时代教育·国外高校优秀教材精选

化学—中心科学

Chemistry—The Central Science

（英文版·原书第 8 版）

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出版说明

随着我国加入 WTO，国际间的竞争越来越激烈，而国际间的竞争实际上也就是人才的竞争、教育的竞争。为了加快培养具有国际竞争力的高水平技术人才，加快我国教育改革的步伐，国家教育部近来出台了一系列倡导高校开展双语教学、引进原版教材的政策。以此为契机，机械工业出版社拟于近期推出一系列国外影印版教材，其内容涉及高等学校公共基础课，以及机、电、信息领域的专业基础课和专业课。

引进国外优秀原版教材，在有条件的学校推动开展英语授课或双语教学，自然也引进了先进的教学思想和教学方法，这对提高我国自编教材的水平，加强学生的英语实际应用能力，使我国的高等教育尽快与国际接轨，必将起到积极的推动作用。

为了做好教材的引进工作，机械工业出版社特别成立了由著名专家组成的国外高校优秀教材审定委员会。这些专家对实施双语教学做了深入细致的调查研究，对引进原版教材提出许多建设性意见，并慎重地对每一本将要引进的原版教材一审再审，精选再精选，确认教材本身的质量水平，以及权威性和先进性，以期所引进的原版教材能适应我国学生的外语水平和学习特点。在引进工作中，审定委员会还结合我国高校教学课程体系的设置和要求，对原版教材的教学思想和方法的先进性、科学性严格把关。同时尽量考虑原版教材的系统性和经济性。

这套教材出版后，我们将根据各高校的双语教学计划，举办原版教材的教师培训，及时地将其推荐给各高校选用。希望高校师生在使用教材后及时反馈意见和建议，使我们更好地为教学改革服务。

机械工业出版社
2002 年 3 月

序

该书是一本已经再版 7 次的普通化学教材，三位作者都曾经多次获得过不同层次的教学奖。其中 Brown 在学术上造诣较深，曾获 Guggenheim 学者奖，美国化学会无机化学研究奖和无机化学进步服务优异奖等。现为 Illinois 大学（Urbana Champain）资深化学教授。LeMay 教授有近 30 年的教学经验，并因此多次获得国家级教学奖。Bursten 教授是 Ohio 大学杰出化学教授，在过渡金属和锕系元素化合物研究方面有较高的水平。从作者水平和该书的再版次数来看，这本书应当是质量比较好的。

该书图文并茂，插图精美。全书共分为 25 章，其内容安排和理论深度与国内现有的普通化学或大学一年级化学相近。应当认为，这类教材是 20 世纪 70 年代以来对我国普通化学或大学一年级化学影响最大的一类国外教材，比较重视化学基础理论的完整性和系统性。该书的初等量子力学和化学热力学部分写得比较适合大学一年级学生的水平。作为化学学科的学习，该书有较好的实用性。

该书设计了一些新的栏目，如关于解题（Problem Solving）设有：化学中实用的策略、例题、章后练习题（包括所附光盘上的 e－媒体练习题）、中心科学演示（学生用 CD－ROM 和网站 http：//www. prenhall. com/brown）；形象化（Visualization）设有：分子结构模型、化合物演示、分子运动三维动画以及中心科学演示；应用（Application）设有：生活和实际应用中的化学、化学新闻、有趣的阅读材料和中心科学演示。从而使教学内容可以方便地扩展到与生活和社会相关的其它方面。

该书可以用作双语基础化学教材。

宋心琦
清华大学化学系
2002 年 10 月

Electrochemistry

20

Electrochemistry relates electricity and chemical reactions. The "chrome" grille of this vintage 1949 automobile was produced by electroplating chromium metal on steel, an example of the chemical process called electrolysis.

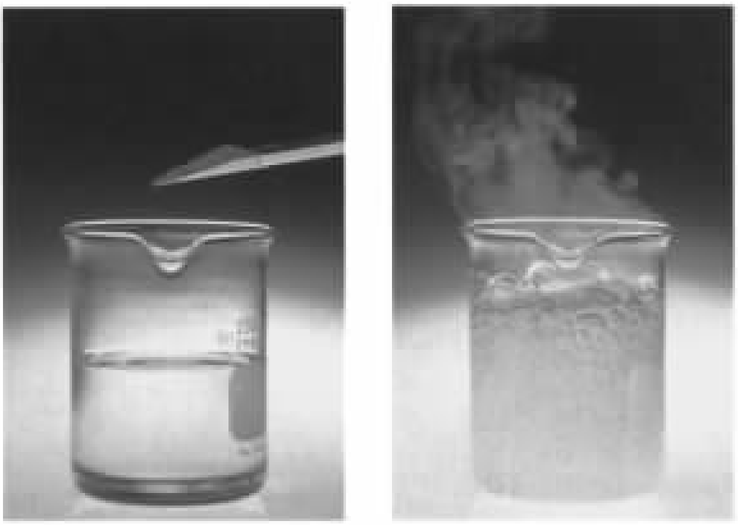
The concept of *oxidation state* or *oxidation number*, which we introduced in Section 4.4, is an extremely useful guide to the changes that occur during chemical reactions. Among the most common and most important chemical reactions are those that involve changes in the oxidation states of atoms. For example, consider the reaction that occurs when zinc metal is added to a strong acid (Figure 20.1 ▶):

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g) \qquad [20.1]$$

During this reaction the oxidation state of zinc increases from 0 in $Zn(s)$ to +2 in $Zn^{2+}(aq)$, whereas that of hydrogen decreases from +1 to 0. Chemical reactions in which the oxidation state of one or more substance changes are called **oxidation-reduction reactions** (or *redox* reactions).

As we discussed earlier, *oxidation* refers to the loss of electrons. Conversely, *reduction* refers to the gain of electrons. ∞ (Section 4.4) We can view oxidation-reduction reactions as involving the transfer of electrons from the atom that is oxidized to the atom that is reduced. In Equation 20.1 electrons are transferred from zinc atoms (zinc is oxidized) to hydrogen ions (hydrogen is reduced).

The transfer of electrons that occurs in the reaction in Figure 20.1 produces energy in the form of heat; the reaction is thermodynamically "downhill" and proceeds spontaneously. The transfer of electrons that occurs during oxidation-reduction reactions can also be used to produce energy in the form of electricity. In other instances we use electrical energy to make certain nonspontaneous chemical processes occur. **Electrochemistry** is the branch of chemistry that deals with the relationships between electricity and chemical reactions. Our discussion of electrochemistry will provide insight into such diverse topics as the construction of batteries, the spontaneity of reactions, electroplating, and the corrosion of metals. We will begin by learning more about oxidation-reduction reactions.



▶ **Figure 20.1** The addition of zinc metal to hydrochloric acid leads to a spontaneous oxidation-reduction reaction: Zinc metal is oxidized to $Zn^{2+}(aq)$, and $H^+(aq)$ is reduced to $H_2(g)$, which produces the vigorous bubbling.

20.1 Oxidation-Reduction Reactions

How do we determine whether a given chemical reaction is an oxidation-reduction reaction? We can do so by keeping track of the oxidation numbers of all the elements involved in the reaction. This procedure tells us which elements (if any) are changing oxidation state. For example, the reaction in Equation 20.1 can be written

$$\underset{\textcircled{0}}{Zn(s)} + \underset{\textcircled{+1}}{2H^+(aq)} \longrightarrow \underset{\textcircled{+2}}{Zn^{2+}(aq)} + \underset{\textcircled{0}}{H_2(g)} \qquad [20.2]$$

By writing the oxidation number of each element under the equation, we can easily see the oxidation state changes that occur: The oxidation state of Zn changes from 0 to +2, and that of H changes from +1 to 0.

In a reaction such as Equation 20.2, a clear transfer of electrons occurs. Zinc loses electrons as $Zn(s)$ is converted to $Zn^{2+}(aq)$, and hydrogen gains electrons as $H^+(aq)$ is turned into $H_2(g)$. In other reactions, the oxidation states change, but we can't say that any substance literally gains or loses electrons. For example, consider the combustion of hydrogen gas:

Oxidation-Reduction Reactions I movie; Oxidation-Reduction Reactions II movie

$$\underset{\textcircled{0}}{2H_2(g)} + \underset{\textcircled{0}}{O_2(g)} \longrightarrow \underset{\textcircled{+1}\;\textcircled{-2}}{2H_2O(g)} \qquad [20.3]$$

Hydrogen has been oxidized from the 0 to the +1 oxidation state, and oxygen has been reduced from the 0 to the −2 oxidation state. Therefore, Equation 20.3 is an oxidation-reduction reaction. However, because water is not an ionic substance, there is not a complete transfer of electrons from hydrogen to oxygen as water is formed. It is important to remember that using oxidation numbers is a convenient form of "bookkeeping." *In general, you should not equate the oxidation state of an atom with its actual charge in a chemical compound.*

In any redox reaction, both oxidation and reduction must occur. In other words, if one substance is oxidized, then another must be reduced. The substance that makes it possible for another substance to be oxidized is called the ox-

idizing agent, or **oxidant**. The oxidizing agent removes electrons from another substance by acquiring them itself; thus, the oxidizing agent is itself reduced. Similarly, a **reducing agent**, or **reductant**, is a substance that gives up electrons, thereby causing another substance to be reduced. The reducing agent is oxidized in the process. In Equation 20.2, $H^+(aq)$ is the oxidizing agent, and $Zn(s)$ is the reducing agent.

SAMPLE EXERCISE 20.1

The nickel-cadmium (nicad) battery, a rechargeable "dry cell" used in battery-operated devices, uses the following redox reaction to generate electricity:

$$Cd(s) + NiO_2(s) + 2H_2O(l) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$

Identify the substances that are oxidized and reduced, and indicate which are oxidizing agents and which are reducing agents.

Solution *First*, we assign oxidation numbers to all the atoms in the reaction:

$$\underset{\textcircled{0}}{Cd}(s) + \underset{\textcircled{+4}}{Ni}\underset{\textcircled{-2}}{O_2}(s) + 2\underset{\textcircled{+1}}{H_2}\underset{\textcircled{-2}}{O}(l) \longrightarrow \underset{\textcircled{+2}}{Cd}(\underset{\textcircled{-2}}{O}\underset{\textcircled{+1}}{H})_2(s) + \underset{\textcircled{+2}}{Ni}(\underset{\textcircled{-2}}{O}\underset{\textcircled{+1}}{H})_2(s)$$

Second, we identify the elements that are changing oxidation numbers. We see that Cd undergoes an increase in oxidation number from 0 to +2 and that Ni undergoes a decrease from +4 to +2.

Third, we apply the definitions of oxidation and reduction. The Cd atom increases oxidation number during the reaction, so it is oxidized; $Cd(s)$ loses electrons, and it therefore serves as the reducing agent. The Ni atom decreases oxidation number as NiO_2 is converted into $Ni(OH)_2$. Ni is reduced, so NiO_2 is the oxidizing agent. (A common mnemonic for remembering oxidation and reduction is "LEO the lion says GER": *l*osing *e*lectrons is *o*xidation; *g*aining *e*lectrons is *r*eduction.)

PRACTICE EXERCISE

Identify the oxidizing and reducing agents in the following oxidation-reduction equation:

$$2H_2O(l) + Al(s) + MnO_4^-(aq) \longrightarrow Al(OH)_4^-(aq) + MnO_2(s)$$

Answer: $Al(s)$ is the reducing agent; $MnO_4^-(aq)$ is the oxidizing agent.

20.2 Balancing Oxidation-Reduction Equations

We know that whenever we balance a chemical equation, we must obey the law of conservation of mass: The amount of each element must be the same on both sides of the equation. As we balance oxidation-reduction reactions, we will see an additional requirement: The gains and losses of electrons must be balanced. In other words, if a substance loses a certain number of electrons during a reaction, then another substance must gain that same number of electrons. In many simple chemical reactions, such as Equation 20.2, this balance of electrons is handled "automatically"; we can balance the equation without explicitly considering the transfer of electrons. However, many redox reactions are more complex than Equation 20.2 and cannot be balanced easily without taking into account the number of electrons lost and gained in the course of the reaction. In this section we examine a systematic procedure for balancing redox equations.

Half-Reactions

Although oxidation and reduction must take place simultaneously, it is often convenient to consider them as separate processes. For example, the oxidation of Sn^{2+} by Fe^{3+}

$$Sn^{2+}(aq) + 2Fe^{3+}(aq) \longrightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$$

can be considered to consist of two processes: (1) the oxidation of Sn^{2+} (Equation 20.4) and (2) the reduction of Fe^{3+} (Equation 20.5).

$$\text{Oxidation:} \quad Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq) + 2e^- \qquad [20.4]$$

$$\text{Reduction:} \quad 2Fe^{3+}(aq) + 2e^- \longrightarrow 2Fe^{2+}(aq) \qquad [20.5]$$

Notice that in the oxidation process electrons are shown as products; in the reduction process electrons are shown on the reactant side of the equation.

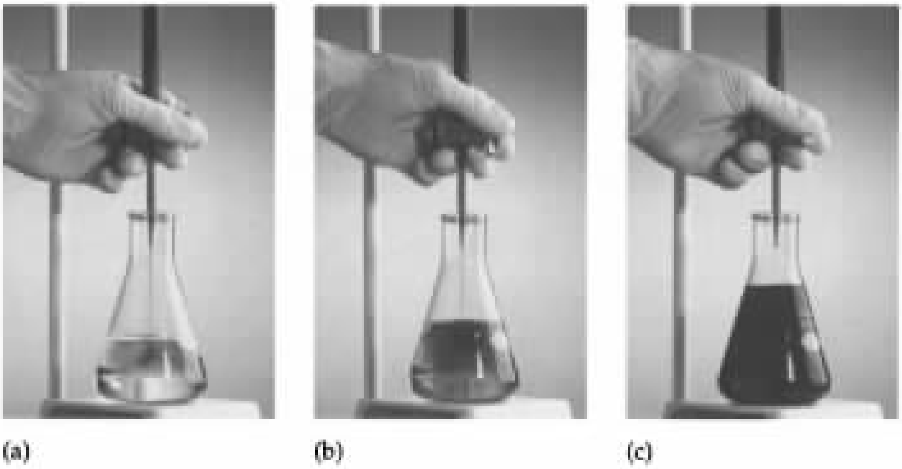
Equations that show either oxidation or reduction alone, as in Equations 20.4 and 20.5, are called **half-reactions**. In the overall redox reaction the number of electrons lost in the oxidation half-reaction must equal the number of electrons gained in the reduction half-reaction. When this condition is met and each half-reaction is balanced, the electrons on each side cancel when the two half-reactions are added to give the overall balanced oxidation-reduction equation.

Balancing Equations by the Method of Half-Reactions

The use of half-reactions provides a general method for balancing oxidation-reduction equations. As an example, let's consider the reaction that occurs between permanganate ion, MnO_4^-, and oxalate ion, $C_2O_4^{2-}$, in acidic aqueous solutions. When MnO_4^- is added to an acidified solution of $C_2O_4^{2-}$, the deep purple color of the MnO_4^- ion fades, as illustrated in Figure 20.2 ▼. Bubbles of CO_2 form, and the solution takes on the pale pink color of Mn^{2+}. We can therefore write the unbalanced equation as follows:

$$MnO_4^-(aq) + C_2O_4^{2-}(aq) \longrightarrow Mn^{2+}(aq) + CO_2(g) \qquad [20.6]$$

Experiments also show that H^+ is consumed and H_2O is produced in the reaction. We will see that these facts can be deduced in the course of balancing the equation.


(a) (b) (c)

▶ **Figure 20.2** Titration of an acidic solution of $Na_2C_2O_4$ with $KMnO_4(aq)$. (a) As the reaction proceeds, deep purple MnO_4^- is rapidly reduced to extremely pale pink Mn^{2+} by $C_2O_4^{2-}$. (b) When all the $C_2O_4^{2-}$ is consumed, the purple color of MnO_4^- persists. The end point corresponds to the faintest discernible purple color in the solution. (c) Beyond the end point, the solution becomes deep purple due to excess MnO_4^-.

To complete and balance Equation 20.6 by the method of half-reactions, we begin with the unbalanced reaction and write two incomplete half-reactions, one involving the oxidant and the other involving the reductant.

$$\mathrm{MnO_4^-}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq)$$

$$\mathrm{C_2O_4^{2-}} \longrightarrow \mathrm{CO_2}(g)$$

We have not explicitly stated which substance is oxidized and which is reduced. This information emerges as we balance the half-reactions.

We can now complete and balance the half-reactions separately. First, the atoms undergoing oxidation or reduction are balanced by adding coefficients on one side or the other as necessary. Then, the remaining elements are balanced in the same way. If the reaction occurs in acidic aqueous solution, H^+ and H_2O can be added either to reactants or to products to balance hydrogen and oxygen. Similarly, in basic solution the equation can be completed using OH^- and H_2O. These species are in large supply in the respective solutions, and their formation as products or their use as reactants can easily go undetected experimentally. In the permanganate half-reaction we already have one manganese atom on each side of the equation. However, we have four oxygens on the left and none on the right side; four H_2O molecules are needed among the products to balance the four oxygen atoms in MnO_4^-:

Formation of Silver Crystals movie

$$\mathrm{MnO_4^-}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\mathrm{H_2O}(l)$$

The eight hydrogen atoms that this introduces among the products can then be balanced by adding $8H^+$ to the reactants:

$$8\mathrm{H^+}(aq) + \mathrm{MnO_4^-}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\mathrm{H_2O}(l)$$

There are now equal numbers of each type of atom on both sides of the equation, but the charge still needs to be balanced. The total charge of the reactants is $8(1+) + (1-) = 7+$, and that of the products is $(2+) + 4(0) = 2+$. To balance the charge, five electrons are added to the reactant side.*

$$5e^- + 8\mathrm{H^+}(aq) + \mathrm{MnO_4^-}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\mathrm{H_2O}(l)$$

For the oxalate half-reaction, we first realize that mass balance requires the production of two CO_2 molecules for each oxalate ion that reacts:

$$\mathrm{C_2O_4^{2-}}(aq) \longrightarrow 2\mathrm{CO_2}(g)$$

Mass is now balanced. We can balance the charge by adding two electrons to the products, giving a balanced half-reaction:

$$\mathrm{C_2O_4^{2-}}(aq) \longrightarrow 2\mathrm{CO_2}(g) + 2e^-$$

Now that we have two balanced half-reactions, we need to multiply each by an appropriate factor so that the number of electrons gained in one half-reaction equals the number of electrons lost in the other. The half-reactions are then added to give the overall balanced equation. In our example the MnO_4^- half-reaction must be multiplied by 2, and the $C_2O_4^{2-}$ half-reaction must be mul-

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* Although the oxidation numbers of the elements need not be used in balancing a half-reaction by this method, oxidation numbers can be used as a check. In this example MnO_4^- contains manganese in a +7 oxidation state. Because manganese changes from a +7 to a +2 oxidation state, it must gain five electrons, as we have just concluded.

tiplied by 5 so that the same number of electrons (10) appears on both sides of the equation:

$$\begin{array}{r}10e^- + 16H^+(aq) + 2MnO_4^-(aq) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) \\ 5C_2O_4^{2-}(aq) \longrightarrow 10CO_2(g) + 10e^- \\ \hline 16H^+(aq) + 2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) \longrightarrow \qquad\qquad \\ 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)\end{array}$$

The balanced equation is the sum of the balanced half-reactions. Note that the electrons on the reactant and product sides of the equation cancel each other.

We can check the balanced equation by counting atoms and charges: There are 16 H, 2 Mn, 28 O, 10 C, and a net charge of 4+ on both sides of the equation, confirming that the equation is correctly balanced.

We can summarize the procedure that we use to balance a redox reaction that occurs in acidic solution:

1. Divide the equation into two incomplete half-reactions, one for oxidation and the other for reduction.
2. Balance each half-reaction.
   - **a.** First, balance the elements other than H and O.
   - **b.** Next, balance the O atoms by adding H_2O.
   - **c.** Then, balance the H atoms by adding H^+.
   - **d.** Finally, balance the charge by adding e^- to the side with the greater overall positive charge.
3. Multiply each half-reaction by an integer so that the number of electrons lost in one half-reaction equals the number gained in the other.
4. Add the two half-reactions and simplify where possible by canceling species appearing on both sides of the equation.
5. Check the equation to make sure that there are the same number of atoms of each kind and the same total charge on both sides.

SAMPLE EXERCISE 20.2

Complete and balance the following equation by the method of half-reactions:

$$Cr_2O_7^{2-}(aq) + Cl^-(aq) \longrightarrow Cr^{3+}(aq) + Cl_2(g) \qquad \text{(acidic solution)}$$

Solution *First*, we divide the equation into two half-reactions:

$$Cr_2O_7^{2-}(aq) \longrightarrow Cr^{3+}(aq)$$
$$Cl^-(aq) \longrightarrow Cl_2(g)$$

Second, we balance each half-reaction. In the first half-reaction the presence of $Cr_2O_7^{2-}$ among the reactants requires two Cr^{3+} among the products. The 7 oxygen atoms in $Cr_2O_7^{2-}$ are balanced by adding 7 H_2O to the products. The 14 hydrogen atoms in 7 H_2O are then balanced by adding 14 H^+ to the reactants:

$$14H^+(aq) + Cr_2O_7^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

Charge is balanced by adding electrons to the left side of the equation so that the total charge is the same on both sides:

$$6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

In the second half-reaction, 2 Cl^- are required to balance one Cl_2:

$$2Cl^-(aq) \longrightarrow Cl_2(g)$$

We add two electrons to the right side to attain charge balance:

$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$$

Third, we equalize the number of electrons transferred in the two half-reactions. To do so, we multiply the second half-reaction by 3 so that the number of electrons gained in the first half-reaction (6) equals the number lost in the second, allowing the electrons to cancel when the reactions are added.

Fourth, the equations are added to give the balanced equation:

$$14H^+(aq) + Cr_2O_7^{2-}(aq) + 6Cl^-(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3Cl_2(g)$$

Fifth, we check the final equation. There are equal numbers of atoms of each kind on both sides of the equation: 14 H, 2 Cr, 7 O, 6 Cl. In addition, the charge is the same on both sides, 6+. Thus, the equation is correctly balanced.

PRACTICE EXERCISE

Complete and balance the following oxidation-reduction equations using the method of half-reactions. Both reactions occur in acidic solution.

(a) $Cu(s) + NO_3^-(aq) \longrightarrow Cu^{2+}(aq) + NO_2(g)$

(b) $Mn^{2+}(aq) + NaBiO_3(s) \longrightarrow Bi^{3+}(aq) + MnO_4^-(aq)$

Answers:

(a) $Cu(s) + 4H^+(aq) + 2NO_3^-(aq) \longrightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$

(b) $2Mn^{2+}(aq) + 5NaBiO_3(s) + 14H^+(aq) \longrightarrow$
$2MnO_4^-(aq) + 5Bi^{3+}(aq) + 5Na^+(aq) + 7H_2O(l)$

Balancing Equations for Reactions Occurring in Basic Solution

If a redox reaction occurs in basic solution, the equation must be completed by using OH^- and H_2O rather than H^+ and H_2O. The half-reactions can be balanced initially as if they occurred in acidic solution. The H^+ ions can then be "neutralized" by adding an equal number of OH^- ions to both sides of the equation. This procedure is shown in Sample Exercise 20.3.

SAMPLE EXERCISE 20.3

Complete and balance the following equation:

$$CN^-(aq) + MnO_4^-(aq) \longrightarrow CNO^-(aq) + MnO_2(s) \qquad \text{(basic solution)}$$

Solution *First*, we write the incomplete and unbalanced half-reactions:

$$CN^-(aq) \longrightarrow CNO^-(aq)$$
$$MnO_4^-(aq) \longrightarrow MnO_2(s)$$

Second, we initially balance each half-reaction as if it took place in acidic solution. The resultant balanced half-reactions are

$$CN^-(aq) + H_2O(l) \longrightarrow CNO^-(aq) + 2H^+(aq) + 2e^-$$
$$3e^- + 4H^+(aq) + MnO_4^-(aq) \longrightarrow MnO_2(s) + 2H_2O(l)$$

Third, because H^+ does not exist in any appreciable concentration in basic solution, we remove it from the equation by adding an appropriate amount of OH^-. In the CN^- half-reaction, 2 OH^- is added to both sides of the equation to neutralize the 2 H^+. The 2 OH^- and 2 H^+ form 2 H_2O:

$$2OH^-(aq) + CN^-(aq) + H_2O(l) \longrightarrow CNO^-(aq) + 2H_2O(l) + 2e^-$$

The half-reaction can be simplified because H_2O occurs on both sides of the equation. The simplified equation is

$$2OH^-(aq) + CN^-(aq) \longrightarrow CNO^-(aq) + H_2O(l) + 2e^-$$

For the MnO_4^- half-reaction, 4 $OH^-(aq)$ is added to both sides of the equation:

$$3e^- + 4H_2O(l) + MnO_4^-(aq) \longrightarrow MnO_2(s) + 2H_2O(l) + 4OH^-(aq)$$

Simplifying gives

$$3e^- + 2H_2O(l) + MnO_4^-(aq) \longrightarrow MnO_2(s) + 4OH^-(aq)$$

Fourth, we multiply the top equation by 3 and the bottom one by 2 to equalize electron loss and gain in the two half-reactions. The half-reactions are then added:

$$\begin{array}{r}
6OH^-(aq) + 3CN^-(aq) \longrightarrow 3CNO^-(aq) + 3H_2O(l) + 6e^- \\
6e^- + 4H_2O(l) + 2MnO_4^-(aq) \longrightarrow 2MnO_2(s) + 8OH^-(aq) \\
\hline
6OH^-(aq) + 3CN^-(aq) + 4H_2O(l) + 2MnO_4^-(aq) \longrightarrow \\
3CNO^-(aq) + 3H_2O(l) + 2MnO_2(s) + 8OH^-(aq)
\end{array}$$

This equation can be simplified because H_2O and OH^- occur on both sides:

$$3CN^-(aq) + H_2O(l) + 2MnO_4^-(aq) \longrightarrow 3CNO^-(aq) + 2MnO_2(s) + 2OH^-(aq)$$

Fifth, the result is checked by counting atoms and charges: There are 3 C, 3 N, 2 H, 9 O, 2 Mn, and a charge of 5− on both sides of the equation.

PRACTICE EXERCISE

Complete and balance the following equations for oxidation-reduction reactions that occur in basic solution:

(a) $NO_2^-(aq) + Al(s) \longrightarrow NH_3(aq) + Al(OH)_4^-(aq)$

(b) $Cr(OH)_3(s) + ClO^-(aq) \longrightarrow CrO_4^{2-}(aq) + Cl_2(g)$

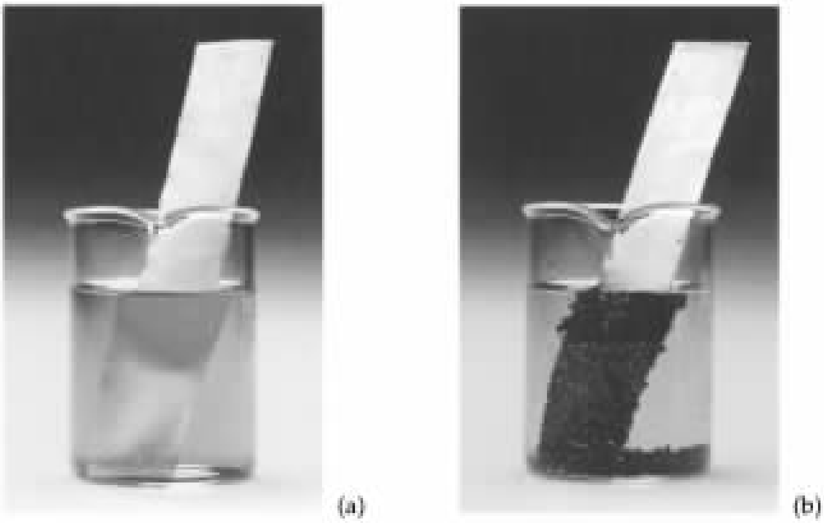
Answers: **(a)** $NO_2^-(aq) + 2Al(s) + 5H_2O(l) + OH^-(aq) \longrightarrow NH_3(aq) + 2Al(OH)_4^-(aq)$; **(b)** $2Cr(OH)_3(s) + 6ClO^-(aq) \longrightarrow 2CrO_4^{2-}(aq) + 3Cl_2(g) + 2OH^-(aq) + 2H_2O(l)$

20.3 Voltaic Cells

The energy released in a spontaneous redox reaction can be used to perform electrical work. This task is accomplished through a **voltaic** (or **galvanic**) **cell**, a device in which the transfer of electrons takes place through an external pathway rather than directly between reactants.

One such spontaneous reaction occurs when a strip of zinc is placed in contact with a solution containing Cu^{2+}. As the reaction proceeds, the blue color of $Cu^{2+}(aq)$ ions fades, and copper metal deposits on the zinc. At the same time, the zinc begins to dissolve. These transformations are shown in Figure 20.3 ▼ and are summarized by Equation 20.7:

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) \qquad [20.7]$$


(a)

(b)

▶ **Figure 20.3** (a) A strip of zinc is placed in a solution of copper(II) sulfate. (b) Electrons are transferred from the zinc to the Cu^{2+} ion, forming Zn^{2+} ions and $Cu(s)$. As the reaction proceeds, the zinc dissolves, the blue color due to $Cu^{2+}(aq)$ fades, and copper metal (the dark material on the zinc strip and on the bottom of the beaker) is deposited.

Figure 20.4 ▶ shows a voltaic cell that uses the redox reaction between Zn and Cu^{2+} in Equation 20.7. Although the setup shown in Figure 20.4 is more complex than that in Figure 20.3, it is important to recognize that the reaction is the same in both cases. Unlike Figure 20.3, in Figure 20.4 the zinc metal and $Cu^{2+}(aq)$ are no longer in direct contact. Consequently, the reduction of the Cu^{2+} can occur only by a flow of electrons through an external circuit, namely the wire that connects the Zn and Cu strips.

▲ **Figure 20.4** A voltaic cell based on the reaction in Equation 20.7. The left compartment contains 1 *M* $CuSO_4$ and a copper electrode. The one on the right contains 1 *M* $ZnSO_4$ and a zinc electrode. The solutions are connected by a porous glass disc, which permits contact of the two solutions. The metal electrodes are connected through a voltmeter, which reads the potential of the cell, 1.10 V.

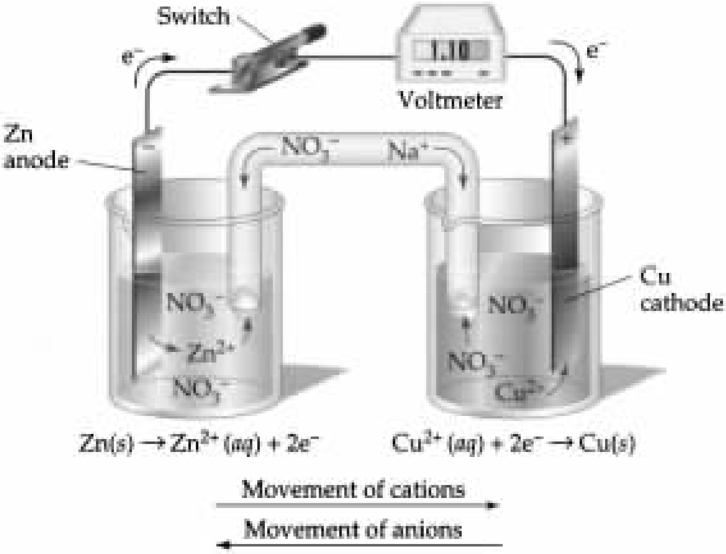
The two solid metals that are connected by the external circuit are called *electrodes*. By definition, the electrode at which oxidation occurs is called the **anode**; the electrode at which reduction occurs is called the **cathode**.* We can think of the voltaic cell as two "half-cells," one corresponding to the oxidation half-reaction and one corresponding to the reduction half-reaction. In our present example Zn is oxidized and Cu^{2+} is reduced:

Anode (oxidation half-reaction): $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Cathode (reduction half-reaction): $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Electrons become available as zinc metal is oxidized at the anode. They flow through the external circuit to the cathode, where they are consumed as $Cu^{2+}(aq)$ is reduced. Because $Zn(s)$ is oxidized in the cell, the zinc electrode loses mass, and the concentration of the Zn^{2+} solution increases as the cell operates. Similarly, the Cu electrode gains mass, and the Cu^{2+} solution becomes less concentrated as Cu^{2+} is reduced to $Cu(s)$.

As the voltaic cell operates, oxidation of Zn introduces additional Zn^{2+} ions into the anode compartment. Unless a means is provided to neutralize this positive charge, no further oxidation can take place. Similarly, the reduction of Cu^{2+} at the cathode leaves an excess of negative charge in solution in that compartment. Electrical neutrality is maintained by a migration of ions through the porous glass disc separating the two compartments, as in Figure 20.4, or through a *salt bridge*, as illustrated in Figure 20.5 ▼. A salt bridge consists of a U-shaped tube that contains an electrolyte solution, such as $NaNO_3(aq)$, whose ions will not react with other ions in the cell or with the electrode materials. The electrolyte is



◀ **Figure 20.5** Voltaic cell that uses a salt bridge to complete the electrical circuit.

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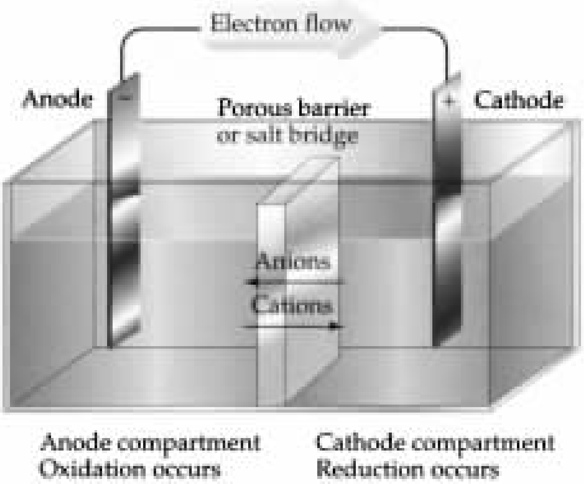
* To help remember these definitions, note that *anode* and *oxidation* both begin with a vowel, and *cathode* and *reduction* both begin with a consonant.



▶ **Figure 20.6** A summary of the terminology used in describing voltaic cells. Oxidation occurs at the anode; reduction occurs at the cathode. The electrons flow spontaneously from the negative anode to the positive cathode. The electrical circuit is completed by the movement of ions in solution. Anions move toward the anode, whereas cations move toward the cathode. The cell compartments can be separated by either a porous glass barrier (as in Figure 20.4) or by a salt bridge (as in Figure 20.5).

often incorporated into a gel so that the electrolyte solution does not run out when the U-tube is inverted. As oxidation and reduction proceed at the electrodes, ions from the salt bridge migrate to neutralize charge in the cell compartments. Anions migrate toward the anode, and cations toward the cathode. In fact, no measurable electron flow will occur through the external circuit unless a means is provided for ions to migrate through the solution from one electrode compartment to another, thereby completing the circuit.

Voltaic Cells I movie

Figure 20.6 ▲ summarizes the relationships among the anode, the cathode, the chemical process occurring in a voltaic cell, the direction of migration of ions in solution, and the motion of electrons in the external circuit. Notice in particular that *in any voltaic cell the electrons flow from the anode through the external circuit to the cathode*. Because the negatively charged electrons flow from the anode to the cathode, the anode in a voltaic cell is labeled with a negative sign and the cathode with a positive sign; we can envision the electrons as being attracted to the positive cathode from the negative anode through the external circuit.*

SAMPLE EXERCISE 20.4

The following oxidation-reduction reaction is spontaneous:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq) \longrightarrow 2Cr^{3+}(aq) + 3I_2(s) + 7H_2O(l)$$

A solution containing $K_2Cr_2O_7$ and H_2SO_4 is poured into one beaker, and a solution of KI is poured into another. A salt bridge is used to join the beakers. A metallic conductor that will not react with either solution (such as platinum foil) is suspended in each solution, and the two conductors are connected with wires through a voltmeter or some other device to detect an electric current. The resultant voltaic cell generates an electric current. Indicate the reaction occurring at the anode, the reaction at the cathode, the direction of electron and ion migrations, and the signs of the electrodes.

Solution Our first step is to divide the chemical equation into half-reactions so that we can identify the oxidation and the reduction processes:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

$$6I^-(aq) \longrightarrow 3I_2(s) + 6e^-$$

---

* Although the anode and cathode are labeled with − and + signs respectively, you should not interpret the labels as charges on the electrodes. The labels simply tell us the electrode at which the electrons are released to the external circuit (the anode) and received from the external circuit (the cathode). The actual charges on the electrodes are essentially zero.

Now we can use the summary in Figure 20.6 to describe the voltaic cell. The first half-reaction is the reduction process, which by definition occurs at the cathode. The second half-reaction is the oxidation, which occurs at the anode. The I^- ions are the source of electrons, and the $Cr_2O_7^{2-}$ ions accept the electrons. Hence, the electrons flow through the external circuit from the electrode immersed in the KI solution (the anode) to the electrode immersed in the $K_2Cr_2O_7$–H_2SO_4 solution (the cathode). The electrodes themselves do not react in any way; they merely provide a means of transferring electrons from or to the solutions. The cations move through the solutions toward the cathode, and the anions move toward the anode. The anode (from which the electrons move) is the negative electrode, and the cathode (toward which the electrons move) is the positive one.

PRACTICE EXERCISE

The two half-reactions in a voltaic cell are

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

$$ClO_3^-(aq) + 6H^+(aq) + 6e^- \longrightarrow Cl^-(aq) + 3H_2O(l)$$

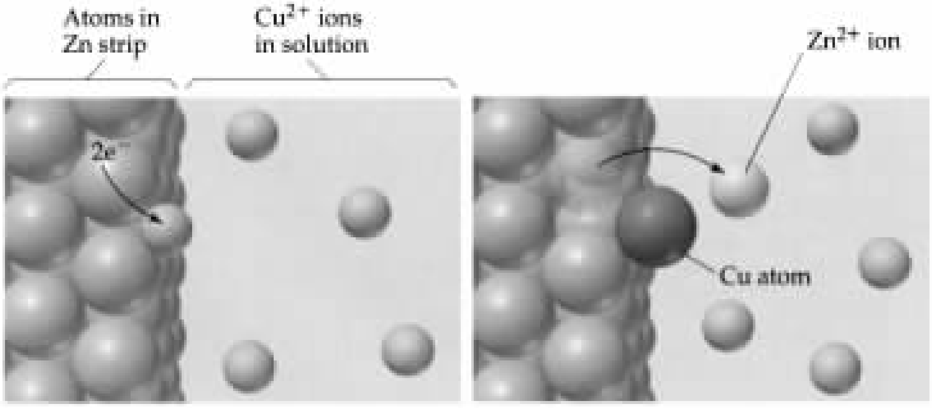
(a) Indicate which reaction occurs at the anode and which at the cathode. **(b)** Which electrode is consumed in the cell reaction? (c) Which electrode is positive? ***Answers:*** **(a)** The first reaction occurs at the anode, the second reaction at the cathode. **(b)** The anode (Zn) is consumed in the cell reaction. **(c)** The cathode is positive.

A Molecular View of Electrode Processes

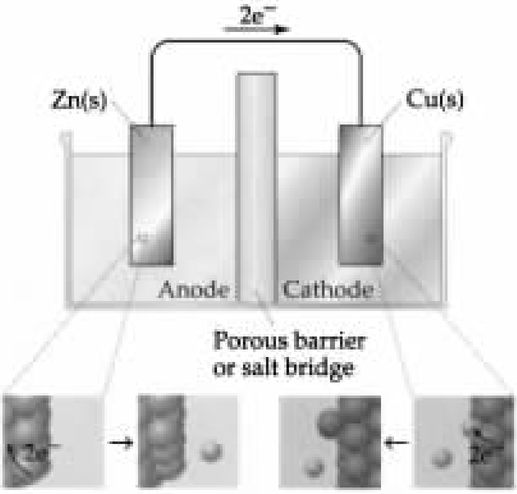
In order to understand better the relationship between voltaic cells and spontaneous redox reactions, it is instructive to look at what happens at the atomic or molecular level. The actual processes involved in the transfer of electrons are quite complex; nevertheless, we can learn much by examining these processes in a simplified way.

Let's first consider the spontaneous redox reaction between Zn(*s*) and Cu^{2+}(*aq*), illustrated in Figure 20.3. During the reaction Zn(*s*) is oxidized to Zn^{2+}(*aq*) and Cu^{2+}(*aq*) is reduced to Cu(*s*). Figure 20.7 ▼ shows a schematic diagram of how these processes occur at the atomic level. We can envision a Cu^{2+} ion coming into contact with the strip of Zn metal, as in Figure 20.7(a). Two elec-

▼ **Figure 20.7** Depiction of the reaction between Zn(*s*) and Cu^{2+}(*aq*) at the atomic level. The water molecules and anions in the solution are not shown. (a) A Cu^{2+} ion comes in contact with the surface of the Zn strip and gains two electrons from a Zn atom; the Cu^{+} ion is reduced, and the Zn atom is oxidized. (b) The resulting Zn^{2+} ion enters the solution, and the Cu atom remains deposited on the strip.



(a) (b)



▶ **Figure 20.8** Depiction of the voltaic cell in Figure 20.5 at the atomic level. At the anode a Zn atom loses two electrons and becomes a Zn^{2+} ion; the Zn atom is oxidized. The electrons travel through the external circuit to the cathode. At the cathode a Cu^{2+} ion gains the two electrons, forming a Cu atom; the Cu^{2+} ion is reduced. Ions migrate through the porous barrier to maintain charge balance between the compartments.

trons are transferred directly from a Zn atom to the Cu^{2+} ion, leading to a Zn^{2+} ion and a Cu atom. The Zn^{2+} ion migrates away into the aqueous solution while the Cu atom remains deposited on the metal strip [Figure 20.7(b)]. As the reaction proceeds, we produce more and more Cu(*s*) and deplete the Cu^{2+}(*aq*), as we saw in Figure 20.3(b).

The voltaic cell in Figure 20.5 also involves the oxidation of Zn(*s*) and the reduction of Cu^{2+}(*aq*). In this case, however, the electrons are not transferred directly between the reacting species. Figure 20.8 ▲ shows qualitatively what happens at each of the electrodes of the cell. At the surface of the anode, a Zn atom "loses" two electrons and becomes a Zn^{2+}(*aq*) ion in the anode compartment. We envision the two electrons traveling from the anode through the wire to the cathode. At the surface of the cathode, the two electrons reduce a Cu^{2+} ion to a Cu atom, which is deposited on the cathode. As we noted earlier, the flow of electrons from the anode to the cathode is possible only if ions are transferred through the salt bridge in order to maintain overall charge balance for each of the two compartments.

We see that the redox reaction between Zn and Cu^{2+} is spontaneous regardless of whether they react directly or in the separate compartments of a voltaic cell. In each case the overall reaction is the same—only the path by which the electrons are transferred from the Zn atom to a Cu^{2+} ion is different. In the next section we will examine *why* this reaction is spontaneous.

20.4 Cell EMF

At this point you may be asking yourself why the electrons flow spontaneously in the way that they do. Why do electrons transfer spontaneously from a Zn atom to a Cu^{2+} ion, either directly as in the reaction of Figure 20.3 or through an external circuit as in the voltaic cell of Figure 20.5? In this section we will examine the "driving force" that pushes the electrons through an external circuit in a voltaic cell.

In a simple sense, we can compare the electron flow caused by a voltaic cell to the flow of water in a waterfall (Figure 20.9 ▶). Water flows spontaneously over a waterfall because of a difference in potential energy between the top of the falls and the stream below. ∞ (Section 5.1) In a similar fashion electrons flow