen atoms.

Sample Problem

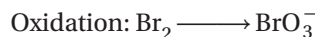
The following unbalanced equation represents a redox reaction that takes place in a basic solution containing KOH. Balance the redox equation.



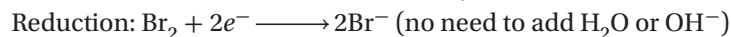
Write the full ionic equation, assign oxidation numbers, and eliminate species whose oxidation numbers do not change. The result is the following equation:



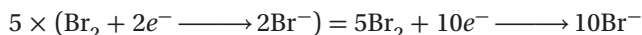
Divide this equation into half-reactions. Note that Br_2 is the reactant in both half-reactions.



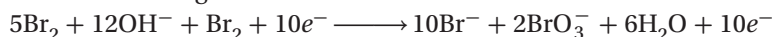
Add H_2O and OH^- to balance atoms in basic solution. Then, add electrons to balance charge.



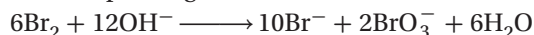
To balance transferred electrons, you must multiply the reduction half-reaction by 5 so that both reactions have $10e^-$.



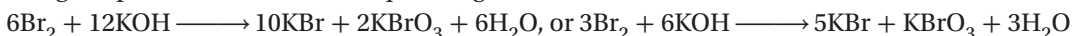
Combining the two half-reactions gives



Combining and canceling common species gives



Returning the potassium ions to the equation gives



Practice

1. Balance the following equation for a redox reaction that takes place in basic solution:
 $\text{MnO}_2(s) + \text{NaClO}_3(aq) + \text{NaOH}(aq) \longrightarrow \text{NaMnO}_4(aq) + \text{NaCl}(aq) + \text{H}_2\text{O}(l)$
2. Balance the following equation for a redox reaction that takes place in basic solution:
 $\text{N}_2\text{O}(g) + \text{KClO}(aq) + \text{KOH}(aq) \longrightarrow \text{KCl}(aq) + \text{KNO}_2(aq) + \text{H}_2\text{O}(l)$

CHAPTER 19 Summary

BIG IDEA In oxidation-reduction reactions atoms and ions change oxidation states, either by losing electrons (oxidizing) or gaining electrons (reducing).

SECTION 1 Oxidation and Reduction

KEY TERMS

- Oxidation numbers are assigned by the set of rules listed in **Figure 1.1**. Oxidation numbers are based on the distribution of electrons in a molecule.
- Oxidation-reduction reactions consist of two half-reactions that must occur simultaneously.
- Oxidation-reduction reactions are identified by examining the changes in the oxidation numbers of atoms in the reactants and products.
- Oxidation involves the loss of electrons, and reduction involves the gain of electrons.
- A species whose oxidation number increases is oxidized. A species whose oxidation number decreases is reduced.

oxidation
oxidized
reduction
reduced
oxidation-reduction reaction
redox reaction
half-reaction

SECTION 2 Balancing Redox Equations

- Charge and mass are conserved in a balanced redox equation.
- In the half-reaction method for balancing equations, the atoms and charge of oxidation and reduction equations are balanced separately. Then, they are combined to give a complete balanced equation.
- In a half-reaction, the charge on the reactant side must equal the charge on the product side, but these charges do not need to be zero.
- For the half-reaction method, the atoms in each half-reaction are balanced by adding H^+ ions and H_2O molecules in acidic solutions. If the solution is basic, OH^- ions and H_2O molecules are added to balance the atoms in each half-reaction.
- The number of electrons lost in the oxidation half-reaction must equal the number of electrons gained in the reduction half-reaction. The two half-reactions must be multiplied by appropriate factors to ensure that the same number of electrons are transferred.

SECTION 3 Oxidizing and Reducing Agents

KEY TERMS

- The substance that is *reduced* in redox reactions is the *oxidizing agent* because it *acquires* electrons from the substance that is oxidized.
- The substance that is *oxidized* in a redox reaction is the *reducing agent* because it *supplies* the electrons to the substance that is reduced.
- Strong reducing agents are substances that easily give up electrons.
- Disproportionation is a process in which a substance is both an oxidizing agent and a reducing agent.

reducing agent
oxidizing agent
disproportionation


SECTION 1

Oxidation and Reduction

REVIEWING MAIN IDEAS

- Distinguish between the processes of oxidation and reduction.
 - Write an equation to illustrate each process.
- Which of the following are redox reactions?
 - $2\text{Na} + \text{Cl}_2 \longrightarrow 2\text{NaCl}$
 - $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$
 - $2\text{H}_2\text{O} \longrightarrow 2\text{H}_2 + \text{O}_2$
 - $\text{NaCl} + \text{AgNO}_3 \longrightarrow \text{AgCl} + \text{NaNO}_3$
 - $\text{NH}_3 + \text{HCl} \longrightarrow \text{NH}_4^+ + \text{Cl}^-$
 - $2\text{KClO}_3 \longrightarrow 2\text{KCl} + 3\text{O}_2$
 - $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{HCl}$
 - $\text{H}_2\text{SO}_4 + 2\text{KOH} \longrightarrow \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$
 - $\text{Zn} + \text{CuSO}_4 \longrightarrow \text{ZnSO}_4 + \text{Cu}$
- For each oxidation-reduction reaction in the previous question, identify what is oxidized and what is reduced. Can an oxidation-reduction reaction also be another type of reaction?

PRACTICE PROBLEMS

- Each of the following atom/ion pairs undergoes the oxidation-number change indicated below. For each pair, determine whether oxidation or reduction has occurred and then write the electronic equation indicating the corresponding number of electrons lost or gained.

a. $\text{K} \longrightarrow \text{K}^+$	e. $\text{H}_2 \longrightarrow \text{H}^+$
b. $\text{S} \longrightarrow \text{S}^{2-}$	f. $\text{O}_2 \longrightarrow \text{O}^{2-}$
c. $\text{Mg} \longrightarrow \text{Mg}^{2+}$	g. $\text{Fe}^{3+} \longrightarrow \text{Fe}^{2+}$
d. $\text{F}^- \longrightarrow \text{F}_2$	h. $\text{Mn}^{2+} \longrightarrow \text{MnO}_4^-$
- Identify the following reactions as redox or nonredox:
 - $2\text{NH}_4\text{Cl}(aq) + \text{Ca}(\text{OH})_2(aq) \longrightarrow 2\text{NH}_3(aq) + 2\text{H}_2\text{O}(l) + \text{CaCl}_2(aq)$
 - $2\text{HNO}_3(aq) + 3\text{H}_2\text{S}(g) \longrightarrow 2\text{NO}(g) + 4\text{H}_2\text{O}(l) + 3\text{S}(s)$
 - $[\text{Be}(\text{H}_2\text{O})_4]^{2+}(aq) + \text{H}_2\text{O}(l) \longrightarrow \text{H}_3\text{O}^+(aq) + [\text{Be}(\text{H}_2\text{O})_3\text{OH}]^+(aq)$
- Arrange the following in order of increasing oxidation number of the xenon atom: CsXeF_8 , Xe , XeF_2 , XeOF_2 , XeO_3 , and XeF .

- Determine the oxidation number of each atom indicated in the following:

a. H_2	f. HNO_3
b. H_2O	g. H_2SO_4
c. Al	h. $\text{Ca}(\text{OH})_2$
d. MgO	i. $\text{Fe}(\text{NO}_3)_2$
e. Al_2S_3	j. O_2

SECTION 2

Balancing Redox Equations

REVIEWING MAIN IDEAS

- Label the following half-reactions as either reduction or oxidation half-reactions.
 - $\text{H}_2\text{S} \longrightarrow \text{S} + 2\text{H}^+ + 2e^-$
 - $\text{SO}_2 + 2\text{H}_2\text{O} + 4e^- \longrightarrow \text{S} + 4\text{OH}^-$
 - $\text{ClO}_3^- + 6\text{H}^+ + 6e^- \longrightarrow \text{Cl}^- + 3\text{H}_2\text{O}$
 - $\text{Mn}(\text{CN})_6^{4-} \longrightarrow \text{Mn}(\text{CN})_6^{3-} + e^-$
- What are the oxidation states of the elements that changed oxidation states in the half-reactions in the above question?
- Balance the equation for the following reaction in a basic solution. Give balanced equations for both half-reactions and a balanced equation for the overall reaction.


PRACTICE PROBLEMS

- For each requested step, use the half-reaction method to balance the oxidation-reduction equation below. (Hint: See Sample Problem A.)

$$\text{K} + \text{H}_2\text{O} \longrightarrow \text{KOH} + \text{H}_2$$
 - Write the ionic equation, and assign oxidation numbers to all atoms to determine what is oxidized and what is reduced.
 - Write the equation for the reduction, and balance it for both atoms and charge.
 - Write the equation for the oxidation, and balance it for both atoms and charge.
 - Multiply the coefficients of the oxidation and reduction equations so that the number of electrons lost equals the number of electrons gained. Add the two equations.
 - Add species as necessary to balance the overall formula equation.

12. Use the method in the previous problem to balance each of the reactions below.
- $\text{HI} + \text{HNO}_2 \longrightarrow \text{NO} + \text{I}_2 + \text{H}_2\text{O}$
 - $\text{FeCl}_3 + \text{H}_2\text{S} \longrightarrow \text{FeCl}_2 + \text{HCl} + \text{S}$
13. Balance the equation for the reaction in which hot, concentrated sulfuric acid reacts with zinc to form zinc sulfate, hydrogen sulfide, and water.

SECTION 3

Oxidizing and Reducing Agents

REVIEWING MAIN IDEAS

14. a. Identify the most active reducing agent among all common elements.
 b. Why are all of the elements in its group in the periodic table very active reducing agents?
 c. Identify the most active oxidizing agent among the common elements.
15. Use **Figure 3.1** to identify the strongest and weakest reducing agents among the substances listed within each of the following groupings:
- Ca, Ag, Sn, Cl^-
 - Fe, Hg, Al, Br^-
 - F^- , Pb, Mn^{2+} , Na
16. Use **Figure 3.1** to respond to each of the following:
- Would Al be oxidized by Ni^{2+} ?
 - Would Cu be oxidized by Ag^+ ?
 - Would Pb be oxidized by Na?
 - Would F_2 be reduced by Cl^- ?
 - Would Br_2 be reduced by Cl^- ?

Mixed Review

REVIEWING MAIN IDEAS

17. Identify the following reactions as redox or nonredox:
- $\text{Mg}(s) + \text{ZnCl}_2(aq) \longrightarrow \text{Zn}(s) + \text{MgCl}_2(aq)$
 - $2\text{H}_2(g) + \text{OF}_2(g) \longrightarrow \text{H}_2\text{O}(g) + 2\text{HF}(g)$
 - $2\text{KI}(aq) + \text{Pb}(\text{NO}_3)_2(aq) \longrightarrow$
 $\text{PbI}_2(s) + 2\text{KNO}_3(aq)$
 - $\text{CaO}(s) + \text{H}_2\text{O}(l) \longrightarrow \text{Ca}(\text{OH})_2(aq)$
 - $3\text{CuCl}_2(aq) + 2(\text{NH}_4)_3\text{PO}_4(aq) \longrightarrow$
 $6\text{NH}_4\text{Cl}(aq) + \text{Cu}_3(\text{PO}_4)_2(s)$
 - $\text{CH}_4(g) + 2\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)$

18. Arrange the following in order of decreasing oxidation number of the nitrogen atom: N_2 , NH_3 , N_2O_4 , N_2O , N_2H_4 , and NO_3^- .
19. Balance the following redox equations:
- $\text{SbCl}_5 + \text{KI} \longrightarrow \text{KCl} + \text{I}_2 + \text{SbCl}_3$
 - $\text{Ca}(\text{OH})_2 + \text{NaOH} + \text{ClO}_2 + \text{C} \longrightarrow$
 $\text{NaClO}_2 + \text{CaCO}_3 + \text{H}_2\text{O}$
20. Balance the following equations in basic solution:
- $\text{PbO}_2 + \text{KCl} \longrightarrow \text{KClO} + \text{KPb}(\text{OH})_3$
 - $\text{KMnO}_4 + \text{KIO}_3 \longrightarrow \text{MnO}_2 + \text{KIO}_4$
 - $\text{K}_2\text{MnO}_4 \longrightarrow \text{MnO}_2 + \text{KMnO}_4$
21. Balance the following equations in acidic solution:
- $\text{MnO}_4^- + \text{Cl}^- \longrightarrow \text{Mn}^{2+} + \text{HClO}$
 - $\text{NO}_3^- + \text{I}_2 \longrightarrow \text{IO}_3^- + \text{NO}_2$
 - $\text{NO}_2^- \longrightarrow \text{NO} + \text{NO}_3^-$

CRITICAL THINKING

22. **Interpreting Graphics** Given the activity table below, determine whether a reaction will occur or not. If the reaction will occur, give the products.

Reducing Agents	
↑	↓
L	L^+
M	M^+
P	P^+
T	T^+
	Oxidizing Agents

- L and M^+
 - P and M^+
 - P and T^+
23. **Drawing Conclusions** A substance has an element in one of its highest possible oxidation states. Is this substance more likely to be an oxidizing agent or a reducing agent? Explain your reasoning.
24. **Drawing Conclusions** Use **Figure 3.2** to decide if a redox reaction would occur between the two species, and if so, write the balanced equation. Explain your reasoning.
- Cl_2 and Br_2
 - Sn^{2+} and Zn
25. **Drawing Conclusions** An element that disproportionates must have at least how many different oxidation states? Explain your reasoning.

USING THE HANDBOOK

26. Several reactions of aluminum are shown in the common reactions section for Group 13 of the *Elements Handbook* (Appendix A). Use these reactions to answer the following:
- Which of the five reactions shown are oxidation-reduction reactions? How do you know?
 - For each redox reaction you listed in item **a**, identify what is oxidized and what is reduced.
 - Write half-reactions for each equation you listed in item **a**.
27. Aluminum is described in Group 13 of the *Elements Handbook* (Appendix A) as a self-protecting metal. This property of aluminum results from a redox reaction.
- Write the redox equation for the oxidation of aluminum.
 - Write the half-reactions for this reaction, and show the number of electrons transferred.
 - What problems are associated with the buildup of aluminum oxide on electrical wiring made of aluminum?

RESEARCH AND WRITING

28. Oxidizing agents are used in the cleaning industry. Research three different oxidizing agents used in this area, and write a report on the advantages and disadvantages of these compounds.
29. Oxidizing and reducing agents play important roles in biological systems. Research the role of one of these agents in a biological process. Write a report describing the process and the role of oxidation and reduction.

ALTERNATIVE ASSESSMENT

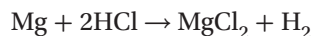
30. Boilers are used to convert water to steam in electric power plants. Dissolved oxygen in the water promotes corrosion of the steel used in boiler parts. Explain how dissolved oxygen is removed from the water in boilers.
31. **Performance** For one day, record situations that show evidence of oxidation-reduction reactions. Identify the reactants and the products, and determine whether there is proof that a chemical reaction has taken place.

Standards-Based Assessment

Record your answers on a separate piece of paper.

MULTIPLE CHOICE

- 1 In the following chemical reaction, which substance is reduced?



- A Mg
 - B H^+
 - C Cl^-
 - D Mg^{2+}
- 2 Which of the following equations shows a redox reaction?
- A $\text{NaI} + \text{KBr} \rightarrow \text{NaBr} + \text{KI}$
 - B $2\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$
 - C $\text{Zn} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2$
 - D $\text{BaCl}_2 + \text{Na}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + 2\text{NaCl}$
- 3 The oxidation number of the sulfur atom in the SO_4^{2-} ion is —
- A +2
 - B -2
 - C +6
 - D +4
- 4 In the following reaction, which is the oxidizing agent?
- $$\text{AgNO}_2 + \text{Cl}_2 + 2\text{KOH} \rightarrow \text{AgNO}_3 + 2\text{KCl} + \text{H}_2\text{O}$$
- A AgNO_2
 - B Cl_2
 - C KOH
 - D KCl

- 5 A half-reaction —
- A involves a change in the oxidation state of an element
 - B always contains H_2O molecules
 - C always contains H^+ ions
 - D all of the above
- 6 What are the oxidation states (in increasing order) of the element that undergoes disproportionation in the following reaction?
- $$\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HOCl}$$
- A -1, 0, +2
 - B -1, 0, +1
 - C -2, -1, 0
 - D none of the above
- 7 Which of the statements best describes the following reaction?
- $$2\text{Pb}(\text{NO}_3)_2 \rightarrow 2\text{PbO} + 4\text{NO}_2 + \text{O}_2$$
- A This reaction is a decomposition reaction and not a redox reaction.
 - B This reaction is between a strong acid and a strong base.
 - C This reaction is a precipitation reaction.
 - D This reaction is a redox reaction in which the nitrogen is reduced and the oxygen is oxidized.

GRIDDED RESPONSE

- 8 Determine the oxidation number for barium in the superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$. Yttrium (Y) has an oxidation number of +3. Give only an integer oxidation number.