#### CHAPTER

# 17 Oxidation, Reduction, and Electrochemistry

f you run out of gasoline in a car, you might have to walk to the nearest gas station for more fuel. But running out of energy when you are millions of kilometers from Earth is a different story! A robot designed to collect data on other bodies in our solar system needs a reliable, portable source of energy that can work in the absence of an atmosphere to carry out its mission. Many of the power sources for these explorer robots are batteries. In this chapter, you will learn about the processes of oxidation and reduction and how they are used in batteries to provide energy. You will also learn how these processes are used to purify metals and protect objects from corrosion.

# START-UPACTIVITY

## **Lights On**

#### PROCEDURE

- **1.** Assemble **batteries**, a **light-emitting diode**, and **wires** so that the diode lights. Make a diagram of your construction.
- **2.** Remove the batteries, and reconnect them in the opposite direction. Record the results.

#### **ANALYSIS**

- 1. A light-emitting diode allows electrons to move through it in only one direction—into the short leg and out of the longer leg. Based on your results, from which end of the battery must electrons leave?
- **2.** How are the atoms changing in the end of the battery from which electrons leave?
- **3.** What must happen to the electrons as they enter into the other end of the battery?
- 4. Why does a battery eventually run down?

# **Pre-Reading Questions**

- What type of charge results from losing electrons? from gaining electrons?
- 2 Name a device that converts chemical energy into electrical energy.
- Why are batteries marked with positive and negative terminals?

#### SAFETY PRECAUTIONS





#### **SECTION 1**

Oxidation-Reduction Reactions

#### **SECTION 2**

Introduction to Electrochemistry

#### **SECTION 3**

**Galvanic Cells** 

SECTION 4 Electrolytic Cells

#### S E C T I O N

# **Oxidation-Reduction Reactions**

#### **Key Terms**

- oxidation
- reduction
- oxidation-reduction reaction
- oxidation number
- half-reaction
- oxidizing agent
- reducing agent

#### **Topic Link**

Refer to the "Ions and Ionic Compounds" and "Covalent Compounds" chapters for more information about chemical bonding.

#### oxidation

a reaction that removes one or more electrons from a substance such that the substance's valence or oxidation state increases

#### **O**BJECTIVES

- Identify atoms that are oxidized or reduced through electron transfer.
- **Assign** oxidation numbers to atoms in compounds and ions.
- **Identify** redox reactions by analyzing changes in oxidation numbers for different atoms in the reaction.
- 4
  - **Balance** equations for oxidation-reduction reactions through the half-reaction method.

# **Electron Transfer and Chemical Reactions**

You already know that atoms with very different electronegativities bond by an electron transfer. For example, sodium chloride is formed by the transfer of electrons from sodium atoms to chlorine atoms in the reaction shown in **Figure 1** and described by the following equation:

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

Though NaCl is the way the formula of sodium chloride is usually written, the compound is made up of ions. Therefore, it might be helpful to think of sodium chloride as if its formula were written  $Na^+Cl^-$  so that you remember the ions.

When the electronegativity difference between the atoms is smaller, a polar covalent bond can form when the atoms join, as shown below.

$$2\mathrm{C}(s) + \mathrm{O}_2(g) \longrightarrow 2\mathrm{CO}(g)$$

The C–O bond has some ionic character because there is an unequal sharing of electrons between the carbon atom and the oxygen atom. The oxygen atom attracts the shared electrons more strongly than the carbon atom does.

#### **Oxidation Involves a Loss of Electrons**

In the examples above, electrons were transferred at least in part from one atom to another. The sodium atom lost an electron to the chlorine atom. The carbon atom lost some of its control over its electrons to the oxygen atom. The loss, wholly or in part, of one or more electrons is called **oxidation**.

Thus, in making NaCl, the sodium atom is oxidized from Na to Na<sup>+</sup>. Likewise, the carbon atom is oxidized when CO forms, even though the carbon atom does not become an ion.



#### **Reduction Involves a Gain of Electrons**

In making NaCl, the electrons lost by the sodium atoms do not just disappear. They are gained by the chlorine atoms. The gain of electrons is described as **reduction.** The chlorine atoms are reduced as they change from  $Cl_2$  to  $2Cl^-$ .

When joining with carbon atoms to make CO, oxygen atoms do not gain electrons but gain only a partial negative charge. But because the electrons in the C—O bonds spend more time near the oxygen atoms, the change is still a reduction.

More than one electron may be gained in a reduction. In the formation of  $Li_3N$ , described by the equation below, three electrons are gained by each nitrogen atom.

 $6\text{Li}(s) + N_2(g) \longrightarrow 2\text{Li}_3N(s)$ 

#### **Oxidation and Reduction Occur Together**

When oxidation happens there must also be reduction taking place. You will learn later in this chapter that oxidation and reduction can happen at different places. In most situations, however, oxidation and reduction happen in a single place. Consider HgO being broken down into its elements, as described by the following equation:

$$2 \text{HgO}(s) \longrightarrow 2 \text{Hg}(l) + \text{O}_2(g)$$

In this reaction, mercury atoms are reduced, while oxygen atoms are oxidized. A single reaction in which an oxidation and a reduction happen is called an **oxidation-reduction reaction** or *redox reaction*.

#### reduction

a chemical change in which electrons are gained, either by the removal of oxygen, the addition of hydrogen, or the addition of electrons



# oxidation-reduction reaction

any chemical change in which one species is oxidized (loses electrons) and another species is reduced (gains electrons); also called *redox reaction* 

#### oxidation number

the number of electrons that must be added to or removed from an atom in a combined state to convert the atom into the elemental form

#### **Oxidation Numbers**

To identify whether atoms are oxidized or reduced, chemists use a model of **oxidation numbers,** which can help them identify differences in an atom of an element in different compounds. By following the set of rules described in **Skills Toolkit 1** below, you can assign an oxidation number to each atom in a molecule or in an ion. **Sample Problem A** shows how to use the rules. You can see three different oxidation numbers for atoms of manganese in **Figure 2**.

By tracking oxidation numbers, you can tell whether an atom is oxidized or reduced. If the oxidation number of an atom increases during a reaction, the atom is oxidized. If the oxidation number decreases, the atom is reduced. Like other models, oxidation numbers have limits. You should consider them a bookkeeping tool to help keep track of electrons. In some cases, additional rules are needed to find values that make sense.

# SKILLS SUDDIN

#### **Assigning Oxidation Numbers**

- 1. Identify the formula.
  - If no formula is provided, write the formula of the molecule or ion.

#### 2. Assign known oxidation numbers.

- Place an oxidation number above each element's symbol according to the following rules.
  - **a.** The oxidation number of an atom of any free (uncombined) element in atomic or molecular form is zero.
  - **b.** The oxidation number of a monatomic ion is equal to the charge on the ion.
  - **c.** The oxidation number of an atom of fluorine in a compound is always –1 because it is the most electronegative element.
  - **d.** An atom of the more electronegative element in a binary compound is assigned the number equal to the charge it would have if it were an ion.
  - **e.** In compounds, atoms of the elements of Group 1, Group 2, and aluminum have positive

oxidation numbers of +1, +2, and +3, respectively.

- f. The oxidation number of each hydrogen atom in a compound is +1, unless it is combined with a metal atom; then it is -1.
- g. The oxidation number of each oxygen atom in compounds is usually -2. When combined with fluorine atoms, oxygen becomes +2. In peroxides, such as H<sub>2</sub>O<sub>2</sub>, an oxygen atom has an oxidation number of -1.

# **3. Calculate remaining oxidation** numbers, and verify the results.

- Use the total oxidation number of each element's atoms (the oxidation number for an atom of the element multiplied by the subscript for the element) and the following rules to calculate missing oxidation numbers.
  - **h.** The sum of the oxidation numbers for all the atoms in a molecule is zero.
  - **i.** The sum of the oxidation numbers for all atoms in a polyatomic ion is equal to the charge on that ion.



#### Figure 2

An atom of manganese in its elemental form has an oxidation number of 0. In  $MnO_2$ , the oxidation number of the manganese atom is +4. In the permanganate ion,  $MnO_4^-$ , the oxidation number of the manganese atom is +7.

## SAMPLE PROBLEM A

#### **Determining Oxidation Numbers**

Assign oxidation numbers to the sulfur and oxygen atoms in the pyrosulfate ion,  $S_2O_7^{2-}$ .

#### **1** Identify the formula.

The pyrosulfate ion has the formula  $S_2O_7^{2-}$ .

#### **2** Assign known oxidation numbers.

According to Rule **g**, the oxidation number of the O atoms is -2, so this number is written above the O symbol in the formula. Because the oxidation number of the sulfur atoms is unknown, x is written above the S symbol. Thus the formula is as follows:

 $\overset{x -2}{S_2O_7^{2-}}$ 

#### **3** Calculate remaining oxidation numbers, and verify the results.

- Multiplying the oxidation numbers by the subscripts, we see that the S atoms contribute 2x and the O atoms contribute 7(-2) = -14 to the total oxidation number. To come up with the correct total charge, (Rule

  i), 2x + (-14) = -2. Solve this equation to find x = +6.
- In  $S_2O_7^{2-}$ , the oxidation number of the S atoms is +6, and the oxidation number of the O atoms is -2. The sum of the total oxidation numbers for each element is 2(+6) + 7(-2) = -2, which is the charge on the ion.

#### **PRACTICE HINT**

In this book, the oxidation number for a single atom is written above its chemical symbol. However, be sure to use the total number of atoms for each element when finding the sum of the oxidation numbers for all atoms in the molecule or ion.

		PRACTICE	
Determine the			
<b>1</b> a. NH <sub>4</sub> <sup>+</sup>	<b>e.</b> H <sub>2</sub>	i. $Ca(OH)_2$	PROBLEM
<b>b.</b> Al	<b>f.</b> PbSO <sub>4</sub>	<b>j</b> . Fe <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	SIGIL
<b>c.</b> H <sub>2</sub> O	g- KClO <sub>3</sub>	<b>k.</b> $H_2PO_4^-$	
<b>d.</b> Pb <sup>2+</sup>	<b>h.</b> BF <sub>3</sub>	I. $NH_4NO_3$	



Figure 3

Zinc metal reacts with hydrochloric acid, making bubbles of hydrogen gas.

#### **Identifying Redox Reactions**

**Figure 3** shows the reaction of Zn with HCl. Is this a redox reaction? Hydrochloric acid is a solution in water of  $Cl^-$ , which plays no part in the reaction, and  $H_3O^+$ . The net change in this reaction is

$$2H_3O^+(aq) + Zn(s) \longrightarrow H_2(g) + 2H_2O(l) + Zn^{2+}(aq)$$

Using rules **a**, **b**, **f**, **g**, **h**, and **i** from **Skills Toolkit 1**, you can give oxidation numbers to all atoms as follows:

$$2\overset{+1}{\mathrm{H}_{3}}\overset{-2}{\mathrm{O}^{+}}(aq) + \overset{0}{\mathrm{Zn}}(s) \longrightarrow \overset{0}{\mathrm{H}_{2}}(g) + 2\overset{+1}{\mathrm{H}_{2}}\overset{-2}{\mathrm{O}}(l) + \overset{+2}{\mathrm{Zn}}^{2+}(aq)$$

Comparing oxidation numbers, you see that the zinc atom changes from 0 to +2 and that two hydrogen atoms change from +1 to 0. So, this is a redox reaction. In a redox reaction, the oxidation numbers of atoms that are oxidized increase, and those of atoms that are reduced decrease.

## **Half-Reactions**

In the reaction shown in **Figure 3**, each zinc atom loses two electrons and is oxidized. One way to show only this half of the overall redox reaction is by writing a **half-reaction** for the change.

$$\operatorname{Zn}(s) \longrightarrow \operatorname{Zn}^{2+}(aq) + 2e^{-}$$

Note that electrons are a product. Of course, there is also a half-reaction for reduction in which electrons are a reactant.

$$2e^- + 2H_3O^+(aq) \longrightarrow H_2(g) + 2H_2O(l)$$

By adding the two half-reactions together, you get the overall redox reaction shown earlier. Notice that enough electrons are in each half-reaction to keep the charges balanced. Keep in mind that free electrons do not actually leave the zinc atoms and float around before being picked up by the hydronium ions. Instead, they are "handed off" directly from one to the other.

#### half-reaction

the part of a reaction that involves only oxidation or reduction

#### **Balancing Oxidation-Reduction Equations**

Equations for redox reactions are sometimes difficult to balance. Use the steps in **Skills Toolkit 2** below to balance redox equations for reactions in acidic aqueous solution. An important step is to identify the key ions or molecules that contain atoms whose oxidation numbers change. These atoms are the starting points of the unbalanced half-reactions. For the reaction of zinc and hydrochloric acid, the unbalanced oxidation and reduction half-reactions would be as follows:

 $\operatorname{Zn}(s) \longrightarrow \operatorname{Zn}^{2+}(aq)$  and  $\operatorname{H}_3O^+(aq) \longrightarrow \operatorname{H}_2(g)$ 

These reactions are then separately balanced. Finally, the balanced equations of the two half-reactions are added together to cancel the electrons.

SKILLS

# **Balancing Redox Equations Using the Half-Reaction Method**

#### 1. Identify reactants and products.

- Write the unbalanced equation in ionic form, excluding any spectator ions.
- Assign oxidation numbers, and identify the atoms that change their oxidation numbers. Ignore all species whose atoms do not change their oxidation number.

#### 2. Write and balance the half-reactions.

- Separate the equation into its two half-reactions.
- For each half-reaction, do the following:
  - **a.** Balance atoms other than hydrogen and oxygen.
  - **b.** Balance oxygen atoms by adding water molecules as needed.
  - **c.** Balance hydrogen atoms by adding one hydronium ion for each hydrogen atom needed and then by adding the same number of water molecules to the other side of the equation.
  - **d.** Balance the overall charge by adding electrons as needed.

#### 3. Make the electrons equal, and combine half-reactions.

- Multiply each half-reaction by an appropriate number so that both half-reactions have the same number of electrons. Now the electrons lost equal the electrons gained, so charge is conserved.
- Combine the half-reactions, and cancel anything that is common to both sides of the equation.

#### 4. Verify your results.

• Double-check that all atoms and charge are balanced.

## SAMPLE PROBLEM B

#### **The Half-Reaction Method**

Write and balance the equation for the reaction when an acidic solution of  $MnO_4^-$  reacts with a solution of  $Fe^{2+}$  to form a solution containing  $Mn^{2+}$  and  $Fe^{3+}$  ions.

#### **1** Identify reactants and products.

• The unbalanced equation in ionic form is as follows:

 $H_3O^+(aq) + MnO_4^-(aq) + Fe^{2+}(aq) \longrightarrow Mn^{2+}(aq) + Fe^{3+}(aq)$ 

• Oxidation numbers for the atoms are as follows:

$${}^{+1}_{H_3}{}^{-2}_{O^+} + {}^{+7}_{Mn}{}^{-2}_{O_4} + {}^{+2}_{Fe}{}^{2+} \longrightarrow {}^{+2}_{Mn}{}^{2+}_{O^+} + {}^{+3}_{Fe}{}^{3-}_{O^+}$$

• Atoms of Mn and Fe change oxidation numbers.

#### **2** Write and balance the half-reactions.

Unbalanced:  $Fe^{2+} \rightarrow Fe^{3+}$  $MnO_4^- \rightarrow Mn^{2+}$ Balance O:  $Fe^{2+} \rightarrow Fe^{3+}$  $MnO_4^- \rightarrow Mn^{2+} + 4H_2O$ Balance H:  $Fe^{2+} \rightarrow Fe^{3+}$  $8H_3O^+ + MnO_4^- \rightarrow Mn^{2+} + 12H_2O$ Balance  $e^-$ :  $Fe^{2+} \rightarrow Fe^{3+} + e^ 5e^- + 8H_3O^+ + MnO_4^- \rightarrow Mn^{2+} + 12H_2O$ 

#### 3 Make the electrons equal, and combine half-reactions.

Multiply the half-reaction that involves iron by 5 to make the numbers of electrons the same in each half-reaction. Add the half-reactions, and cancel the electrons to get the final balanced equation:

 $8\mathrm{H}_{3}\mathrm{O}^{+}(aq) + \mathrm{MnO}_{4}^{-}(aq) + 5\mathrm{Fe}^{2+}(aq) \longrightarrow \mathrm{Mn}^{2+}(aq) + 5\mathrm{Fe}^{3+}(aq) + 12\mathrm{H}_{2}\mathrm{O}(l)$ 

#### **4** Verify your results.

Note that there are equal numbers of all atoms and a net charge of +17 on each side of the equation.

#### PRACTICE

Use the half-reaction method to write a balanced equation for each of the following reactions in acidic, aqueous solution.

- The reactants are Fe(s) and  $O_2(aq)$ , and the products are  $Fe^{3+}(aq)$  and  $H_2O(l)$ .
- **2** Al(*s*) is placed in the acidic solution and forms  $H_2(g)$  and Al<sup>3+</sup>(*aq*).
- 3 The reactants are sodium bromide and hydrogen peroxide, and the products are bromine and water.
- 4 The reactants are manganese dioxide and a soluble copper(I) salt, and the products are soluble manganese(II) and copper(II) salts.

#### **PRACTICE HINT**

To help avoid confusion between charges and oxidation numbers, the sign of a charge is written last and the sign of an oxidation number is written first. Thus the  $Fe^{2+}$  ion has a 2+ charge and a +2 oxidation number.



#### **Identifying Agents in Redox Reactions**

In **Sample Problem B**, the permanganate ion caused the oxidation of the iron(II) ion. Substances that cause the oxidation of other substances are called **oxidizing agents.** They accept electrons easily and so are reduced. Common oxidizing agents are oxygen, hydrogen peroxide, and halogens.

**Reducing agents** cause reduction to happen and are themselves oxidized. The iron(II) ion caused the reduction of the permanganate ion and was the reducing agent. Common ones are metals, hydrogen, and carbon.

#### oxidizing agent

the substance that gains electrons in an oxidation-reduction reaction and is reduced

#### reducing agent

a substance that has the potential to reduce another substance

# **O** Section Review

#### **UNDERSTANDING KEY IDEAS**

- **1.** Explain oxidation and reduction in terms of electron transfer.
- **2.** How can you identify a reaction as a redox reaction?
- **3.** Describe how an oxidation-reduction reaction may be broken down into two half-reactions, and explain why the latter are useful in balancing redox equations.
- **4.** Compare the number of electrons lost in an oxidation half-reaction with the number of electrons gained in the corresponding reduction half-reaction.
- **5.** Describe what an oxidizing agent and a reducing agent are.

#### **PRACTICE PROBLEMS**

**6.** Assign oxidation numbers to the atoms in each of the following:

a. 
$$H_2SO_3$$
 c.  $SF_6$ 

**b.** 
$$Cl_2$$
 **d.**  $NO_3^-$ 

- **7.** Assign oxidation numbers to the atoms in each of the following:
  - **a.** CH<sub>4</sub> **c.** NaHCO<sub>3</sub>
  - **b.**  $HSO_3^-$  **d.**  $NaBiO_3$
- Identify the oxidation number of a Cr atom in each of the following: CrO<sub>3</sub>, CrO, Cr(s), CrO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, and CrO<sub>4</sub><sup>2-</sup>.

**9.** Which of the following equations represent redox reactions? For each redox reaction, determine which atom is oxidized and which is reduced, and identify the oxidizing agent and the reducing agent.

**a.** MgO(s) + H<sub>2</sub>CO<sub>3</sub>(aq) 
$$\rightarrow$$

$$MgCO_3(s) + H_2O(l)$$

**b.** 
$$2KNO_3(s) \longrightarrow 2KNO_2(s) + O_2(g)$$

**c.** 
$$H_2(g) + CuO(s) \longrightarrow Cu(s) + H_2O(l)$$

**d.** NaOH
$$(aq)$$
 + HCl $(aq)$   $\rightarrow$ 

 $NaCl(aq) + H_2O(l)$ 

**e.** 
$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

**f.** 
$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

**10.** Use the half-reaction method in acidic, aqueous solution to balance each of the following redox reactions:

**a.** 
$$\operatorname{Cl}^{-}(aq) + \operatorname{Cr}_{2}\operatorname{O}_{7}^{2-}(aq) \longrightarrow$$
  
 $\operatorname{Cl}_{2}(g) + \operatorname{Cr}^{3+}(aq)$   
**b.**  $\operatorname{Cu}(s) + \operatorname{Ag}^{+}(aq) \longrightarrow \operatorname{Cu}^{2+}(aq) + \operatorname{Ag}(s)$   
**c.**  $\operatorname{Br}_{2}(l) + \operatorname{I}^{-}(aq) \longrightarrow \operatorname{I}_{2}(s) + \operatorname{Br}^{-}(aq)$ 

- **d.**  $I^{-}(aq) + NO_{2}^{-}(aq) \longrightarrow NO(g) + I_{2}(s)$
- **11.** Determine which atom is oxidized and which is reduced, and identify the oxidizing agent and the reducing agent for each reaction in item 10.

#### **CRITICAL THINKING**

**12.** How is it possible for hydrogen peroxide to be both an oxidizing agent and a reducing agent?

#### S E C T I O N



# Introduction to Electrochemistry

#### **Key Terms**

- electrochemistry
- voltage
- electrode
- electrochemical cell
- cathode
- anode

#### electrochemistry

the branch of chemistry that is the study of the relationship between electric forces and chemical reactions



#### Figure 4

When the switch of a flashlight is closed, electrons "pushed" by the battery are forced through the thin tungsten filament of the bulb. This flow of electrons makes the filament hot enough to emit light.

#### **O**BJECTIVES

**Describe** the relationship between voltage and the movement of electrons.

- **Identify** the parts of an electrochemical cell and their functions.
- Write electrode reactions for cathodes and anodes.

# **Chemistry Meets Electricity**

The science of **electrochemistry** deals with the connections between chemistry and electricity. It is an important subject because it is involved in many of the things you use every day. Electrochemical devices change electrical energy into chemical energy and vice versa. A simple flashlight is an everyday example of something that converts chemical energy into electrical energy, which is then converted into light energy.

**Figure 4** shows the components of a typical flashlight. The power source is two batteries or cells. Each cell has a metal terminal at each end. If you examine a battery, you will find a  $\oplus$  or + symbol near the top identifying the positive terminal. The bottom is the negative terminal, and is possibly unmarked or marked with a  $\ominus$  or – symbol. By closing the switch, you turn the flashlight on. Electrons move from the negative terminal of the lower battery, through a metal circuit that includes the light bulb, and continue to the positive terminal of the upper battery. The circuit is completed by electrons and ions moving charge through each of the batteries and electrons moving charge from the upper battery to the lower one. When you turn off the flashlight, you break the pathway, and the movement of electrons and ions stops.

#### "Electrical Pressure" Is Expressed in Volts

Electrochemical reactions in a battery cause a greater electron density in the negative terminal than in the positive terminal. Electrons repel each other, so there is a higher "pressure" on the electrons in the negative terminal, which drives the electrons out of the battery and through the flashlight.

Electrical "pressure," often called *electric potential*, or **voltage**, is expressed in units of *volts*. The voltage of an ordinary flashlight cell is 1.5 volts or 1.5 V. When two cells are placed end-to-end, as in **Figure 4**, the voltages add together, so the overall voltage driving electrons is 3.0 V. The movement of electrons or other charged particles is described as *electric current* and is expressed in units of *amperes*.

## **Components of Electrochemical Cells**

A flashlight battery is an electrochemical cell. An **electrochemical cell** consists of two electrodes separated by an electrolyte. An **electrode** is a conductor that connects with a nonmetallic part of a circuit. You have learned about two kinds of conductors. One kind includes metals, which conduct electric current through moving electrons. The second kind includes electrolyte solutions, which conduct through moving ions.

#### **The Cathode Is Where Reduction Occurs**

*Electrode reactions* happen on the surfaces of electrodes. **Figure 5** shows half of an electrochemical cell. The copper strip is an electrode because it is a conductor in contact with the electrolyte solution. The reaction on this electrode is the reduction described by the following equation:

$$\operatorname{Cu}^{2+}(aq) + 2e^{-} \longrightarrow \operatorname{Cu}(s)$$

The copper electrode is a **cathode** because reduction happens on it.

#### voltage

the potential difference or electromotive force, measured in volts; it represents the amount of work that moving an electric charge between two points would take

#### electrochemical cell

a system that contains two electrodes separated by an electrolyte phase

#### electrode

a conductor used to establish electrical contact with a nonmetallic part of a circuit, such as an electrolyte

#### cathode

the electrode on whose surface reduction takes place





#### **The Anode Is Where Oxidation Occurs**

The electrons that cause reduction at the cathode are pushed there from a reaction at the second electrode of a cell. The **anode** is the electrode on which oxidation occurs. **Figure 6** shows the second half of the electrochemical cell. The zinc strip is an electrode because it is a conductor in contact with the solution. The reaction on this electrode is the oxidation described by the following equation:

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$$

The zinc electrode is an anode because oxidation happens on it.

The electrode reactions described here would have been called halfreactions in the last section. The difference is that a half-reaction is a helpful model, but the electrons shown are never really free. An electrode reaction describes reality because the electrons actually move from one electrode to another to continue the reaction.

#### **Pathways for Moving Charges**

The electrode reactions cannot happen unless the electrodes are part of a complete circuit. So, a cell must have pathways to move charges. Wires are often used to connect the electrodes through a meter or a light bulb. Electrons carry charges in the wires and electrodes.

Ions in solution carry charges between the electrolytes to complete the circuit. A porous barrier, as shown in **Figure 7**, or a salt bridge keeps the solutions from mixing, but lets the ions move. In the cell shown, charge is carried through the barrier by a combination of  $Zn^{2+}(aq)$  ions moving to the right and  $SO_4^{2-}(aq)$  ions moving to the left. Understand that positive charge may be carried from left to right through this cell either by negative particles (electrons or anions) moving from right to left or by cations moving from left to right.

#### anode

the electrode on whose surface oxidation takes place; anions migrate toward the anode, and electrons leave the system from the anode



Electrodes Porous barrier

#### **Figure 7**

The light bulb is powered by the reaction in this cell.

#### **The Complete Cell**

**Figure 7** shows a complete cell composed of the electrodes shown separately in earlier figures. The overall process when the anode reaction is added to the cathode reaction for this cell is the same as the following redox reaction:

$$\operatorname{Zn}(s) + \operatorname{Cu}^{2+}(aq) \longrightarrow \operatorname{Zn}^{2+}(aq) + \operatorname{Cu}(s)$$

Although the two electrode reactions occur at the same time, they occur at different places in the cell. This is an important distinction from the redox reactions discussed in the last section.



#### **UNDERSTANDING KEY IDEAS**

- **1.** What is voltage?
- **2.** How does voltage relate to the movement of electrons?
- **3.** List the components of an electrochemical cell, and describe the function of each.
- **4.** What are the names of the electrodes in an electrochemical cell? What type of reaction happens on each?
- **5.** Describe the difference in how charge flows in wires and in electrolyte solutions.
- **6.** A 12 V car battery has six cells connected end-to-end. What is the voltage of a single cell?
- **7.** Will the reaction below happen at an anode or a cathode? Explain.

 $\operatorname{Fe}(\operatorname{CN})_6^{3-}(aq) + e^- \longrightarrow \operatorname{Fe}(\operatorname{CN})_6^{4-}(aq)$ 

**8.** Describe the changes in oxidation number that happen in an anode reaction and in a cathode reaction.

#### **CRITICAL THINKING**

- **9.** What would happen if you put one of the batteries in backward in a two-cell flashlight?
- **10.** What would happen if you put both batteries in backward in a two-cell flashlight?



- 12. Write an electrode reaction in which you change  $Br^{-}(aq)$  to  $Br_{2}(aq)$ . Would this reaction happen at an anode or a cathode?
- **13.** Write an electrode reaction in which  $\operatorname{Sn}^{4+}(aq)$  is changed to  $\operatorname{Sn}^{2+}(aq)$ . Would this reaction happen at an anode or a cathode?
- **14.** If you wanted to use an electrochemical cell to deposit a thin layer of silver metal onto a bracelet, which electrode would you make the bracelet? Explain using the equation for the electrode reaction that would occur.
- 15. What would happen at each electrode if batteries were connected to the cell in Figure 7 so that electrons flowed in the opposite direction of the direction described in the text?
- **16.** Compare the equations for electrode reactions with the equations for half-reactions.
- 17. Write the electrode reactions for a cell that involves only Cu(s) and Cu<sup>2+</sup>(aq) in which the anode reaction is the reverse of the cathode reaction. What is the net result of operating this cell?
- **18.** Is it correct to say that the net chemical result of an electrochemical cell is a redox reaction? Explain.

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#### S E C T I O N



# **Galvanic Cells**

#### **Key Terms**

- corrosion
- standard electrode potential

#### **OBJECTIVES**

- **Describe** the operation of galvanic cells, including dry cells, lead-acid batteries, and fuel cells.
- Identify conditions that lead to corrosion and ways to prevent it.
- **Calculate** cell voltage from a table of standard electrode potentials.

# **Types of Galvanic Cells**

A battery is one kind of *galvanic cell*, a device that can change chemical energy into electrical energy. In these cells, a spontaneous reaction happens that causes electrons to move. **Figure 8** shows a kind of galvanic cell known as a Daniell cell. Daniell cells were used as energy sources in the early days of electrical research. Of course, Daniell cells would be impractical to use in a radio or portable computer today. There are many other kinds of galvanic cells. These include dry cells, lead-acid batteries, and fuel cells.

#### Figure 8

As a result of the reaction in a galvanic cell, the bulb lights up as electrons move in the wires from the anode to the cathode.





#### **Dry Cells**

Although the Daniell cell was useful for supplying energy in the lab, it wasn't very portable because it held solutions. The energy source that you know as a *battery* and use in radios and remote controls is a dry cell. In a dry cell, moist electrolyte pastes are used instead of solutions. This cell was invented over a century ago by Georges Leclanché, a French chemist. His original design was close to that shown on the left in **Figure 9.** A carbon rod, the battery's positive terminal, connects with a wet paste of carbon; ammonium chloride, NH<sub>4</sub>Cl; manganese(IV) oxide, MnO<sub>2</sub>; starch; and water. When the cell is used, the carbon rod is the cathode, and the following electrode reaction happens:

Cathode:  $2MnO_2(s) + 2NH_4^+(aq) + 2e^- \rightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$ 

The zinc case serves as the negative terminal of the battery. When the cell is used, zinc dissolves in the following electrode reaction:

Anode: 
$$\operatorname{Zn}(s) + 4\operatorname{NH}_3(aq) \longrightarrow 2e^- + \operatorname{Zn}(\operatorname{NH}_3)_4^{2+}(aq)$$

The white powder that you see on old corroded batteries is the chloride salt of this  $Zn(NH_3)_4^{2+}(aq)$  complex ion.

The  $NH_4^+(aq)$  ion is a weak acid, and for this reason the Leclanché cell is called the *acidic* version of the dry cell. The *alkaline cell*, shown in **Figure 9**, is a newer, better version. The ingredients of the alkaline cell are similar to the acidic version, but the carbon cathode is replaced by a piece of brass, and ammonium chloride is replaced by potassium hydroxide. The presence of this strong base gives the alkaline cell its name. The electrode reactions that occur when the cell is used are described by the equations below.

Cathode: 
$$2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$$
  
Anode:  $Zn(s) + 2OH^-(aq) \rightarrow 2e^- + Zn(OH)_2(s)$ 

A sturdy steel shell is needed to prevent the caustic contents from leaking out of the battery. Because of this extra packaging, alkaline cells are more expensive than cells of the older, acidic version. **Figure 9** Two familiar kinds of dry cells use different electrolytes. The electrolytes make the cell on the left acidic and the cell on the right alkaline.



# Listen Up

#### PROCEDURE

- 1. Press a zinc strip and a copper strip into a raw potato. The strips should be about 0.5 cm apart but should not touch one another.
- 2. While listening to the earphone, touch one wire from the earphone to one of the

metal strips and the other wire from the earphone to the second metal strip using **alligator clips.** Record your observations.

**3.** While listening to the earphone, touch both wires to a single metal strip. Record your observations.

#### SAFETY PRECAUTIONS



#### ANALYSIS

- Compare your results from step 2 with your results from step 3. Suggest an explanation for any similarities or differences.
- **2.** Suggest an explanation for the sound.

#### **Lead-Acid Batteries**

The batteries just discussed are called *dry cells* because the water is not free, but absorbed in pastes. In contrast, the Daniell cell and the lead-acid battery use aqueous solutions of electrolytes, so they should be used in an upright position.

Most car batteries are lead-acid storage batteries. Usually they have six cells mounted side-by-side in a single case, as shown in **Figure 10**. Though many attempts have been made to replace the heavy lead-acid battery by lighter alternatives, no other material has been found that can reliably and economically give the large surges of electrical energy needed to start a cold engine.

A fully charged lead-acid cell is made up of a stack of alternating lead and lead(IV) oxide plates isolated from each other by thin porous separators. All these components are in a concentrated solution of sulfuric acid. The positive terminal of one cell is linked to the negative terminal of the next cell in the same way that the batteries in the flashlight were connected. This arrangement of cells causes the outermost terminals of the lead-acid battery to have a voltage of 12.0 V. When the cell is used, it acts as a galvanic cell with the following reactions:

Cathode: 
$$PbO_2(s) + HSO_4^-(aq) + 3H_3O^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 5H_2O(l)$$

Anode:  $Pb(s) + HSO_4(aq) + H_2O(l) \rightarrow 2e^- + PbSO_4(s) + H_3O^+(aq)$ 

Notice that PbSO<sub>4</sub> is produced at both electrodes.

Unlike the Daniell and Leclanché cells, the lead-acid cell is rechargeable. So, when the battery runs down, you do not need to replace it. Instead, an electric current is applied in a direction opposite to that discussed above. As a result of the input of energy, the reactions are reversed. The cell is eventually restored to its charged state. During recharge, the cell functions as an *electrolytic cell*, which you will learn about in the next section.





#### Figure 10

The lead-acid battery is used to store energy in almost all vehicles. Although the cutaway view shows a single  $PbO_2$  plate and a single Pb plate in each cell, there are actually several of each.

#### **Fuel Cells**

In a *fuel cell*, the oxidizing and reducing agents are brought in, often as gases, from outside of the cell, rather than being part of it. Unlike a dry cell, a fuel cell can work forever, in principle, changing chemical energy into electrical energy. **Figure 11** models a fuel cell that uses the reactions below.

Cathode:  $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ 

Anode:  $2H_2(g) + 4OH^-(aq) \rightarrow 4e^- + 4H_2O(l)$ 

Because fuel cells directly change chemical energy into electrical energy, they are very efficient and are cleaner than the burning of fuels in power plants to generate electrical energy. Research into fuel cells continues, and fuel cells are used in a few experimental power plants.



#### Figure 11

The reactions in this fuel cell take place at carbon electrodes that contain metal catalysts. The water formed is removed as a gas.

#### **Corrosion Cells**

Oxygen is so reactive that many metals spontaneously oxidize in air. Fortunately, many of these reactions are slow. The disintegration of metals is called **corrosion.** Usually  $O_2(g)$  is the oxidizing agent, but the direct reaction of  $O_2$  with the metal is not usually how corrosion happens.

Water is usually involved in corrosion. Consider the corrosion of iron. Hydrated iron(III) oxide, or rust, forms by the following overall reaction:

$$4\text{Fe}(s) + 3\text{O}_2(aq) + 4\text{H}_2\text{O}(l) \longrightarrow 2\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}(s)$$

However, the reaction mechanism is more complicated than this equation suggests. An even simpler version of what happens is shown in **Figure 12.** The iron dissolves by the oxidation half-reaction

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^{-}$$

 $Fe^{2+}$  then gets oxidized to  $Fe^{3+}$  in a further reaction. Any oxidation must be accompanied by a reduction taking place at the same time, but not necessarily at the same location. In fact, the electrons produced by the oxidation are consumed by the reduction of oxygen at a cathodic site elsewhere on the iron's surface. The reduction half-reaction is

$$O_2(aq) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

Electrons move in the metal and ions move in the water layer between the two reaction sites, as in an electrochemical cell. In fact, a corrosion cell is an unwanted galvanic cell. Chemical energy is converted into electrical energy, which heats the metal.

The three ingredients—oxygen, water, and ions—needed for the corrosion of metals are present almost everywhere on Earth. Even pure rainwater contains a few  $H_3O^+$  and  $HCO_3^-$  ions from dissolved carbon dioxide. Higher ion concentrations—from airborne salt near the ocean, from acidic air pollutants, or from salts spread on icy roads—make corrosion worse in certain areas.



#### corrosion

the gradual destruction of a metal or alloy as a result of chemical processes such as oxidation or the action of a chemical agent



#### Figure 13

The Alaskan oil pipeline is cathodically protected by a parallel zinc cable.

#### **Methods to Prevent Corrosion**

Corrosion is a major economic problem. About 20% of all the iron and steel produced is used to repair or replace corroded structures. That is why the prevention of corrosion is a major focus of research in materials science and electrochemistry. An obvious response to corrosion is to paint the metal or coat it with some other material that does not corrode. However, once a crack or scrape occurs in the coating, corrosion can begin and often spread even faster than on an uncoated surface.

Some metals corrode more easily than others do. Electronegativity is one factor. Gold, the metal with the highest electronegativity, is the most corrosion resistant. The alkali metals, with the lowest electronegativities, easily corrode. The properties of the metal oxides that form are also important. Despite having low electronegativities, aluminum, chromium, and titanium are corrosion-resistant metals. This is because the oxides of these metals form layers that cover the underlying metal, stopping oxidation. In contrast, rust is a porous powder that flakes off, so it does not protect the iron surface.

Surprisingly, it is better to coat steel with another metal that does corrode. Trash cans, for example, are made of zinc-coated steel. This coating does not stop corrosion. But the zinc corrodes first, making the steel underneath last much longer than it would without the zinc layer.

Whenever two metals are in electrical contact, a corrosion cell is likely to form. In fact, the metal that is the anode in the cell corrodes faster than it would if it were not connected to another metal. This idea explains the use of sacrificial anodes on ships and pipelines, as shown in Figure 13. As the anode corrodes, it gives electrons to the cathode. The corrosion of the anode slows or stops the corrosion of the important structural metal in a process called cathodic protection.



#### Figure 14

It would be difficult to measure every possible combination of electrodes using a technique like the one shown here. This is why the SHE is used as a reference for all other electrodes.



# **Determining the Voltage of a Cell**

A voltmeter is an electronic instrument that measures the voltage between its two leads. The student in **Figure 14** is using the meter to measure the difference in potentials between the electrodes in a Daniell cell. With such a meter, measuring the voltage of a cell is easy. However, the voltage of a cell depends on such factors as temperature and concentration. And because there are so many combinations of electrode reactions, it would be very difficult to measure the voltage for each combination.

#### **Standard Electrode Potentials**

Picking one electrode as a standard and determining electrode potentials in reference to that standard is much easier than measuring the potential between every combination of electrodes is. The electrode that has been chosen as a standard is the *standard hydrogen electrode* (SHE). It consists of a platinum electrode in a 1.00 M  $H_3O^+$  solution in the presence of  $H_2$  gas at 1 atm pressure and 25°C. The SHE is assigned a potential of 0.0000 V and its reaction is

$$2H_3O^+(aq) + 2e^- \rightleftharpoons H_2(g) + 2H_2O(l)$$

When measuring potentials, a salt bridge, a narrow tube filled with a concentrated solution of a salt, must be used to link the compartments. When a SHE is joined to another electrode by a salt bridge, a voltmeter can be used to determine the **standard electrode potential**,  $E^{\circ}$ , for the electrode. Some standard electrode potentials are shown in **Table 1**, on the last page of this section.

The standard electrode potential is sometimes called the standard reduction potential because it is listed by the reduction half-reactions. However, a voltmeter allows no current in the cell during the measurement. Therefore, the conditions are neither galvanic nor electrolytic—the cell is at equilibrium. As a result, the half-reactions listed in the table are shown as reversible. If the reaction occurs in the opposite direction, as an oxidation half-reaction,  $E^{\circ}$  will have the opposite sign.

# standard electrode potential

the potential developed by a metal or other material immersed in an electrolyte solution relative to the potential of the hydrogen electrode, which is set at zero

#### **Calculating the Voltage of a Cell**

Think of  $E^{\circ}$  as a measure of the ability of an electrode to gain electrons. A more positive value means the electrode is more likely to be a cathode. The standard cell voltage—the voltage of a cell under standard conditions—can be found by subtracting the standard potentials of the two electrodes, as follows:

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$$

To determine the reaction that will happen naturally, use the electrode with the most positive  $E^{\circ}$  value as the cathode, as shown in **Sample Problem C.** Otherwise, a given reaction happens naturally if  $E^{\circ}_{cell}$  is positive. If  $E^{\circ}_{cell}$  is negative, the reaction could be made to happen if energy is added.

#### SAMPLE PROBLEM C

## **Calculating Cell Voltage**

Calculate the voltage of a cell for the naturally occurring reaction between a liquid mercury electrode in a solution of mercury(I) nitrate and a cadmium metal electrode in a solution of cadmium nitrate.

#### 1 Gather information.

From Table 1 the standard electrode potentials are

 $Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l) \qquad E^\circ = +0.7973 \text{ V}$  $Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s) \qquad E^\circ = -0.4030 \text{ V}$ 

#### **2** Plan your work.

The mercury electrode has the more positive  $E^{\circ}$ , so it is the cathode.

#### **3** Calculate.

 $E^{\circ}_{cell} = E^{\circ}_{Hg} - E^{\circ}_{Cd} = (+0.7973 \text{ V}) - (-0.4030 \text{ V}) = +1.2003 \text{ V}$ 

#### 4 Verify your results.

The positive value of  $E_{cell}^{\circ}$  shows that the reaction is spontaneous and will occur naturally with the mercury electrode as the cathode.

# Use data from Table 1 to answer the following: Calculate the voltage of a cell if the reactions are as follows: Fe(s) → Fe<sup>3+</sup>(aq) + 3e<sup>-</sup> O<sub>2</sub>(g) + 2H<sub>2</sub>O(l) + 4e<sup>-</sup> → 4OH<sup>-</sup>(aq) Calculate the voltage of a cell for the naturally occurring reaction between a copper electrode in a copper(II) solution and a zinc electrode in a solution containing zinc ions. Calculate the voltage of a cell for the naturally occurring reaction between a silver electrode in a solution containing silver ions and a copper electrode in a copper(II) solution.

## When asked to calculate

**PRACTICE HINT** 

the voltage of a cell for a particular chemical equation, you must determine which atom is oxidized and which is reduced based on the change of oxidation numbers.



#### Table 1 Standard Electrode Potentials

Electrode reaction	<i>E</i> °(V)	Electrode reaction	<i>E</i> °(V)
$\operatorname{Li}^+(aq) + e^- \rightleftharpoons \operatorname{Li}(s)$	-3.0401	$\operatorname{Cu}^{2+}(aq) + 2e^{-} \rightleftharpoons \operatorname{Cu}(s)$	+0.3419
$\mathrm{K}^+(aq) + e^- \rightleftharpoons \mathrm{K}(s)$	-2.931	$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.401
$\operatorname{Na}^+(aq) + e^- \rightleftharpoons \operatorname{Na}(s)$	-2.71	$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.5355
$2\mathrm{H}_{2}\mathrm{O}(l) + 2e^{-} \rightleftharpoons \mathrm{H}_{2}(g) + 2\mathrm{OH}^{-}(aq)$	-0.828	$\operatorname{Fe}^{3+}(aq) + e^{-} \rightleftharpoons \operatorname{Fe}^{2+}(aq)$	+0.771
$\operatorname{Zn}^{2+}(aq) + 2e^{-} \rightleftharpoons \operatorname{Zn}(s)$	-0.7618	$\mathrm{Hg}_{2}^{2+}(aq) + 2e^{-} \rightleftharpoons 2\mathrm{Hg}(l)$	+0.7973
$\operatorname{Fe}^{2+}(aq) + 2e^{-} \rightleftharpoons \operatorname{Fe}(s)$	-0.447	$\operatorname{Ag}^+(aq) + e^- \rightleftharpoons \operatorname{Ag}(s)$	+0.7996
$PbSO_{4}(s) + H_{3}O^{+}(aq) + 2e^{-} \rightleftharpoons$ $Pb(s) + HSO_{4}^{-}(aq) + H_{2}O(l)$	-0.42	$\operatorname{Br}_2(l) + 2e^- \rightleftharpoons 2\operatorname{Br}^-(aq)$	+1.066
$\operatorname{Cd}^{2+}(aq) + 2e^{-} \rightleftharpoons \operatorname{Cd}(s)$	-0.4030	$\operatorname{Cl}_2(g) + 2e^- \rightleftharpoons 2\operatorname{Cl}^-(aq)$	+1.358
$Pb^{2+}(aq) + 2e^{-} \rightleftharpoons Pb(s)$	-0.1262	$PbO_2(s) + 4H_3O^+(aq) + 2e^- \rightleftharpoons$ $Pb^{2+}(aq) + 6H_2O(l)$	+1.455
$\operatorname{Fe}^{3+}(aq) + 3e^{-} \rightleftharpoons \operatorname{Fe}(s)$	-0.037	$PbO_{2}(s) + HSO_{4}^{-}(aq) + 3H_{3}O^{+}(aq) + 2e^{-} \rightleftharpoons PbSO_{4}(s) + 5H_{2}O(l)$	+1.691
$2\mathrm{H}_{3}\mathrm{O}^{+}(aq) + 2e^{-} \rightleftharpoons \mathrm{H}_{2}(g) + 2\mathrm{H}_{2}\mathrm{O}(l)$	0.0000	$\operatorname{Ce}^{4+}(aq) + e^{-} \rightleftharpoons \operatorname{Ce}^{3+}(aq)$	+1.72
$\operatorname{AgCl}(s) + e^{-} \rightleftharpoons \operatorname{Ag}(s) + \operatorname{Cl}^{-}(aq)$	+0.222	$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.866

Refer to Appendix A for additional standard electrode potentials.

# **3** Section Review

#### UNDERSTANDING KEY IDEAS

- **1.** How does a fuel cell differ from a battery?
- **2.** How do an acidic dry cell and an alkaline dry cell differ?
- **3.** Of the metals Zn, Fe, and Ag, which will corrode the easiest? Explain.
- **4.** Describe how a standard electrode potential is measured.

#### **PRACTICE PROBLEMS**

**5.** Calculate the voltage and identify the anode for a cell in which the following electrode reactions take place:

$$Ag(s) + Cl^{-}(aq) \longrightarrow AgCl(s) + e^{-}$$
$$Cl_{2}(g) + 2e^{-} \longrightarrow 2Cl^{-}(aq)$$

**6.** Calculate the voltage and identify the cathode for a cell in which the natural reaction between the following electrodes happens:

 $Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s)$ 2H<sub>2</sub>O(*l*) + 2e<sup>-</sup> \equiv H<sub>2</sub>(g) + 2OH<sup>-</sup>(aq)

#### **CRITICAL THINKING**

- 7. Write the overall equation for the reaction occurring in a lead-acid cell during discharge. What happens to the sulfuric acid concentration during this process? Why is it possible to use a hydrometer, which measures the density of a liquid, to determine if a lead-acid cell is fully charged?
- **8.** A sacrificial anode is allowed to corrode. Why is use of a sacrificial anode considered to be a way to prevent corrosion?

# SCIENCE AND TECHNOLOGY





A small pump sends a precise e

sample size into the fuel cell

inside this device.

# **Fuel Cells** Historical Perspective

In 1839, Sir William Robert Grove, a British lawyer and physicist, built the first fuel cell. More than 100 years later, fuel cells finally found a practical application—in space exploration. During short space missions, batteries can provide enough energy to keep the astronauts warm and to run electrical systems. But longer missions need energy for much longer periods of time, and fuel cells are better suited for this than batteries are. Today, fuel cells

are critical to the space shuttle missions and to future missions on the international space station.

# **Blood Alcohol Testing**

A more down-to-Earth use of fuel cells is found in traffic-law enforcement. Police officers need quick and simple ways to determine a person's blood alcohol level in the field. In the time it takes to bring a person to the station or to a hospital for a blood or urine test, the person's blood alcohol content (BAC) might change. Fuel cells, such as the one in the device shown above, provide a quick and accurate way to measure BAC from a breath sample. The alcohol ethanol from the person's breath is oxidized to acetic acid at the anode. At the cathode, gaseous oxygen is reduced and combined with hydronium ions (released from the anode) to form water. The reactions generate an electric current. The size of this current is related to the BAC.

## Questions

- **1.** Research at least two more uses for fuel cells. Identify the reactants and products for the cell in each use.
- **2.** Research careers open to chemical engineers. Determine the level of education, the approximate salaries, and the areas of study needed to become a chemical engineer.

#### **CAREER APPLICATION**



# **Chemical Engineer**

Chemical engineers do much of the ongoing fuel-cell research. There are many careers open to chemical engineers. They can work to find alternative, renewable fuel sources, to design new recyclable materials, and to devise new recycling methods. These scientists combine knowledge of chemistry, physics, and mathematics to link laboratory chemistry with its industrial applications. As with any scientist, they also must be good problem solvers.

Chemical engineers use lab techniques that you may know, including distillation, separation, and mixing. The chemical engineer in the photo is part of a team that is developing a compound to help locate explosives, such as those used in land mines. The compound detects small amounts of nitrogen-containing compounds in the air that are often found with explosives. The bright fluorescence of the compound dims when it contacts these compounds.



#### S E C T I O N



# **Electrolytic Cells**

#### **Key Terms**

- electrolytic cell
- electrolysis
- electroplating

#### **O**BJECTIVES

- **Describe** how electrolytic cells work.
- 2
- **Describe** the process of electrolysis in the decomposition of water and in the production of metals.
- **Describe** the process of electroplating.

# **Cells Requiring Energy**

Galvanic cells generate electrical energy, but another kind of cell *consumes* electrical energy. This energy is used to drive a chemical reaction. The cell shown in **Figure 15** is a laboratory-scale version of the industrial process used to refine copper. The anode is impure copper, which includes such metals as zinc, silver, and gold. The oxidation reaction at the anode changes Cu atoms in the impure sample to  $Cu^{2+}(aq)$ . The opposite reaction happens at the cathode. The  $Cu^{2+}(aq)$  ions are reduced to Cu atoms. Pure copper is formed, adding to the pure copper cathode.

Impurities such as Zn and other active metals also dissolve as cations. But they are not reduced at the cathode. Inactive metals, such as Au and Ag, fall to the bottom as an *anode sludge*. This sludge is a valuable source of these more-expensive metals in the industrial process.



#### **Figure 15** The experiment shown

here mirrors the industrial refining of copper.

#### **Electrolysis**

In an **electrolytic cell**, chemical changes are brought about by driving electrical energy through an electrochemical cell. In fact, the words *electrolysis* and *electrolytic* mean "splitting by electricity" and **electrolysis** does refer to the decomposition of a compound, usually into its elements. However, many changes other than decomposition can happen when you use an electrolytic cell. For example, adiponitrile, one of the raw materials used to make nylon, is synthesized in an electrolytic cell. What makes an electrolytic cell useful is that the overall reaction is a *nonspontaneous* process that is forced to happen by an input of energy.

#### **Electrolysis of Water**

The electrolysis of water, shown in **Figure 16**, leads to the overall reaction in which H<sub>2</sub>O is broken down into its elements, H<sub>2</sub> and O<sub>2</sub>. Pure water does not have enough ions in it and is not conductive enough for electrolysis. An electrolyte, such as sodium sulfate, must be added. The Na<sup>+</sup>(*aq*) and SO<sub>4</sub><sup>2-</sup>(*aq*) ions play no part in the electrode reactions, which are as follows:

> Anode:  $6H_2O(l) \rightarrow 4e^- + O_2(g) + 4H_3O^+(aq)$ Cathode:  $4H_2O(l) + 4e^- \rightarrow 2H_2(g) + 4OH^-(aq)$

As always, oxidation happens on the anode, while reduction happens on the cathode. Note that hydronium ions form at the anode. Thus, the solution near the anode becomes acidic. But hydroxide ions form at the cathode. So, the solution near the cathode becomes basic.

**Figure 16** Electrical energy from the battery is used to break down water. Hydrogen forms at the cathode, and oxygen forms at

the anode.



#### electrolytic cell

an electrochemical device in which electrolysis takes place when an electric current is in the device

#### electrolysis

the process in which an electric current is used to produce a chemical reaction, such as the decomposition of water

## Topic Link 🧹

Refer to the "Causes of Change" chapter for more information about spontaneous and nonspontaneous reactions.

#### **Sodium Production by Electrolysis**

Sodium is such a reactive metal that preparing it through a chemical process can be dangerous. Sir Humphry Davy first isolated it in 1807 by the electrolysis of molten sodium hydroxide. Today, sodium is made by the electrolysis of molten sodium chloride in a Downs cell, as shown in **Figure 17**.

Pure sodium chloride melts at  $801^{\circ}$ C. The addition of calcium chloride, CaCl<sub>2</sub>, to the NaCl lowers the melting point. The Downs cell can then work at 590°C, and less energy is needed to run the cell. The equations below describe the major reactions that occur.

Anode: 
$$2\operatorname{Cl}^{-}(l) \longrightarrow 2e^{-} + \operatorname{Cl}_{2}(g)$$
  
Cathode:  $2\operatorname{Na}^{+}(l) + 2e^{-} \longrightarrow 2\operatorname{Na}(s)$ 

Because chlorine reacts with most metals, the anode is made of graphite. The cathode is steel. Because sodium melts at 98°C and is less dense than the molten salts, it floats to the top and can be removed.

In addition to sodium, a small amount of calcium also forms at the cathode by the reaction:

Cathode: 
$$\operatorname{Ca}^{2+}(l) + 2e^{-} \longrightarrow \operatorname{Ca}(s)$$

The calcium is more dense than the molten salts, so it falls to the bottom of the cell, where it slowly changes back to  $Ca^{2+}$  by the following reaction:

$$Ca(l) + 2Na^{+}(l) \longrightarrow 2Na(l) + Ca^{2+}(l)$$



#### **Aluminum Production by Electrolysis**

Aluminum is the most abundant metal in Earth's crust. Aluminum is light, weather resistant, and easily worked. You have seen aluminum in use in drink cans, in food packaging, and even in airplanes. However, aluminum is never found in nature as a pure metal. Instead, it is isolated from its ore through electrolysis.

The process used to get aluminum from its ore, bauxite, is the electrochemical Hall-Héroult process. This process is the largest single user of electrical energy in the United States—nearly 5% of the national total. This need for energy makes the manufacture of aluminum expensive. Recycling aluminum saves almost 95% of the cost! Aluminum recycling is one of the most economically worthwhile recycling programs that has been developed.

The bauxite is processed to extract and purify hydrated alumina,  $Al_2O_3$ . The alumina is fed into huge carbon-lined tanks, like the one in **Figure 18.** There the alumina dissolves in molten cryolite,  $Na_3AlF_6$ , at 970°C. Liquid aluminum forms at the cathode. Being more dense than the molten cryolite, aluminum sinks to the floor of the tank. As reduction continues, the level of aluminum rises. As needed, the liquid aluminum is drained and allowed to cool.

Carbon rods serve as the anode. The carbon is oxidized during the anodic reaction, forming  $CO_2$ . The rods are eaten away by this oxidation and must be replaced from time to time.

The Hall-Héroult process has been in use for more than a century. But scientists do not completely understand how alumina dissolves and what exactly the species are that participate in the electrode reactions. Although scientists still debate how the process works, they agree that the overall reaction is

$$2Al_2O_3(l) + 3C(s) \longrightarrow 4Al(l) + 3CO_2(g)$$



The Hall-Héroult process is used to make aluminum by the electrolysis of dissolved alumina,  $Al_2O_3$ .



#### electroplating

the electrolytic process of plating or coating an object with a metal



## **Electroplating**

Many of the metal things that you use every day—forks and spoons, cans for food and drinks, plumbing fixtures, jewelry and decorative ornaments, automobile and appliance parts, nails, nuts, and bolts—have been treated to change their surfaces. Often this involves putting a layer of another metal on top of the main metal. **Electroplating** is one way of applying these finishes. Forks, spoons, and jewelry are often electroplated to give the objects the appearance of silver or gold while still keeping the cost of the objects low. The chrome parts on automobiles have been electroplated to improve the parts' appearance and protect them from corrosion. Electroplating is also used for many electronic and computer parts to give them a certain physical property or to make them last longer by protecting them against corrosion.

To electroplate a bracelet with silver, as shown in the simplified model in **Figure 19**, the bracelet is made the cathode of an electrolytic cell. The anode is a strip of pure silver metal. Both electrodes are placed in a solution of silver ions. The net reactions that happen are very simple. The anode slowly dissolves by the following oxidation reaction:

Anode: 
$$Ag(s) \rightarrow e^- + Ag^+(aq)$$

The cathode reaction on the surface of the bracelet is the reverse of the anode reaction.

Cathode: 
$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$

The result is that a thin coating of silver forms on the bracelet. The longer the plating is continued, the thicker the silver layer becomes.



#### **Benefits and Concerns About Electroplating**

A major benefit of electroplating a metal is that it becomes more resistant to corrosion. Chrome-plated car parts and zinc-plated food cans are two uses of electroplating to reduce corrosion. Another benefit of electroplating is that it improves the appearance of an object. An item that is gold-plated or silver-plated is much cheaper than the same item in solid gold or silver but looks the same.

However, there are also drawbacks with the electroplating process. In practice, electroplating is not as simple as the description above suggests. It is difficult to get metal to deposit in depressions, so the metal layer often is not uniform. Sometimes, deposits are loose and powdery. Additives are used and conditions such as temperature and pH are carefully controlled to overcome these problems. Over time, impurities build up in the solutions used for electroplating. Eventually, the spent solutions must be discarded. They can contain high concentrations of such toxic metals as cadmium or chromium and require careful disposal to protect the environment.

# Section Review

#### **UNDERSTANDING KEY IDEAS**

- **1.** How does an electrolytic cell differ from a galvanic cell?
- **2.** What chemical process occurs at the anode of an electrolytic cell?
- **3.** What chemical process occurs at the cathode of an electrolytic cell?
- **4.** What form of energy is used to drive an electrolytic cell?
- **5.** List three commercial products made by using electrolytic cells.
- 6. What does *electrolysis* mean?
- **7.** Write the equation for the cathodic reaction that occurs in the Downs cell used to make sodium.
- 8. How is aluminum manufactured?
- 9. Describe the electroplating process.

#### **CRITICAL THINKING**

**10.** In the copper refining process, why does zinc not also deposit on the cathode?

- Elemental aluminum was first prepared in 1827 by the reaction of aluminum chloride with potassium.
  - **a.** Write the balanced equation for this reaction.
  - **b.** Determine if the reaction is a redox reaction.
  - **c.** Would this reaction need to happen in an electrolytic cell? Explain.
- **12.** Cryolite,  $Na_3AlF_6$ , is an ionic mineral used in the preparation of aluminum. Explain why the sodium ions are not reduced during the electrolytic process that produces aluminum.
- **13.** The following reaction happens naturally:

 $\operatorname{Zn}(s) + \operatorname{Cu}^{2+}(aq) \longrightarrow \operatorname{Cu}(s) + \operatorname{Zn}^{2+}(aq)$ 

Explain why it is necessary to use an electric current to deposit a layer of zinc on a copper bracelet.

- **14.** Explain why a galvanic cell is often used in an electrolytic cell. What function does the galvanic cell serve?
- **15.** Why is it so important to recycle rather than discard aluminum products?

# **CHAPTER HIGHLIGHTS**

#### **KEY IDEAS**

#### SECTION ONE Oxidation-Reduction Reactions

- The loss or gain of electrons in a chemical reaction is called *oxidation* or *reduction*, respectively.
- In a redox reaction, oxidation and reduction occur at the same time.
- An oxidation number may be assigned to each atom in a molecule or ion.
- Half-reactions, in which only the oxidation or the reduction is described, are useful in balancing redox equations.
- Reducing agents readily donate electrons; oxidizing agents readily accept electrons.

#### SECTION TWO Introduction to Electrochemistry

- An electrochemical cell is made up of two electrodes linked by one or more ionic conductors.
- When electric current is in a cell, electrode reactions take place.
- Oxidation happens at the anode. Reduction happens at the cathode.

#### SECTION THREE Galvanic Cells

- Many examples of galvanic cells are power sources that generate electrical energy from chemical energy.
- Fuel cells differ from batteries in that their oxidizing and reducing agents are gases introduced to the cell from outside.
- The corrosion of metals generally happens in a galvanic cell.
- Whether there is electric current or not, the electrodes of a cell have different potentials. The difference between these is the voltage of the cell.

#### **SECTION FOUR** Electrolytic Cells

- Electrical energy is used to power an electrolytic cell.
- In electrolysis, a compound is decomposed, usually to its elements; H<sub>2</sub>, O<sub>2</sub>, Al, Na, and Cl<sub>2</sub> are among the elements that can be isolated by electrolysis.
- A layer of a second metal is deposited cathodically in electroplating.

#### **KEY TERMS**

oxidation reduction oxidation-reduction reaction oxidation number half-reaction oxidizing agent reducing agent

electrochemistry voltage electrode electrochemical cell cathode anode

corrosion standard electrode potential

electrolytic cell electrolysis electroplating

#### KEY SKILLS

Assigning Oxidation Numbers Skills Toolkit 1 p. 606 Sample Problem A p. 607 **Balancing Redox Equations Using the Half-Reaction Method** Skills Toolkit 2 p. 609 Sample Problem B p. 610 **Calculating Cell Voltage** Sample Problem C p. 623



#### **USING KEY TERMS**

- **1.** What is a redox reaction?
- **2.** Explain the terms *oxidation* and *reduction* in terms of electrons.
- **3.** Explain how oxidation numbers are used to identify redox reactions?
- **4.** Explain what half-reactions are and why they are useful.
- 5. Define *electrochemistry*.
- **6.** Define *electrode*, *anode*, and *cathode*.
- **7.** Explain voltage and current in terms of electrons.
- **8.** Distinguish between galvanic and electrolytic cells.
- 9. What is a fuel cell?
- **10.** What is corrosion, and what is a corrosion cell?
- **11.** Why does a sacrificial anode provide cathodic protection?
- **12.** What is electroplating?

#### **UNDERSTANDING KEY IDEAS**

#### **Oxidation-Reduction Reactions**

- **13.** Assign oxidation numbers to the atoms in the ionic compound  $MgBr_2(s)$ .
- **14.** Assign oxidation numbers to the atoms in the ionic compound  $NH_4NO_3(s)$ .
- **15.** Assign oxidation numbers to the atoms in the ion  $PF_{6}^{-}(aq)$ .

- **16.** Identify each of the following half-reactions as oxidation or reduction reactions.
  - **a.**  $K(s) \rightarrow e^- + K^+(aq)$

**b.** 
$$\operatorname{Cu}^{2+}(aq) + e^{-} \longrightarrow \operatorname{Cu}^{+}(aq)$$

- **c.**  $\operatorname{Br}_2(l) + 2e^- \longrightarrow 2\operatorname{Br}^-(aq)$
- **17.** Is the reaction below a redox reaction? Explain your answer.

 $Ca(s) + Cl_2(g) \longrightarrow CaCl_2(s)$ 

- **18.** Describe how to identify the oxidizing agent and the reducing agent in a reaction.
- **19.** Nitrogen monoxide, NO(g), reacts with phosphorus,  $P_4(s)$ , to produce nitrogen,  $N_2(g)$ , and diphosphorus pentoxide,  $P_2O_5$ . Write the balanced equation for this reaction. Identify the atoms that have been oxidized and reduced, and identify the oxidizing and reducing agents.

#### **Introduction to Electrochemistry**

- **20.** What is the distinction between a half-reaction and an electrode reaction?
- **21.** Describe the components of an electrochemical cell.
- **22.** Identify which of the following reactions (as written) is an anodic reaction and which is a cathodic reaction. Write the balanced overall ionic equation for the redox reaction of the cell.

$$Cd(s) \longrightarrow Cd^{2+}(aq) + 2e^{-}$$
$$Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)$$

- **23.** What is the significance of the ⊕ symbol on a dry cell or battery?
- **24.** What reaction happens at the cathode of an electrochemical cell?

- **25.** In an electrochemical cell, what role does the porous barrier play? What would happen without it?
- **26.** Explain why the combination of the two electrode reactions of an electrochemical cell always gives the equation of a redox reaction.

#### **Galvanic Cells**

- **27.** Describe a galvanic cell, and give an example.
- **28.** Write the equations of the two electrode reactions that occur when a Daniell cell is in use. Identify the anode reaction and the cathode reaction.
- **29.** What is the essential advantage of a fuel cell over other types of galvanic cells that are used to generate electrical energy?
- **30.** Explain why a corrosion cell is a galvanic cell.
- **31.** Discuss methods of reducing corrosion.
- **32.** The standard electrode potential for the reduction of  $Zn^{2+}(aq)$  to Zn(s) is -0.762 V. What does this value indicate?
- **33.** Which half-reaction would be more likely to be an oxidation: one with a standard electrode potential of -0.42 V, or one with a standard electrode potential of +0.42 V? Explain your answer.

#### **Electrolytic Cells**

- **34.** Define *electrolytic cell*, and give an example.
- **35.** Describe the apparatus used in the electrolysis of water.
- **36.** Explain why sodium can be prepared by electrolysis.
- **37.** Describe some benefits of electroplating.
- **38.** What are some problems in the electroplating industry?

#### **PRACTICE PROBLEMS**



#### **Determining Oxidation Numbers**

- **39.** Determine the oxidation number of each atom in  $CO_2$ .
- **40.** Determine the oxidation number of each atom in CoO.
- **41.** Determine the oxidation number of each atom in BaCl<sub>2</sub>.
- **42.** Determine the oxidation number of each atom in  $K_2SO_4$ .
- **43.** Determine the oxidation number of each atom in CaCO<sub>3</sub>.
- **44.** Determine the oxidation number of each atom in  $PtCl_6^{2-}$ .
- **45.** Determine the oxidation number of each atom in  $\text{COCl}_2$ .
- **46.** Determine the oxidation number of each atom in  $PO_4^{3-}$ .

#### The Half-Reaction Method

- **47.** Write the balanced half-reaction for the conversion of Fe(s) to  $Fe^{2+}(aq)$ .
- **48.** Write the balanced half-reaction for the conversion of  $Cl_2(g)$  to  $Cl^-(aq)$ .
- **49.** Combine the half-reactions from items 47 and 48 into a single reaction.
- **50.** Write the balanced half-reaction for the conversion of HOBr(aq) to  $Br_2(aq)$  in acidic solution.
- **51.** Write the balanced half-reaction for the conversion of  $H_2O(l)$  to  $O_2(aq)$  in acidic solution.
- **52.** Combine the half-reactions from items 50 and 51 into a single reaction.
- **53.** Write the balanced half-reaction for the change of  $O_2(aq)$  to  $H_2O(l)$  in acidic solution.

- **54.** Write the balanced half-reaction for the change of  $SO_2(aq)$  to  $HSO_4^-(aq)$  in acidic solution.
- **55.** Combine the reactions from items 53 and 54 into a single reaction.
- **56.** Using half-reactions, balance the redox equation of Zn(s) and  $Fe^{3+}(aq)$  reacting to form  $Zn^{2+}(aq)$  and  $Fe^{2+}(aq)$ .

#### **Calculating Cell Voltage**

**57.** The standard electrode potentials of two electrodes in a cell are 1.30 V and 0.45 V. What is the voltage of the cell?

Use the information from Table 1 to answer the following items.

**58.** Calculate the voltage of a cell for the naturally occurring reaction between the following electrodes:

$$\operatorname{AgCl}(s) + e^{-} \rightleftharpoons \operatorname{Ag}(s) + \operatorname{Cl}^{-}(aq)$$

 $2H_3O^+(aq) + 2e^- \rightleftharpoons 2H_2O(l) + H_2(g)$ 

**59.** Calculate the voltage of a cell that has the following electrode reactions:

$$2H_3O^+(aq) + 2e^- \longrightarrow 2H_2O(l) + H_2(g)$$
$$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$$

**60.** Calculate the voltage of a cell in which the overall reaction is

 $2\mathrm{Fe}^{3+}(aq) + \mathrm{Cd}(s) \longrightarrow \mathrm{Cd}^{2+}(aq) + 2\mathrm{Fe}^{2+}(aq)$ 

**61.** Calculate the voltage of a cell that has the following electrode reactions:

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$
  
 $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$ 

- **62.** Calculate the voltage of a cell in which the two electrode reactions are the reduction of chlorine gas to chloride ions and the oxidation of copper metal to copper(II) ions.
- **63.** Calculate the voltage of a cell in which the two electrode reactions are those of the lead-acid battery.

#### **MIXED REVIEW**

- 64. Assign an oxidation number to the N atom in each of the following oxides of nitrogen: N<sub>2</sub>O, NO, NO<sub>2</sub>, N<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O<sub>4</sub>, and N<sub>2</sub>O<sub>5</sub>.
- **65.** Refer to the figure below to answer the following questions:



- **a.** What observations suggest that a chemical reaction has taken place?
- **b.** Write a balanced equation for the reaction taking place, and explain how you can identify it as a redox reaction.
- **c.** Identify what is oxidized and what is reduced in the reaction.
- **d.** Describe how the quantity of zinc metal and of copper metal will change as the reaction continues.
- **e.** Describe the role of the chloride ions in the reaction.
- **66.** What name is given to an electrode at which oxidation occurs? at which reduction occurs?
- **67.** Using half-reactions, balance the equation for the redox reaction when  $\operatorname{Cr}_2\operatorname{O}_7^{2-}(aq)$  and  $\operatorname{Fe}^{2+}(aq)$  react to form  $\operatorname{Cr}^{3+}(aq)$  and  $\operatorname{Fe}^{3+}(aq)$  in acidic solution.
- **68.** Calculate the voltage of a cell in which the overall reaction is the electrolysis of aqueous cadmium chloride into its elements.
- **69.** Calculate the voltage of a cell in which the overall reaction is the electrolysis of solid AgCl into its elements.

#### **CRITICAL THINKING**

- **70.** Suggest how the word *oxidation* might have come to be the general term for a loss of electrons.
- **71.** Think of ammonium nitrite as  $(NH_4^+)(NO_2^-)$ , and assign oxidation numbers within each ion. Now think of ammonium nitrate as  $N_2H_4O_2$ , and assign oxidation numbers. Which assignment makes more sense?
- **72.** Why is the negative battery terminal the one with the greater "electron pressure"?
- **73.** What is different about electric current in metals compared with current in electrolyte solutions?
- 74. The activity of the halogens decreases as you move down the group on the periodic table. Use the information in Table 1 to explain this trend.
- 75. A fuel cell uses methanol, CH<sub>3</sub>OH, as fuel. Assuming complete oxidation of the fuel to CO<sub>2</sub> and H<sub>2</sub>O in acidic aqueous solution, how many electrons are transferred per CH<sub>3</sub>OH molecule?
- **76.** Using **Table 1**, calculate the voltage of a cell for the naturally occurring reaction between the electrodes below. If a wire were connected between the Ag and Cu, which way would electrons travel? Which electrode would be the anode?

$$\operatorname{Ag}^{+}(aq) + e^{-} \rightleftharpoons \operatorname{Ag}(s)$$
$$\operatorname{Cu}^{2+}(aq) + 2e^{-} \rightleftharpoons \operatorname{Cu}(s)$$

**77.** How does the oxidation number of an atom of Mn change in the reaction below?

 $4\text{Mn}^{2+}(aq) + \text{MnO}_{4}^{-}(aq) + 8\text{H}_{3}\text{O}^{+}(aq) + \\15\text{H}_{2}\text{P}_{4}\text{O}_{7}^{2-}(aq) \longrightarrow 12\text{H}_{2}\text{O}(l) + \\5\text{Mn}(\text{H}_{2}\text{P}_{4}\text{O}_{7})_{3}^{3-}(aq)$ 

#### **ALTERNATIVE ASSESSMENT**

- **78.** Consumer use of rechargeable batteries is growing. Nickel-cadmium batteries, a common type of rechargeable battery, are used in cellular phones, electric shavers, and portable video-game systems. Make a list of the items with which you come into contact that use nickel-cadmium batteries or other rechargeable batteries. Write a short essay about technology that was not and could not have been available before the development of the nickel-cadmium battery.
- **79.** Read the book *Apollo 13* on which the movie of the same title was based, and report information about the power sources in the spacecraft.
- **80.** Research metals other than copper, sodium, and aluminum that are manufactured or refined electrochemically.
- 81. Using a voltmeter from home or one borrowed from your teacher, devise a method of measuring the voltage of a flashlight battery *while it is delivering power to the bulb*. Compare that voltage with that of a new battery. Also record the voltage as the battery "runs down." Write a report on your results.
- 82. Manufacturers often claim that their batteries are "heavy duty" or "long lasting." Design an experiment to test the value and efficacy of AA batteries. If your teacher approves, carry out your procedure.
- **83.** Carpentry nails are steel, but some are plated with a second metal. Obtain a variety of nails and evaluate their tendency to rust by laying them on a piece of cloth moistened by water containing salt and vinegar, so they are exposed both to the liquid and to air. After two weeks, report your findings.

#### **CONCEPT MAPPING**



**84.** Use the following terms to create a concept map: *cathode, electrodes, electrochemical cell, anode, oxidation,* and *reduction.* 



Study the graph below, and answer the questions that follow. For help in interpreting graphs, see Appendix B, "Study Skills for Chemistry."



- **85.** What is the rate of production, in g/h, for each metal?
- **86.** What is the rate of production, in mol/h, for each metal?
- **87.** How much time is needed for 1.00 mol of electrons to be absorbed?
- **88.** Write the half-reaction for the production of silver metal from silver ions. Write the half-reaction for the production of gold metal from gold(III) ions. Using these half-reactions, provide an explanation for the difference in the rates of production of the metals.

# TECHNOLOGY AND LEARNING

#### **89. Graphing Calculator**

Calculate the Equilibrium Constant, using the Standard Cell Voltage

The graphing calculator can run a program that calculates the equilibrium constant for an electrochemical cell using an equation called the Nernst equation, given the standard potential and the number of electrons transferred. Given that the standard potential is 2.041 V and that two electrons are transferred, you will calculate the equilibrium constant. The program will be used to make the calculations. **Go to Appendix C.** If you are using a TI-83 Plus, you can download the program NERNST and data and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. After you have run the program, answer the following questions.

- **a.** What is the equilibrium constant when the standard potential is 0.099?
- **b.** What is the equilibrium constant when the standard potential is 1.125?
- **c.** What is the equilibrium constant when the standard potential is 2.500?

# STANDARDIZED TEST PREP



## UNDERSTANDING CONCEPTS

Directions (1-3): For each question, write on a separate sheet of paper the letter of the correct answer.

- A cell contains two electrodes—a strip of zinc metal in a solution containing zinc ions and a strip of copper metal in a solution containing copper ions. What happens when this cell operates as a galvanic cell?
  - **A.** Cu is oxidized and  $Zn^{2+}$  is reduced.
  - **B.** Cu is reduced and  $Zn^{2+}$  is oxidized.
  - **C.** Zn is oxidized and  $Cu^{2+}$  is reduced.
  - **D.** Zn is reduced and  $Cu^{2+}$  is oxidized.
  - What is the function of sulfuric acid in the electrolysis of water?
    - **F.** to react with the water
    - **G.** to increase the conductivity
    - **H.** to prevent corrosion of the anode
    - **I.** to supply the energy needed for the reaction
  - What is the oxidation number of the sulfur atom in the  $SO_4^{2-}$  ion?

A.	0	С.	+4
B.	+2	D.	+6

#### Directions (4–6): For each question, write a short response.



4 Explain how a particular pair of half-cells can be used either as an electrolytic cell or as an electrochemical cell.



6 Write a balanced half reaction for the reduction of chlorine gas to chloride ions.

## **READING SKILLS**

Directions (7–9): Read the passage below. Then answer the questions.

The steel hulls of ships are subject to corrosion by the reaction of water and oxygen with iron to form rust. Although painting the surface of the steel can provide some protection, even a small scrape that removes paint can allow corrosion to start. Many ships use blocks of zinc attached to the hull to protect the steel from corrosion. The zinc becomes the "sacrificial" anode of a cell, losing electrons, and going into solution, while the iron in the steel acts as a cathode, gaining electrons as water is reduced. As the cathode, iron does not corrode.

- 7 Why could gold not be used as a sacrificial electrode on a ship, even if it were as inexpensive as zinc?
  - **F.** Pure gold is too soft to use for this purpose.
  - G. Gold oxidizes easier than iron, so it would not be suitable.
  - **H.** If gold were used, it would become the anode, increasing the corrosion of iron.
  - **I.** Gold forms ions with a +2 charge, while iron forms ions with a + 3 charge.

8 Which of these is a balanced equation that describes the situation above?

- **A.**  $Zn + O_2 + H_2O \longrightarrow Zn^{+2} + 2OH^{-1}$
- **B.**  $Zn + O_2 + 2H_2O \longrightarrow Zn^{+2} + 4OH^{-1}$
- **C.**  $2Zn + O_2 + H_2O \rightarrow 2Zn^{+2} + 3OH^{-1}$
- **D.**  $2Zn + O_2 + 2H_2O \longrightarrow Zn^{+2} + 4OH^{-1}$
- Attaching a block of zinc to the side of an 9 old car would not protect it from corrosion. Why does zinc protect a ship but not a car?

#### **INTERPRETING GRAPHICS**

*Directions (10-13):* For *each* question below, record the correct answer on a separate sheet of paper.

The illustration below is a simplified model of electroplating a bracelet with silver. Use it to answer questions 10 through 13.



**10** What happens to the silver strip as the bracelet is electroplated?

- **F.** There is no noticeable change to the silver strip.
- **G.** The silver strip becomes larger as silver ions are deposited on it.
- **H.** The silver strip becomes smaller as silver ions enter the solution.
- **I.** The effect on the silver strip varies, depending on the voltage applied from the battery.

Which of the following conditions will cause this electroplating process to stop?

- A. The solution becomes saturated with electrons.
- **B.** All of the  $CN^-$  ions in the solution are consumed.
- **C.** The reaction inside the battery consumes its entire anode.
- **D.** The bracelet becomes completely covered with a one atom thick layer of silver.

12 Which of the following statements is false?

- **F.** Electroplating can improve corrosion resistance.
- G. Electroplating can enhance the appearance of metal objects.
- **H.** Electroplating can make a polyethylene object look like metal.
- **I.** Electroplating changes the electrical properties of an object.

What are the half reactions at the cathode and the anode of this cell?



When using a diagram to answer a question, look in the image for evidence that supports your potential answer.



# CHAPTER



# NUCLEAR CHEMISTRY