17 Electrochemistry

Most "silver" tableware like the ones in the painting are not made of pure silver but rather are silver-plated using an electrolytic cell.

Suzanne C. Ouellette

If by fire,
Of sooty coal th' empiric
Alchymist
Can turn, or holds it possible
to turn
Metals of drossiest Ore to
Perfect Gold.

—JOHN MILTON
Paradise Lost (Book V, Lines 439–442)

Chapter Outline

Cathode = reduction; anode = oxidation. The consonants go together, as do the vowels.

Electrochemistry is the study of the interconversion of electrical and chemical energy. This conversion takes place in an electrochemical cell that may be a(n)

- **voltaic (galvanic) cell** (Section 17-2), in which a spontaneous reaction generates electrical energy.
- **electrolytic cell** (Section 17-6), in which electrical energy is used to bring about a nonspontaneous reaction.

All of the reactions considered in this chapter are of the oxidation-reduction type. You will recall from Chapter 4 that such a reaction can be split into two half-reactions. In one half-reaction, referred to as ***reduction,*** electrons are consumed; in the other, called ***oxidation,*** electrons are produced. There can be no net change in the number of electrons; the number of electrons consumed in reduction must be exactly equal to the number produced in the oxidation half-reaction. These two half-reactions combine to give a balanced redox reaction (Section 17-1).

In an electrochemical cell, these two half-reactions occur at two different **electrodes,** which most often consist of metal plates or wires. Reduction occurs at the **cathode;** a typical half-reaction might be

$$\text{cathode:} \qquad Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$

Oxidation takes place at the **anode,** where a species such as zinc metal produces electrons:

$$\text{anode:} \qquad Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$

It is always true that in an electrochemical cell, *anions* move to the *anode; cations* move to the *cathode*.

One of the most important characteristics of a cell is its *voltage,* which is a measure of reaction spontaneity. Cell voltages depend on the nature of the half-reactions

occurring at the electrodes (Section 17-3) and on the concentrations of species involved (Section 17-5). From the voltage measured at standard concentrations, it is possible to calculate the standard free energy change and the equilibrium constant (Section 17-4) of the reaction involved.

The principles discussed in this chapter have a host of practical applications. Whenever you start your car, turn on your cell phone, or use a remote control for your television or other devices, you are making use of a voltaic cell. Many of the most important elements, including hydrogen and chlorine, are prepared in electrolytic cells. These applications, among others, are discussed in Section 17-7.

17-1 Oxidation-Reduction Reactions Revisited

In Chapter 4, redox reactions were introduced as one of the three important types of reactions in aqueous solutions. In this section, we will review some of the terminology introduced in Chapter 4 and then go on to describe how to balance redox equations by first learning how to balance redox half-reactions.

Review of Oxidation-Reduction Terminology and Concepts

- A **redox reaction** involves a transfer of electrons between two species.
- **Oxidation** occurs when a species loses electrons and increases its oxidation number (O. N.). An equation that shows this loss is called an *oxidation half-reaction*. In this half-reaction, the electrons are in the product side.
- **Reduction** occurs when a species gains electrons and decreases its oxidation number (O. N.). An equation that shows this gain is called a *reduction half-reaction*. In this half-reaction, the electrons are in the reactant side.
- The ion or molecule that donates the electrons (i.e., oxidized) is called the **reducing agent**.
- The ion or molecule that accepts the electrons (i.e., reduced) is called the **oxidizing agent**.
- Oxidation and reduction occur together in the same reaction. There is no net change in the number of electrons, just an exchange of electrons.

Balancing Half-Equations (Oxidation or Reduction)

Before you can balance an overall redox equation, you have to be able to balance two **half-equations,** one for oxidation (electron loss) and one for reduction (electron gain). Sometimes that's easy. Given the oxidation half-equation

$$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) \qquad (\text{O.N. Fe: } +2 \longrightarrow +3)$$

it is clear that mass and charge balance can be achieved by adding an electron to the right:

$$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$$

In another case, this time a reduction half-equation,

$$Cl_2(g) \longrightarrow Cl^-(aq) \qquad (\text{O.N. Cl: } 0 \longrightarrow -1)$$

mass balance is obtained by writing a coefficient of 2 for Cl^-; charge is then balanced by adding two electrons to the left. The balanced half-equation is

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

Sometimes, though, it is by no means obvious how a given half-equation is to be balanced. This commonly happens when elements other than those being oxidized or reduced take part in the reaction. Most often, these elements are oxygen (O.N. = −2) and hydrogen (O.N. = +1). Consider, for example, the half-equation for the reduction of the permanganate ion,

$$MnO_4^-(aq) \longrightarrow Mn^{2+}(aq) \qquad (\text{O.N. Mn: } +7 \longrightarrow +2)$$

or the oxidation of chromium(III) hydroxide,

$$Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq) \qquad (\text{O.N. Cr: } +3 \longrightarrow +6)$$

To balance half-equations such as these, proceed as follows:

(a) ***Assign oxidation numbers to each element.***
(b) ***Balance the atoms of each element being oxidized or reduced.***
(c) ***Multiply the oxidation number by the number of atoms that have that oxidation number. This gives you the "total" oxidation number.***
The number of atoms is indicated either by the coefficient that you used to balance the atoms or by the subscript of the atom.
(d) ***Balance oxidation number by adding electrons.***
Electrons are added to the left for a reduction half-equation and to the right for an oxidation half-equation.
The number of electrons added should equal the change in "total" number from part (c).
(e) ***Balance charge by adding H^+ ions in acidic solution and OH^- ions in basic solution.***
(f) ***Balance hydrogen by adding H_2O molecules.***
(g) ***Check to make sure that oxygen is balanced.***
If it is, the half-equation is almost certainly balanced correctly with respect to mass and charge.

Figure 17.1 is a flowchart schematically showing the steps described above. Example 17.1 shows how these rules are applied to balance half-equations.

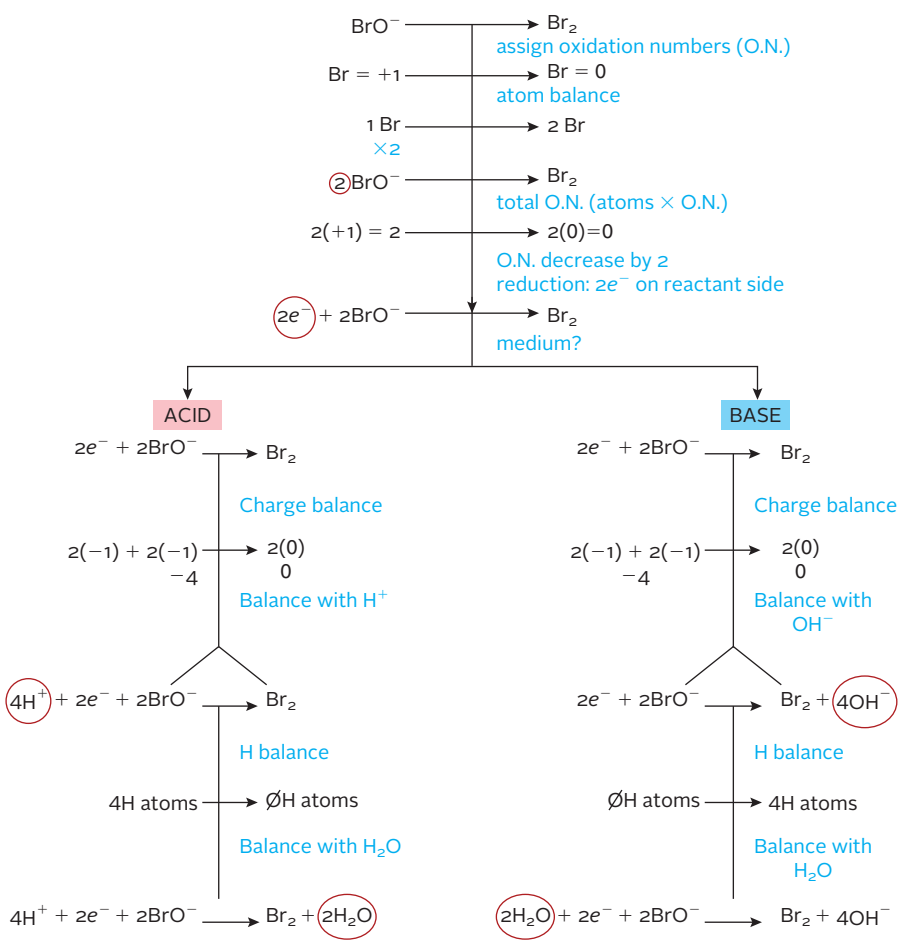

Figure 17.1 Flowchart for balancing half-reactions in acid or base medium.

EXAMPLE 17.1

Balance the following half-equations. Follow the steps outlined in the order given.

a $NO_3^-(aq) \rightarrow NO(g)$ (basic solution)

SOLUTION

1. Oxidation numbers	N: $+5 \rightarrow +2$; O: $-2 \rightarrow -2$; N is reduced.
2. Atom balance	1 N on each side; no adjustment is required.
3. "total oxidation" number	N: $5(1) \rightarrow$ N: $2(1)$
4. Add electrons	The oxidation number for N goes from +5 to +2. It is reduced by 3. Add 3 electrons to the reactant side. $NO_3^-(aq) + 3e^- \rightarrow NO(g)$
5. Balance charge	reactants: $-1 + 3(-1) = -4$ products: 0 basic medium: add OH^-. To balance, add $4OH^-$ on the right. $NO_3^-(aq) + 3e^- \rightarrow NO(g) + 4OH^-(aq)$ reactants: $-1 + 3(-1) = -4$ products: $4(-1) = -4$
6. Balance H	reactants: 0 H products: 4 H To balance, add $2H_2O$ on the left. $NO_3^-(aq) + 3e^- + 2H_2O \rightarrow NO(g) + 4OH^-(aq)$ reactants: 4 H products: 4 H
7. Check O:	reactants: $3 + 2 = 5$ products: $4 + 1 = 5$
The half-equation is balanced:	$NO_3^-(aq) + 3e^- \rightarrow NO(g) + 4OH^-(aq)$

b $Cl_2(g) \rightarrow ClO_3^-(aq)$ (acidic solution)

SOLUTION

1. Oxidation numbers	Cl: $0 \rightarrow +5$; O: $-2 \rightarrow -2$; Cl is oxidized.
2. Atom balance	reactant: 2 Cl product: 1 Cl Multiply ClO_3^- by 2. $Cl_2(g) \rightarrow 2ClO_3^-(aq)$
3. "total oxidation" number	Cl: $0(2) = 0 \rightarrow$ Cl: $5(2) = 10$
4. Add electrons	The oxidation number for Cl goes from 0 to 10. The oxidation number increases by 10. Add 10 electrons to the product side. $Cl_2(g) \rightarrow 2ClO_3^-(aq) + 10e^-$
5. Balance charge	reactants: 0 products: $2(-1) + 10(-1) = -12$ acidic medium: add H^+. To balance, add 12 H^+ on the right. $Cl_2(g) \rightarrow 2ClO_3^-(aq) + 10e^- + 12H^+(aq)$ reactants: 0 products: $2(-1) + 10(-1) + 12(+1) = 0$
6. Balance H	reactants: 0 H products: 12 H To balance, add $6H_2O$ on the left. $Cl_2(g) + 6H_2O \rightarrow 2ClO_3^-(aq) + 10e^- + 12H^+(aq)$ reactants: 12 H products: 12 H
7. Check O:	reactants: 6 products: $2(3) = 6$
The half-equation is balanced:	$Cl_2(g) + 6H_2O \rightarrow 2ClO_3^-(aq) + 10e^- + 12H^+(aq)$

Balancing Redox Equations

The process used to balance an overall redox equation is relatively straightforward, provided you know how to balance half-equations. Follow a systematic,

four-step procedure:

1. ***Split the equation into two half-equations,*** one for reduction, the other for oxidation.
2. ***Balance one of the half-equations*** with respect to both atoms and charge as described above (steps a through e).
3. ***Balance the other half-equation.***
4. ***Combine the two half-equations in such a way as to eliminate electrons.*** Suppose, for example, the two balanced half-equations are

$$A(s) \longrightarrow A^{2+}(aq) + 2e^-$$
$$B^{3+}(aq) + 3e^- \longrightarrow B(s)$$

Multiplying the first half-equation by 3, the second by 2, and adding gives

$$3A(s) + 2B^{3+}(aq) \longrightarrow 3A^{2+}(aq) + 2B(s)$$

The electrons, six on both sides, cancel.

EXAMPLE 17.2

Balance the following redox reactions by following the four-step process outlined above.

a $Fe_2^+(aq) + NO_3^-(aq) \rightarrow Fe_3^+(aq) + NO(g)$ (basic solution)

SOLUTION

1. Split into two half-equations.	$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$ $NO_3^-(aq) \rightarrow NO(g)$
2–3. Balance the half-equations.	Check the text. This has been done earlier. $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$ $NO_3^-(aq) + 3e^- + 2H_2O \rightarrow NO(g) + 4OH^-(aq)$
4. Eliminate electrons.	Multiply the oxidation half-equation by 3. $3[Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-]$
Combine half-equations.	$NO_3^-(aq) + 3Fe^{2+}(aq) + 2H_2O \rightarrow NO(g) + 4OH^-(aq) + 3Fe^{3+}(aq)$

b $MnO_4^-(aq) + Cl_2(g) \rightarrow Mn_2^+(aq) + ClO_3^-(aq)$ (acidic solution)

SOLUTION

1. Split into two half-equations.	$MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$ $Cl_2(g) \rightarrow ClO_3^-(aq)$
2–3. Balance the half-equations.	The oxidation half-equation is balanced in Example 17.1. $Cl_2(g) + 6H_2O \rightarrow 2ClO_3^-(aq) + 10e^- + 12H^+(aq)$ Try to balance the reduction half-equation. $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O$
4. Eliminate electrons.	Multiply the reduction half-equation by 2. $2[MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O]$
Combine half-equations.	$Cl_2(g) + 6H_2O + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow$ $2ClO_3^-(aq) + 12H^+(aq) + 2Mn^{2+}(aq) + 8H_2O$
Net ionic equation	$6H_2O \rightarrow 8H_2O = 2H_2O$ (product side) $16H^+ \rightarrow 12H^+ = 4H^+$ (reactant side)
Balanced net ionic equation	$Cl_2(g) + 2MnO_4^-(aq) + 4H^+(aq) \rightarrow 2ClO_3^-(aq) + 2Mn^{2+}(aq) + 2H_2O$

continued

END POINT

It is a good idea to check both mass and charge balance in the final balanced net ionic equation. In (2), for example:

	Cl Atoms	Mn Atoms	O Atoms	H Atoms	Charge
Left	2	2	2(4) = 8	4	+0 − 2 + 4 = +2
Right	2	2	2(3) + 2 = 8	2(2) = 4	−2 + 4 + 0 = +2

17-2 Voltaic Cells

In principle at least, any spontaneous redox reaction can serve as a source of energy in a **voltaic (galvanic) cell.** The cell must be designed in such a way that oxidation occurs at one electrode (anode) with reduction at the other electrode (cathode). The electrons produced at the anode must be transferred to the cathode, where they are consumed. To do this, the electrons move through an external circuit, where they do electrical work.

To understand how a voltaic cell operates, let us start with some simple cells that are readily made in the general chemistry laboratory.

The Zn-Cu^{2+} Cell

When a piece of zinc is added to a water solution containing Cu^{2+} ions, the following redox reaction takes place:

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

In this reaction, copper metal plates out on the surface of the zinc. The blue color of the aqueous Cu^{2+} ion fades as it is replaced by the colorless aqueous Zn^{2+} ion (Figure 17.2). Clearly, this redox reaction is spontaneous; it involves electron transfer from a Zn atom to a Cu^{2+} ion.

To design a voltaic cell using the Zn-Cu^{2+} reaction as a source of electrical energy, the electron transfer must occur indirectly; that is, the electrons given off by zinc atoms must be made to pass through an external electric circuit before

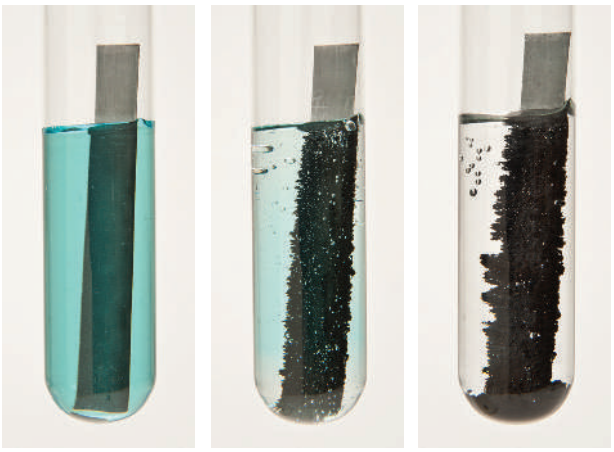

Figure 17.2 Zn-Cu^{2+} spontaneous redox reaction. The blue of the Cu^{2+} ion in solution fades *(from left to right)* as the ion is reduced to metallic Cu that deposits on the zinc strip in the solution.

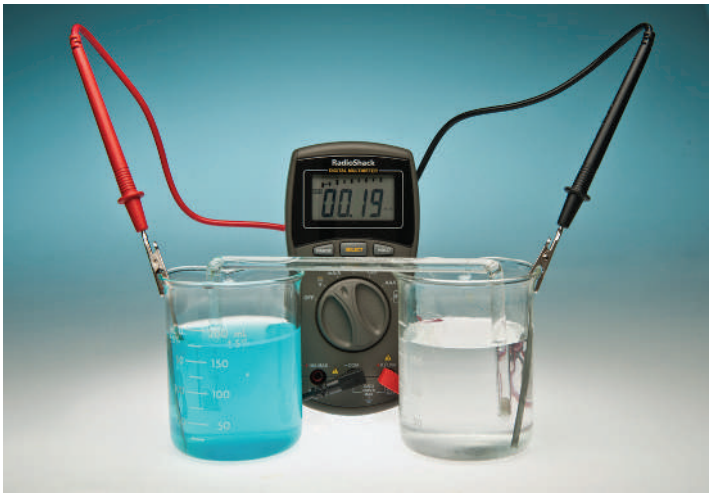

Figure 17.3 A Zn-Cu^{2+} voltaic cell. In this voltaic cell, a voltmeter *(left)* is connected to a half-cell consisting of a Cu cathode in a solution of blue Cu^{2+} ions and a half-cell consisting of a Zn anode in a solution of colorless Zn^{2+} ions. The following spontaneous reaction takes place in this cell: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$. The salt bridge allows ions to pass from one solution to the other to complete the circuit and prevents direct contact between Zn atoms and the Cu^{2+} ions.

The Zn electrode must not come in contact with Cu^{2+} ions. Why?

they reduce Cu^{2+} ions to copper atoms. Figure 17.3 shows one way to do this. The voltaic cell consists of an anode **half-cell** and a cathode **half-cell**:

- a Zn anode dipping into a solution containing Zn^{2+} ions, seen in the beaker at the far right.
- a Cu cathode dipping into a solution containing Cu^{2+} ions (blue), seen in the other beaker in Figure 17.3.

The "external circuit" consists of a voltmeter with leads (red and black) to the anode and cathode.

Let us trace the flow of electric current through the cell.

1. At the zinc *anode* (connected to the black wire in Figure 17.3), electrons are produced by the oxidation half-reaction

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

This electrode, which "pumps" electrons into the external circuit, is ordinarily marked as the negative pole of the cell.

2. Electrons generated at the anode move through the external circuit (right to left in Figure 17.3) to the copper *cathode,* connected through the red wire to the voltmeter. At the cathode, the electrons are consumed, reducing Cu^{2+} ions present in the solution around the electrode:

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

The copper electrode, which "pulls" electrons from the external circuit, is considered to be the positive pole of the cell.

3. As the above half-reactions proceed, a surplus of positive ions (Zn^{2+}) tends to build up around the zinc electrode. The region around the copper electrode tends to become deficient in positive ions as Cu^{2+} ions are consumed. To maintain electrical neutrality, cations must move toward the copper cathode or, alternatively, anions must move toward the zinc anode. In practice, both migrations occur.

In the cell in Figure 17.3, movement of ions occurs through a **salt bridge** connecting the two beakers. The salt bridge is an inverted glass U-tube, plugged with glass wool at each end. The tube is filled with a solution of a salt that takes no part in the electrode reactions; potassium nitrate, KNO_3, is frequently used. As current is drawn from the cell, K^+ ions move from the salt bridge into the cathode half-cell. At the same time, NO_3^- ions move into the anode half-cell. In this way, electrical neutrality is maintained without Cu^{2+} ions coming in contact with the Zn electrode, which would short-circuit the cell.

The cell in Figure 17.3 is often abbreviated as

$$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$$

Anode ‖ cathode.

In this notation,

- the *anode* reaction *(oxidation)* is shown at the left. Zn atoms are oxidized to Zn^{2+} ions.
- the salt bridge (or other means of separating the half cells) is indicated by the symbol ‖.
- the *cathode* reaction *(reduction)* is shown at the right. Cu^{2+} ions are reduced to Cu atoms.
- a single vertical line indicates a phase boundary, such as that between a solid electrode and an aqueous solution.

Notice that the anode half-reaction comes first in the cell notation, just as the letter *a* comes before *c*.

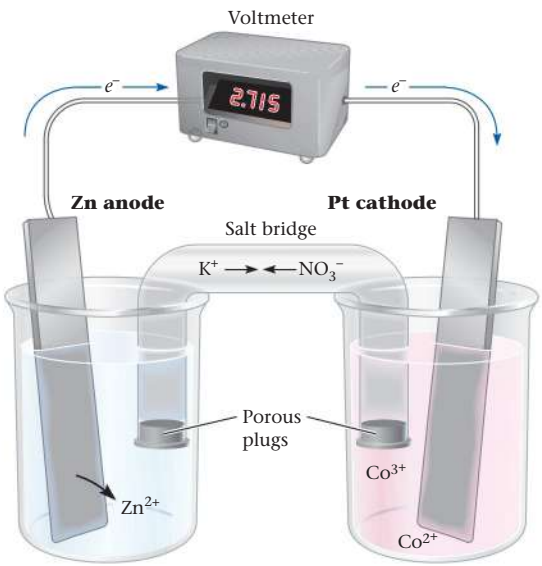

Figure 17.4 A Zn-Co^{3+} voltaic cell. A platinum electrode is immersed in a solution containing Co^{3+} and Co^{2+} ions. The spontaneous cell reaction is

$$Zn(s) + 2Co^{3+}(aq) \longrightarrow Zn^{2+}(aq) + 2Co^{2+}(aq)$$

The platinum electrode does not participate in the reaction. The zinc electrode does.

Other Salt Bridge Cells

Cells similar to that in Figure 17.3 can be set up for many different spontaneous redox reactions. Consider, for example, the reaction

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

This reaction, like that between Zn and Cu^{2+}, can serve as a source of electrical energy in a voltaic cell. The cell is similar to the one in Figure 17.3 except that, in the anode compartment, a nickel electrode is surrounded by a solution of a nickel(II) salt, such as $NiCl_2$ or $NiSO_4$. The cell notation is $Ni \mid Ni^{2+} \parallel Cu^{2+} \mid Cu$.

Another spontaneous redox reaction that can serve as a source of electrical energy is that between zinc metal and Co^{3+} ions:

$$Zn(s) + 2Co^{3+}(aq) \longrightarrow Zn^{2+}(aq) + 2Co^{2+}(aq)$$

A voltaic cell using this reaction is similar to the Zn-Cu^{2+} cell; the $Zn \mid Zn^{2+}$ half-cell and the salt bridge are the same. Because no metal is involved in the cathode half-reaction, an *inert* electrode that conducts an electric current is used. Frequently, the cathode is made of platinum (Figure 17.4). In the cathode, Co^{3+} ions are provided by a solution of $Co(NO_3)_3$. The half-reactions occurring in the cell are

Nichrome or graphite can also be used.

$$\text{anode:} \quad Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \quad \text{(oxidation)}$$

$$\text{cathode:} \quad Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq) \quad \text{(reduction)}$$

The cell notation is $Zn \mid Zn^{2+} \parallel Co^{3+}, Co^{2+} \mid Pt$. Note that a comma separates the half-cell components that are in the *same* phase. The symbol Pt is used to indicate the presence of an inert platinum electrode. A single vertical line separates Pt (a solid) from the components of the half-cell, which are in the liquid phase.

EXAMPLE 17.3

When chlorine gas is bubbled through an aqueous solution of NaBr, chloride ions and liquid bromine are the products of the spontaneous reaction.

(a) Draw a sketch of the cell, labeling the anode, the cathode, and the direction of electron flow.

(b) Write the half-reaction that takes place at the anode and at the cathode.

(c) Write a balanced equation for the cell reaction.

(d) Write an abbreviated notation for the cell.

STRATEGY

1. Split the equation into two half-reactions.
2. Recall that the anode
   - is where oxidation takes place.
   - is the electrode toward which anions move.
   - is where electrons are produced.
3. The cathode
   - is where reduction takes place.
   - is the electrode toward which cations move.
   - is where electrons are released by the anode through an external circuit.

SOLUTION

(a) Sketch of the cell

See Figure 17.5, where all the appropriate parts are labeled and the direction of electron flow is indicated.

(b) Half-reactions

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

anode: $2Br^-(aq) \longrightarrow Br_2(l) + 2e^-$ (oxidation)

(c) Balanced equation

$$Cl_2(g) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(l)$$

(d) Abbreviated cell notation

$$Pt \mid Br_2, Br^- \parallel Cl^- \mid Cl_2 \mid Pt$$

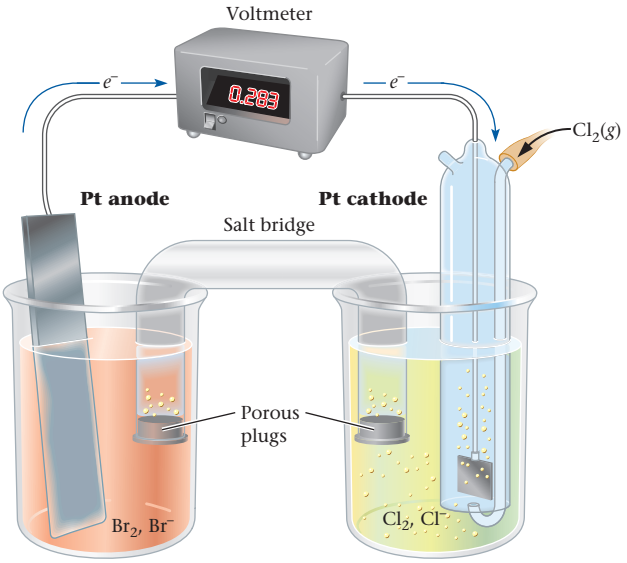

Figure 17.5 A Cl_2-Br_2 voltaic cell. In this cell the spontaneous cell reaction is

$$Cl_2(g) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(l)$$

Both electrodes are platinum, with the anode at the left and the cathode at the right.

To summarize our discussion of the structure of voltaic cells,

- *a voltaic cell consists of two half-cells.* They are joined by an external electric circuit through which electrons move and a salt bridge through which ions move.
- *each half-cell consists of an electrode dipping into a water solution.* If a metal participates in the cell reaction, either as a product or as a reactant, it is ordinarily used as the electrode; otherwise, an inert electrode such as platinum is used.
- *in one half-cell, oxidation occurs at the anode; in the other, reduction takes place at the cathode.* The overall cell reaction is the sum of the half-reactions taking place at the anode and cathode.

17-3 Standard Voltages

The driving force behind the spontaneous reaction in a voltaic cell is measured by the cell voltage, which is an *intensive* property, independent of the number of electrons passing through the cell. **Cell voltage** depends on the nature of the redox reaction and the concentrations of the species involved; for the moment, we'll concentrate on the first of these factors.

The **standard cell voltage ($E°$)** (also referred to as the *standard voltage*) for a given cell is that measured when the current flow is essentially zero, ***all ions and molecules in solution are at a concentration of 1 M, and all gases are at a pressure of 1 atm.*** To illustrate, consider the Zn-H^+ cell. Let us suppose that the half-cells are set up in such a way that the concentrations of Zn^{2+} and H^+ are both 1 *M* and the pressure of $H_2(g)$ is 1 atm. Under these conditions, the cell voltage at very low current flow is +0.762 V. This quantity is referred to as the standard voltage and is given the symbol $E°$.

$$Zn(s) + 2H^+(aq, 1\ M) \longrightarrow Zn^{2+}(aq, 1\ M) + H_2(g, 1\ \text{atm}) \qquad E° = +0.762\ \text{V}$$

$E°_{red}$ and $E°_{ox}$

Any redox reaction can be split into two half-reactions, an oxidation and a reduction. It is possible to associate the standard voltages, **standard oxidation voltage ($E°_{ox}$)** and **standard reduction voltage ($E°_{red}$)**, with the oxidation and reduction half-reactions. The standard voltage for the overall reaction, $E°$, is the sum of these two quantities

$$E° = E°_{red} + E°_{ox} \qquad (17.1)$$

You need two half-cells to measure a voltage.

To illustrate, consider the reaction between Zn and H^+ ions, for which the standard voltage is +0.762 V.

$$+0.762\ \text{V} = E°_{red}(H^+ \longrightarrow H_2) + E°_{ox}(Zn \longrightarrow Zn^{2+})$$

There is no way to measure the standard voltage for a half-reaction; only $E°$ can be measured directly. To obtain values for $E°_{ox}$ and $E°_{red}$, the value zero is arbitrarily assigned to the standard voltage for reduction of H^+ ions to H_2 gas:

$$2H^+(aq, 1\ M) + 2e^- \longrightarrow H_2(g, 1\ \text{atm}) \qquad E°_{red}(H^+ \longrightarrow H_2) = 0.000\ \text{V}$$

Using this convention, it follows that the standard voltage for the oxidation of zinc must be +0.762 V; that is,

$$Zn(s) \longrightarrow Zn^{2+}(aq, 1\ M) + 2e^- \qquad E°_{ox}(Zn \longrightarrow Zn^{2+}) = +0.762\ \text{V}$$

As soon as one half-reaction voltage is established, others can be calculated. For example, the standard voltage for the Zn-Cu^{2+} cell shown in Figure 17.3 is found to be +1.101 V. Knowing that $E°_{ox}$ for zinc is +0.762 V, it follows that

$$\begin{aligned} E°_{red}(Cu^{2+} \longrightarrow Cu) &= E° - E°_{ox}(Zn \longrightarrow Zn^{2+}) \\ &= 1.101\ \text{V} - 0.762\ \text{V} = +0.339\ \text{V} \end{aligned}$$

Standard half-cell voltages are ordinarily obtained from a list of standard voltages such as those in Table 17.1. The unit for the electric potential is the **volt**. Each **standard potential** listed is the standard voltage for a given half-reaction, that is

$$\text{standard potential} = E^\circ_{\text{red}}$$

For example, the standard potentials listed in the table for $Zn^{2+} \longrightarrow Zn$ and $Cu^{2+} \longrightarrow Cu$ are -0.762 V and $+0.339$ V, respectively; it follows that at 25°C

$$Zn^{2+}(aq, 1\ M) + 2e^- \longrightarrow Zn(s) \qquad E^\circ_{\text{red}} = -0.762 \text{ V}$$
$$Cu^{2+}(aq, 1\ M) + 2e^- \longrightarrow Cu(s) \qquad E^\circ_{\text{red}} = +0.339 \text{ V}$$

Standard potential = E°_{red}.

To obtain the standard voltage for an oxidation half-reaction, all you have to do is ***change the sign of the standard potential*** *listed in Table 17.1.* For example, knowing that

$$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s) \qquad E^\circ_{\text{red}} = -0.762 \text{ V}$$

it follows that

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \qquad E^\circ_{\text{ox}} = +0.762 \text{ V}$$

Again, we have

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \qquad E^\circ_{\text{red}} = +0.339 \text{ V}$$

so,

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^- \qquad E^\circ_{\text{ox}} = -0.339 \text{ V}$$

Another way to express this principle is to say that ***standard voltages for forward and reverse half-reactions are equal in magnitude but opposite in sign.***

Strength of Oxidizing and Reducing Agents

As pointed out in Section 17-1, an oxidizing agent is a species that can gain electrons; it is a reactant in a reduction half-reaction. Table 17.1 lists reduction half-reactions from left to right; it follows that ***oxidizing agents are in the left column of the table.*** All of the species appearing in that column (Li^+, . . . , F_2) are, in principle, oxidizing agents. A "strong" oxidizing agent is one that has a strong attraction for electrons and hence *can readily oxidize other species.* In contrast, a "weak" oxidizing agent does not gain electrons readily. It is capable of reacting only with those species that are very easily oxidized.

The strength of an oxidizing agent is directly related to the standard voltage for its reduction, E°_{red}. ***The more positive E°_{red} is, the stronger the oxidizing agent.*** Looking at Table 17.1, you can see that ***oxidizing strength increases moving down the left column.*** The Li^+ ion, at the top of that column, is a very weak oxidizing agent with a large negative reduction voltage ($E^\circ_{\text{red}} = -3.040$ V). In practice, cations of the Group 1 metals (Li^+, Na^+, K^+, . . .) and the Group 2 metals (Mg^{2+}, Ca^{2+}, . . .) never act as oxidizing agents in water solution.

Further down the left column of Table 17.1, the H^+ ion ($E^\circ_{\text{red}} = 0.000$ V) is a reasonably strong oxidizing agent. It is capable of oxidizing many metals, including magnesium and zinc:

$$Mg(s) + 2H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2(g) \qquad E^\circ = +2.357 \text{ V}$$
$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g) \qquad E^\circ = +0.762 \text{ V}$$

The strongest oxidizing agents are those at the bottom of the left column. Species such as $Cr_2O_7^{2-}$ ($E^\circ_{\text{red}} = +1.33$ V) and Cl_2 ($E^\circ_{\text{red}} = +1.360$ V) are commonly used as oxidizing agents in the laboratory. The fluorine molecule, at the bottom of the left column, should be the strongest of all oxidizing agents. In practice, fluorine is seldom used as an oxidizing agent in water solution. The F_2

Table 17.1 Standard Potentials in Water Solution at 25°C

Acidic Solution, $[H^+] = 1\ M$

		$E°_{red}$ (V)
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.040
$K^+(aq) + e^-$	$\longrightarrow K(s)$	−2.936
$Ba^{2+}(aq) + 2e^-$	$\longrightarrow Ba(s)$	−2.906
$Ca^{2+}(aq) + 2e^-$	$\longrightarrow Ca(s)$	−2.869
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.714
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.357
$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.68
$Mn^{2+}(aq) + 2e^-$	$\longrightarrow Mn(s)$	−1.182
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.762
$Cr^{3+}(aq) + 3e^-$	$\longrightarrow Cr(s)$	−0.744
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.409
$Cr^{3+}(aq) + e^-$	$\longrightarrow Cr^{2+}(aq)$	−0.408
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.402
$PbSO_4(s) + 2e^-$	$\longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.356
$Tl^+(aq) + e^-$	$\longrightarrow Tl(s)$	−0.336
$Co^{2+}(aq) + 2e^-$	$\longrightarrow Co(s)$	−0.282
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.236
$AgI(s) + e^-$	$\longrightarrow Ag(s) + I^-(aq)$	−0.152
$Sn^{2+}(aq) + 2e^-$	$\longrightarrow Sn(s)$	−0.141
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.127
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0.000
$AgBr(s) + e^-$	$\longrightarrow Ag(s) + Br^-(aq)$	0.073
$S(s) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2S(aq)$	0.144
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.154
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	$\longrightarrow SO_2(g) + 2H_2O$	0.155
$Cu^{2+}(aq) + e^-$	$\longrightarrow Cu^+(aq)$	0.161
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.339
$Cu^+(aq) + e^-$	$\longrightarrow Cu(s)$	0.518
$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.534
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.769
$Hg_2^{2+}(aq) + 2e^-$	$\longrightarrow 2Hg(l)$	0.796
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.799
$2Hg^{2+}(aq) + 2e^-$	$\longrightarrow Hg_2^{2+}(aq)$	0.908
$NO_3^-(aq) + 4H^+(aq) + 3e^-$	$\longrightarrow NO(g) + 2H_2O$	0.964
$AuCl_4^-(aq) + 3e^-$	$\longrightarrow Au(s) + 4Cl^-(aq)$	1.001
$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.077
$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O$	1.229
$MnO_2(s) + 4H^+(aq) + 2e^-$	$\longrightarrow Mn^{2+}(aq) + 2H_2O$	1.229
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O$	1.33
$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.360
$ClO_3^-(aq) + 6H^+(aq) + 5e^-$	$\longrightarrow \frac{1}{2}Cl_2(g) + 3H_2O$	1.458
$Au^{3+}(aq) + 3e^-$	$\longrightarrow Au(s)$	1.498
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O$	1.512
$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	$\longrightarrow PbSO_4(s) + 2H_2O$	1.687
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O$	1.763
$Co^{3+}(aq) + e^-$	$\longrightarrow Co^{2+}(aq)$	1.953
$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	2.889

Increasing strength of oxidizing agents ↓

Increasing strength of reducing agents ↑

Basic Solution, $[OH^-] = 1\ M$

		$E°_{red}$ (V)
$Fe(OH)_2(s) + 2e^-$	$\longrightarrow Fe(s) + 2OH^-(aq)$	−0.891
$2H_2O + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.828
$Fe(OH)_3(s) + e^-$	$\longrightarrow Fe(OH)_2(s) + OH^-(aq)$	−0.547
$S(s) + 2e^-$	$\longrightarrow S^{2-}(aq)$	−0.445
$NO_3^-(aq) + 2H_2O + 3e^-$	$\longrightarrow NO(g) + 4OH^-(aq)$	−0.140
$NO_3^-(aq) + H_2O + 2e^-$	$\longrightarrow NO_2^-(aq) + 2OH^-(aq)$	0.004
$ClO_4^-(aq) + H_2O + 2e^-$	$\longrightarrow ClO_3^-(aq) + 2OH^-(aq)$	0.398
$O_2(g) + 2H_2O + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.401
$ClO_3^-(aq) + 3H_2O + 6e^-$	$\longrightarrow Cl^-(aq) + 6OH^-(aq)$	0.614
$ClO^-(aq) + H_2O + 2e^-$	$\longrightarrow Cl^-(aq) + 2OH^-(aq)$	0.890

Lithium is the strongest reducing agent.

Lithium and fluorine are very dangerous materials to work with.

O = strongest oxidizing agent; R = strongest reducing agent.

Lithium and fluorine are very dangerous materials to work with.

Fluorine is the strongest oxidizing agent.

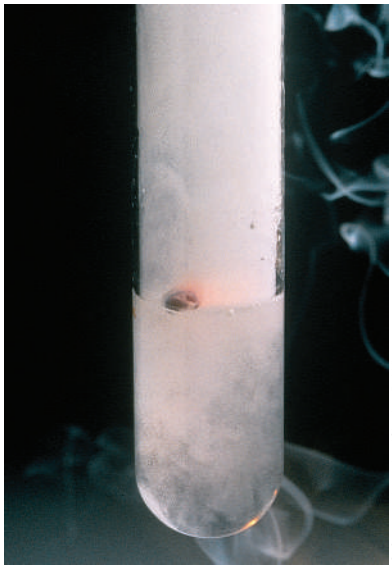

Figure 17.6 Lithium as a reducing agent. Lithium, the strongest reducing agent listed in Table 17.1, is shown reacting with water. The heat of reaction is igniting the hydrogen produced.

molecule takes electrons away from just about anything, including water, often with explosive violence.

The arguments we have just gone through can be applied, in reverse, to ***reducing agents, which are in the column to the right of Table 17.1*** (Li, . . . , F^-). In principle, at least, all of them can supply electrons to another species in a redox reaction. Their strength as reducing agents is directly related to their E°_{ox} values. ***The more positive E°_{ox} is, the stronger the reducing agent.*** Looking at the values, and remembering that $E^\circ_{ox} = -E^\circ_{red}$,

$$\begin{aligned} Li(s) &\longrightarrow Li^+(aq) + e^- & E^\circ_{ox} &= +3.040\ V \\ H_2(g) &\longrightarrow 2H^+(aq) + 2e^- & E^\circ_{ox} &= \ \ 0.000\ V \\ 2F^-(aq) &\longrightarrow F_2(g) + 2e^- & E^\circ_{ox} &= -2.889\ V \end{aligned}$$

It should be clear that ***reducing strength decreases moving down the table.*** Actually, the five metals at the top of the right column (Li, K, Ba, Ca, Na) cannot be used as reducing agents in water solution because they react directly with water, reducing it to hydrogen gas (Figure 17.6):

$$Li(s) + H_2O \longrightarrow Li^+(aq) + OH^-(aq) + \tfrac{1}{2}H_2(g)$$
$$Ba(s) + 2H_2O \longrightarrow Ba^{2+}(aq) + 2OH^-(aq) + H_2(g)$$

EXAMPLE 17.4 CONCEPTUAL

Consider the following species in acidic solution: MnO_4^-, I^-, NO_3^-, H_2S, and Fe^{2+}.

a Using Table 17.1, classify each of these as an oxidizing and/or reducing agent.

STRATEGY

Recall that the oxidizing agents are located in the left column of Table 17.1 and the reducing agents are in the right column of the same table.

SOLUTION

MnO_4^-	found in the left column, oxidizing agent
I^-	found in the right column, reducing agent
NO_3^-	found in the left column, oxidizing agent
H_2S	found in the right column, reducing agent
Fe^{2+}	found in both the left column and right column, oxidizing and reducing agent

b Arrange the oxidizing agents and the reducing agents in order of increasing strength.

STRATEGY AND SOLUTION

Going *down* the left column, the oxidizing agents increase in strength.

$Fe^{2+} < NO_3^- < MnO_4^-$

Going *up* the right column, the reducing agents increase in strength.

$Fe^{2+} < I^- < H_2S$

Calculation of E° from E°_{red} and E°_{ox}

As pointed out earlier, the standard voltage for a redox reaction is the sum of the standard voltages of the two half-reactions, reduction and oxidation; that is,

$$E^\circ = E^\circ_{red} + E^\circ_{ox}$$

This simple relation makes it possible, using Table 17.1, to calculate the standard voltages for more than 3000 different redox reactions.

EXAMPLE 17.5 GRADED

Consider the voltaic cell in which the reaction is

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

a Use Table 17.1 to calculate $E°$ for the voltaic cell.

STRATEGY

1. Assign oxidation numbers to each element so you can decide which element is reduced and which one is oxidized.
2. Write the oxidation and reduction half-reactions together with the corresponding $E°_{ox}$ and $E°_{red}$. Recall that $E°_{ox} = -(E°_{red})$.
3. Add both half-reactions (make sure you cancel electrons) and take the sum of $E°_{ox}$ and $E°_{red}$ to obtain $E°$ for the cell.

SOLUTION

1. Oxidation numbers

   Ag: $+1 \longrightarrow 0$ (reduction)

   Cd: $0 \longrightarrow +2$ (oxidation)

2. Half-reactions

   $2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s)$ $\quad E°_{red} = +0.799$ V

   $Cd(s) \longrightarrow Cd^{2+}(aq) + 2e^-$ $\quad E°_{ox} = -(E°_{red}) = -(-0.402\text{ V}) = +0.402$ V

3. $E°$

   $Cd(s) + 2Ag^+(aq) \longrightarrow Cd^{2+}(aq) + 2Ag(s)$ $\quad E° = 0.799\text{ V} + 0.402\text{ V} = 1.201$ V

b If the value zero is arbitrarily assigned to the standard voltage for the reduction of Ag^+ ions to Ag, what is $E°_{red}$ for the reduction of Cd^{2+} ions to Cd?

STRATEGY AND SOLUTION

$E°$ for the cell does not change. It does not matter what you choose to be $E°_{red}$ of the half-reaction. Naturally, $E°_{ox}$ will also change and you cannot choose to change that.

If you choose $E°_{red}$ to be zero, then

$$E°_{red} + E°_{ox} = 1.201\text{ V}$$

$0 + E°_{ox} = 1.201$ V; $E°_{ox}$ for the half-reaction $Cd(s) \longrightarrow Cd^{2+}(aq) + 2e^- = 1.201$ V

Since $E°_{red}$ for Cd^{2+} is asked for, then $E°_{red} = -(E°_{ox}) = -1.201$ V

Example 17.5 illustrates two general points concerning cell voltages.

1. The calculated voltage, $E°$, is always a positive quantity for a reaction taking place in a voltaic cell.
2. The quantities $E°$, $E°_{ox}$, and $E°_{red}$ are independent of how the equation for the cell reaction is written. You *never* multiply the voltage by the coefficients of the balanced equation.

It would be nice if you could double the voltage by rewriting the equation, but you can't.

Spontaneity of Redox Reactions

To determine whether a given redox reaction is spontaneous, apply a simple principle:

If the calculated voltage for a redox reaction is a positive quantity, the reaction will be spontaneous. If the calculated voltage is negative, the reaction is not spontaneous.

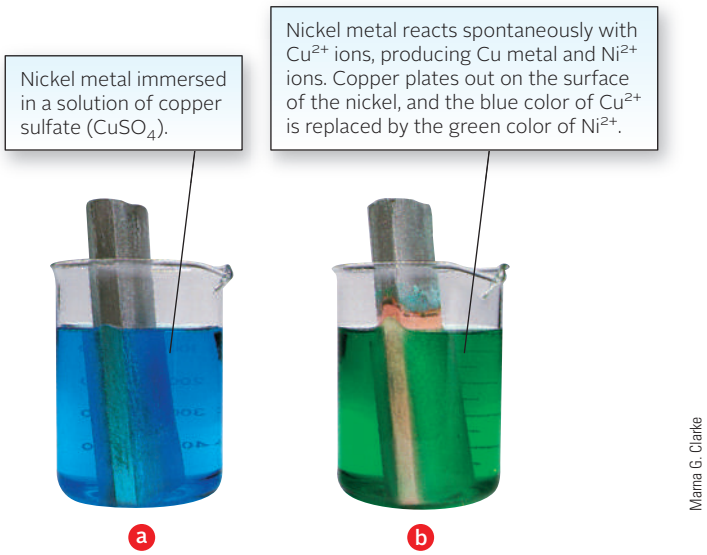

Figure 17.7 Oxidation of Ni by Cu^{2+}.

Ordinarily, this principle is applied at standard concentrations (1 atm for gases, 1 *M* for species in aqueous solution). Hence it is the sign of $E°$ that serves as the criterion for spontaneity. To show how this works, consider the problem of oxidizing nickel metal to Ni^{2+} ions. This cannot be accomplished by using 1 *M* Zn^{2+} ions:

$$Ni(s) + Zn^{2+}(aq, 1\ M) \longrightarrow Ni^{2+}(aq, 1\ M) + Zn(s)$$

$$E° = E°_{ox}\ Ni + E°_{red}\ Zn^{2+} = +0.236\ V - 0.762\ V = -0.526\ V$$

Since you add to obtain $E°$, it makes no difference which you write first, $E°_{red}$ or $E°_{ox}$.

Sure enough, if you immerse a bar of nickel in a solution of 1 *M* $ZnSO_4$, nothing happens. Suppose, however, you add the nickel bar to a solution of 1 *M* $CuSO_4$ (Figure 17.7; left beaker). As time passes, the nickel is oxidized and the Cu^{2+} ions reduced (Figure 17.7; right beaker) through the spontaneous redox reaction

$$Ni(s) + Cu^{2+}(aq, 1\ M) \longrightarrow Ni^{2+}(aq, 1\ M) + Cu(s)$$

$$E° = E°_{ox}\ Ni + E°_{red}\ Cu^{2+} = +0.236\ V + 0.339\ V = +0.575\ V$$

EXAMPLE 17.6

Consider Fe^{2+} at standard conditions.

a Will the reaction below occur?

$$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(s)$$

ANALYSIS

Information given:	equation for the reaction ($2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(s)$)
Information implied:	Table 17.1 (standard reduction potentials)
Asked for:	Will the reaction occur?

continued

STRATEGY

1. Assign oxidation numbers.
2. Write oxidation and reduction half-reactions. Include E°_{ox} and E°_{red}.
3. Find E°. The reaction will occur if $E^\circ > 0$.

SOLUTION

1. oxidation numbers	Fe: $+3 \longrightarrow +2$ reduction I: $-1 \longrightarrow 0$ oxidation
2. half-reactions	$2Fe^{3+}(aq) + 2e^- \longrightarrow 2Fe^{2+}(aq)$ $\quad E^\circ_{red} = +0.769$ V $2I^-(aq) \longrightarrow I_2(s) + 2e^-$ $\quad E^\circ_{ox} = -0.534$ V
3. E°	$E^\circ = 0.769\text{ V} + (-0.534\text{ V}) = +0.235$ V $E^\circ > 0$, the reaction will occur at standard conditions.

b Can Fe(s) be oxidized to Fe^{2+} by treatment with hydrochloric acid?

ANALYSIS

Information given:	oxidation half-reaction ($Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$)
Information implied:	Table 17.1 (standard reduction potentials)
Asked for:	Will HCl oxidize Fe?

STRATEGY

1. $HCl(aq)$ is made up of two ions, H^+ and Cl^-. Since an oxidizing agent is needed (to oxidize Fe to Fe^{2+}), find either H^+ or Cl^- (or both) in the left column of Table 17.1.
2. Write the possible half-reactions.
3. Write the redox reaction and find E°.

SOLUTION

1. Oxidizing agent	Only H^+ appears in the left column.
2. Half-reactions	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$ $\quad E^\circ_{red} = 0.000$ V $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$ $\quad E^\circ_{ox} = 0.409$ V
3. Redox reaction	$Fe(s) + 2H^+(aq) \longrightarrow Fe^{2+}(aq) + H_2(g)$ $\quad E^\circ = 0.409$ V $E^\circ > 0$, HCl will oxidize Fe at standard conditions (Figure 17.8).

c What redox reactions occur when the following species are mixed in acidic solution: Cl^-, Fe^{2+}, Cr^{2+}, I_2?

ANALYSIS

Information given:	ions in acidic solution (Cl^-, Fe^{2+}, Cr^{2+}, I_2)
Information implied:	Table 17.1
Asked for:	Will a redox reaction occur when the ions are mixed?

STRATEGY

1. Check the left column of Table 17.1 to determine which of the ions are oxidizing agents (i.e., they are reduced). Write the reduction half-reactions of the oxidizing agents.
2. Check the right column of Table 17.1 to determine which of the ions are reducing agents (i.e., they are oxidized). Write the reduction half-reactions of the reducing agents.
3. Write all possible combinations of oxidation and reduction half-reactions. The combination(s) that give positive E° values are possible.
4. Write the redox equation(s) for the reaction(s) that occur.

continued

SOLUTION		
1. Oxidizing agents	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$ $I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	$E^\circ_{red} = -0.409$ V $E^\circ_{red} = +0.534$ V
2. Reducing agents	$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$ $Cr^{2+}(aq) \longrightarrow Cr^{3+}(aq) + e^-$ $Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$	$E^\circ_{ox} = -1.360$ V $E^\circ_{ox} = +0.408$ V $E^\circ_{ox} = -0.769$ V
3. Possible combinations	$Fe^{2+} + Cl^-$: $E^\circ < 0$ $Fe^{2+} + Cr^{2+}$: $E^\circ < 0$ $Fe^{2+} + Fe^{2+}$: $E^\circ < 0$	$I_2 + Cl^-$: $E^\circ < 0$ $I_2 + Cr^{2+}$: $E^\circ > 0$ ✔ $I_2 + Fe^{2+}$: $E^\circ < 0$
4. Redox reaction	$I_2(s) + 2Cr^{2+}(aq) \longrightarrow 2I^-(aq) + 2Cr^{3+}(aq)$	$E^\circ = 0.942$ V

Figure 17.8 Oxidation of Fe by H^+. Finely divided iron in the form of steel wool reacts with hydrochloric acid to evolve hydrogen: $Fe(s) + 2H^+(aq) \longrightarrow Fe^{2+}(aq) + H_2(g)$. The hydrogen gas is creating foam as it is produced along the strands of the steel wool.

$F = 9.648 \times 10^4$ C/mol
$= 9.648 \times 10^4$ J/mol·V

17-4 Relations Between $E°$, $\Delta G°$, and K

As pointed out previously, the value of the standard cell voltage, $E°$, is a measure of the spontaneity of a cell reaction. In Chapter 16, we showed that the standard free energy change, $\Delta G°$, is a general criterion for reaction spontaneity. As you might suppose, these two quantities have a simple relation to one another and to the equilibrium constant, K, for the cell reaction.

$E°$ and $\Delta G°$

It can be shown by a thermodynamic argument that we will not go through here that these two quantities are related by the equation

$$\Delta G° = -nFE° \qquad (17.2)$$

where

- $\Delta G°$ is the standard free energy change (gases at 1 atm, species in solution at 1 M) for the reaction.
- $E°$ is the standard voltage for the cell reaction.
- n is the number of moles of electrons transferred in the reaction.
- F, called the **Faraday constant,** has the following value: 9.648×10^4 J/mol·V (J = joule, V = volt).

Notice from this equation that $\Delta G°$ and $E°$ have opposite signs. This is reasonable; a spontaneous reaction is one for which $\Delta G°$ is *negative* but $E°$ is *positive*.

$E°$ and K

Redox reactions, like all reactions, eventually reach a state of equilibrium. It is possible to calculate the equilibrium constant for a redox reaction from the standard voltage. To do that, we start with the relation obtained in Chapter 16:

$$\Delta G° = -RT \ln K$$

We have just seen that $\Delta G° = -nFE°$. It follows that

$$RT \ln K = nFE°$$

that is,

$$E° = \frac{RT}{nF} \ln K$$

The quantity RT/F is readily evaluated at 25°C, the temperature at which standard potentials are tabulated.

$$\frac{RT}{F} = \frac{8.31 \text{ J/mol} \cdot \text{K} \times 298 \text{ K}}{9.648 \times 10^4 \text{ J/mol} \cdot \text{V}} = 0.0257 \text{ V}$$

Hence

$$E° = \frac{(0.0257 \text{ V})}{n} \ln K \qquad \text{(at 25°C)} \qquad (17.3)$$

Notice that if the standard voltage is positive, ln K is also positive, and K is greater than 1. Conversely, if the standard voltage is negative, ln K is also negative, and K is less than 1.

Spontaneous reaction: $E° > 0$, $\Delta G° < 0$, $K > 1$.

EXAMPLE 17.7

Consider the following reaction at 25°C:

$$3Ag(s) + NO_3^-(aq) + 4H^+(aq) \longrightarrow 3Ag^+(aq) + NO(g) + 2H_2O$$

a Find $\Delta G°$.

ANALYSIS

Information given:	reaction: $(3Ag(s) + NO_3^-(aq) + 4H^+(aq) \longrightarrow 3Ag^+(aq) + NO(g) + 2H_2O)$ temperature (25°C)
Information implied:	Table 17.1 (standard reduction potentials) Faraday constant (F)
Asked for:	$\Delta G°$

STRATEGY

1. Assign oxidation numbers.
2. Split the redox reaction into oxidation and reduction half-reactions and find $E°$.
3. Determine the number of electrons cancelled out when balancing the equation to find n.
4. Substitute into Equation 17.2. Note that $\Delta G°$ will be in joules since the Faraday constant is in joules.

SOLUTION

1. oxidation numbers

N: $+5 \longrightarrow +2$ reduction

Ag: $0 \longrightarrow +1$ oxidation

2. half-reactions

$$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O \qquad E°_{red} = 0.964 \text{ V}$$
$$Ag(s) + e^- \longrightarrow Ag^+(aq) \qquad E°_{ox} = -0.799 \text{ V}$$
$$E° = 0.964 \text{ V} + (-0.799 \text{ V}) = 0.165 \text{ V}$$

3. n

Multiply the oxidation half-reaction by 3 to cancel out the three electrons in the reduction half-reaction.

Three electrons cancel out: $n = 3$

4. $\Delta G°$

$$\Delta G° = -nFE = (-3 \text{ mol})(9.648 \times 10^4 \frac{\text{J}}{\text{mol} \cdot \text{V}})(0.165 \text{ V}) = -4.78 \times 10^4 \text{ J}$$
$$= -47.8 \text{ kJ}$$

b Find K.

ANALYSIS

Information given:	From part (a): $E°$ (0.165 V); n (3 mol)
Asked for:	K

continued

STRATEGY	
Substitute into Equation 17.3.	
SOLUTION	
K	$E° = \frac{0.0257\ \text{V}}{n} \ln K;\ 0.165\ \text{V} = \frac{0.0257\ \text{V}}{3} \ln K;\ \ln K = 19.3$ $K = e^{19.3} = 2.4 \times 10^8$

Table 17.2 Relation Between $E°$, K, and $\Delta G°$ ($n = 2$)

$E°$ (V)	K	$\Delta G°$ (kJ)	$E°$ (V)	K	$\Delta G°$ (kJ)
+2.00	4×10^{67}	−400	−2.00	3×10^{-68}	+400
+1.00	6×10^{33}	−200	−1.00	2×10^{-34}	+200
+0.50	8×10^{16}	−100	−0.50	1×10^{-17}	+100
+0.25	3×10^{8}	−50	−0.25	4×10^{-9}	+50
+0.10	2×10^{3}	−20	−0.10	0.0004	+20
+0.05	50	−10	−0.05	0.02	+10
0.00	1	0			

The approach used in Example 17.7 to find the number of moles of electrons transferred, n, is generally useful. What you do is to break down the equation for the cell reaction into two half-equations, oxidation and reduction. The quantity n is the number of electrons appearing in either half-equation.

Table 17.2 lists values of K and $\Delta G°$ corresponding to various values of $E°$ with $n = 2$. Notice that:

- if $E°$ is greater than about +0.10 V, K is very large, and the reaction goes virtually to completion.
- if $E°$ is smaller than about −0.10 V, K is very small, so the reaction does not proceed to any appreciable extent.

Most redox reactions either go to completion or not at all.

Only if the standard voltage falls within a rather narrow range, say +0.10 to −0.10 V, will the value of K (and that of $\Delta G°$) be such that the reaction will produce an equilibrium mixture containing appreciable amounts of both reactants and products.

17-5 Effect of Concentration on Voltage

To this point, we have dealt only with "standard" voltages, that is, voltages when all gases are at 1 atm pressure and all species in aqueous solution are at a concentration of 1 *M*. When the concentration of a reactant or product changes, the voltage changes as well. Qualitatively, the direction in which the voltage shifts is readily predicted when you realize that cell voltage is directly related to reaction spontaneity.

1. Voltage will *increase* if the concentration of a reactant is increased or that of a product is decreased. Either of these changes increases the driving force behind the redox reaction, making it more spontaneous.
2. Voltage will *decrease* if the concentration of a reactant is decreased or that of a product is increased. Either of these changes makes the redox reaction less spontaneous.

When a voltaic cell operates, supplying electrical energy, the concentration of reactants decreases and that of the products increases. As time passes, the voltage drops steadily. Eventually it becomes zero, and we say that the cell is "dead." At that point, the redox reaction taking place within the cell is at equilibrium, and there is no driving force to produce a voltage.

That's what happens when you leave your car lights on, unless your car turns them off automatically.

Nernst Equation

To obtain a quantitative relation between cell voltage and concentration, it is convenient to start with the general expression for the free energy change discussed in Chapter 16:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where Q is the reaction quotient in which products appear in the numerator, reactants in the denominator. But $\Delta G^\circ = -nFE^\circ$ and $\Delta G = -nFE$, so we have

$$-nFE = -nFE^\circ + RT \ln Q$$

Solving for the cell voltage E,

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

This relationship is known as the **Nernst equation**, after Walther Nernst (1864–1941), a brilliant and egocentric colleague of Arrhenius, who first proposed it in 1888. Recalling that, at 25°C, the quantity RT/F is 0.0257 V,

Nernst won the Nobel Prize in Chemistry in 1920.

$$E = E^\circ - \frac{(0.0257\ \text{V})}{n} \ln Q \qquad \text{at } 25^\circ\text{C} \qquad (17.4)$$

In this equation, E is the cell voltage, E° is the standard voltage, n is the number of moles of electrons exchanged in the reaction, and Q is the reaction quotient. Notice that:

- if $Q > 1$, which means that the concentrations of products are high relative to those of reactants, ln Q is positive and $E < E^\circ$.
- if $Q < 1$ (concentrations of products low relative to reactants), ln Q is negative and $E > E^\circ$.
- if $Q = 1$, as is the case under standard conditions, ln $Q = 0$ and $E = E^\circ$.

Remember that gases enter Q as their partial pressures in atmospheres. Species in water solution enter as their molar concentrations. Pure liquids and solids do not appear in the expression for Q. For example,

$$a\text{A}(s) + b\text{B}(aq) \longrightarrow c\text{C}(aq) + d\text{D}(g) \qquad Q = \frac{[\text{C}]^c(\text{P}_\text{D})^d}{[\text{B}]^b}$$

EXAMPLE 17.8 GRADED

Consider a voltaic cell in which the following reaction occurs:

$$O_2(g, 0.98\ \text{atm}) + 4H^+(aq, \text{pH} = 1.24) + 4Br^-(aq, 0.15\ M) \longrightarrow 2H_2O + 2Br_2(l)$$

a Calculate E for the cell at 25°C.

ANALYSIS

Information given:	reaction: $(O_2(g) + 4H^+(aq) + 4Br^-(aq) \longrightarrow 2Br_2(l) + 2H_2O)$ P_{O_2} (0.98 atm); $[H^+]$ (pH = 1.24); $[Br^-]$ (0.15 M) temperature (25°C)
Information implied:	Table 17.1 (standard reduction potentials)
Asked for:	E

continued

STRATEGY

1. Change pH to $[H^+]$ and find Q.
2. Assign oxidation numbers, write oxidation and reduction half-reactions, and cancel electrons to find n.
3. Find $E°$. $(E°_{red} + E°_{ox})$
4. Substitute into the Nernst equation (Equation 17.4) for $T = 25°C$

$$E = E° - \frac{0.0257}{n} \ln Q$$

SOLUTION

1. $[H^+]$	$1.24 = -\log_{10}[H^+]$; $[H^+] = 0.058\ M$
Q	$Q = \dfrac{1}{(P_{O_2})[H^+]^4[Br^-]^4} = \dfrac{1}{(0.98)(0.058)^4(0.15)^4} = 1.8 \times 10^8$
2. Oxidation numbers	O: $0 \longrightarrow -2$ (reduction); Br: $-1 \longrightarrow 0$ (oxidation)
Half-reactions	$O_2(g) + 4H^+(aq) + 4e^-(aq) \longrightarrow 2H_2O$ $2Br^-(aq) \longrightarrow Br_2(l) + 2e^-$
n	The oxidation half-reaction must be multiplied by 2 to cancel out the four electrons in the reduction half-reaction. $n = 4$
3. $E°$	$E°_{red}$ for $O_2 = 1.229$ V; $E°_{ox}$ for $Br^- = -1.077$ V $E° = 1.229\ V + (-1.077\ V) = 0.152\ V$
4. E	$E = 0.152\ V - \dfrac{0.0257}{4} \ln (1.8 \times 10^8) =$ **0.030 V**

b When the voltaic cell is at 35°C, E is measured to be 0.039 V. What is $E°$ at 35°C?

ANALYSIS

Information given:	E (0.039 V) at T (35°C) From part (a): Q (1.8×10^8); n (4 moles)
Information implied:	R and F values in joules
Asked for:	$E°$ at 35°C

STRATEGY

Substitute into the Nernst equation.

$$E = E° - \frac{RT}{nF} \ln Q$$

SOLUTION

$E°$	$0.039\ V = E° - \dfrac{(8.31\ J/mol \cdot K)(308\ K)}{4\ (9.648 \times 10^4\ J/mol \cdot V)} \ln (1.8 \times 10^8)$ $E° = 0.039\ V + 0.126\ V =$ **0.165 V**

The Nernst equation can also be used to determine the effect of changes in concentration on the voltage of an individual half-cell, $E°_{red}$ or $E°_{ox}$. Consider, for example, the half-reaction

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O \qquad E°_{red} = +1.512\ V$$

The Nernst equation takes the form

$$E_{red} = +1.512\ V - \frac{(0.0257\ V)}{5} \ln \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

where E_{red} is the observed reduction voltage corresponding to any given concentrations of Mn^{2+}, MnO_4^-, and H^+.

Use of the Nernst Equation to Determine Ion Concentrations

In chemistry, the most important use of the Nernst equation lies in the experimental determination of the concentrations of ions in solution. Suppose you measure the cell voltage E and know the concentration of all but one species in the two half-cells. It should then be possible to calculate the concentrations of that species by using the Nernst equation (Example 17.9).

EXAMPLE 17.9

Consider a voltaic cell at 25°C in which the reaction is

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

It is found that the voltage is +0.560 V when $[Zn^{2+}] = 0.85\ M$ and $P_{H_2} = 0.988$ atm. What is the pH in the H_2-H half-cell?

ANALYSIS

Information given:	reaction: $(Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g))$ E (0.560 V); T (25°C) P_{H_2} (0.988 atm); $[Zn^{2+}](0.85\ M)$ temperature (25°C)
Information implied:	Table 17.1 (standard reduction potentials)
Asked for:	pH

STRATEGY

1. Assign oxidation numbers, write oxidation and reduction half-reactions, and cancel electrons to find n.
2. Find $E°$. $(E°_{red} + E°_{ox})$
3. Substitute into the Nernst equation (Equation 17.4) for $T = 25$°C and find Q.
4. Write the Q expression and substitute given concentrations and pressures to find $[H^+]$. Change $[H^+]$ to pH.

SOLUTION

1. Oxidation numbers	Zn: $0 \longrightarrow +2$ oxidation; H^+: $+1 \longrightarrow 0$ reduction
Half-reactions	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$ $\quad$ $Zn(s) \longrightarrow 2e^- + Zn^{2+}(aq)$
n	2 electrons cancel out so $n = 2$.
2. $E°$	$E° = E°_{ox}\ Zn + E°_{red}\ H^+ = 0.762\ V + 0\ V = 0.762\ V$
3. Q	$E = E° - \frac{0.0257}{n} \ln Q$; $0.560\ V = 0.762\ V - \frac{0.0257}{2} \ln Q$
	$\frac{0.0257}{2} \ln Q = 0.762\ V - 0.560\ V$; $\ln Q = 15.7$; $Q = 6.7 \times 10^6$
4. $[H^+]$	$Q = \frac{[Zn^{2+}](P_{H_2})}{[H^+]^2}$; $[H^+] = \left[\frac{(0.85)(0.988)}{6.7 \times 10^6}\right]^{\frac{1}{2}} = 3.5 \times 10^{-4}$
pH	$pH = -\log_{10}(3.5 \times 10^{-4}) = 3.45$

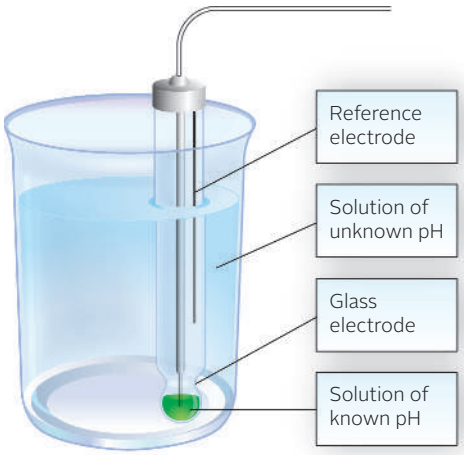

Figure 17.9 Electrode for a pH meter. The pH of a solution can be determined with the aid of a "glass electrode." The voltage between the glass electrode and the reference electrode is directly related to pH. The leads from the electrodes are connected to a pH meter.

As Example 17.9 implies, the $Zn|Zn^{2+}\|H^+|H_2|Pt$ cell can be used to measure the concentration of H^+ or pH of a solution. Indeed, cells of this type are commonly used to measure pH; Figure 17.9 shows a schematic diagram of a cell used with a pH meter. The pH meter, referred to in Chapter 13, is actually a high-resistance voltmeter calibrated to read pH rather than voltage. The cell connected to the pH meter consists of two half-cells. One of these is a reference half-cell of known voltage. The other half-cell contains a solution of known pH separated by a thin, fragile *glass electrode* from a solution whose pH is to be determined. The voltage of this cell is a function of the pH of the solution in the beaker.

Specific ion electrodes, similar in design to the glass electrode, have been developed to analyze for a variety of cations and anions. One of the first to be used extensively was a fluoride ion electrode that is sensitive to F^- at concentrations as low as 0.1 part per million and hence is ideal for monitoring fluoridated water supplies. An electrode that is specific for Cl^- ions is used to diagnose cystic fibrosis. Attached directly to the skin, it detects the abnormally high concentrations of sodium chloride in sweat that are a characteristic symptom of this disorder. Diagnoses that used to require an hour or more can now be carried out in a few minutes; as a result, large numbers of children can be screened rapidly and routinely.

The general approach illustrated by Example 17.9 is widely used to determine equilibrium constants for solution reactions. The pH meter in particular can be used to determine acid or base equilibrium constants by measuring the pH of solutions containing known concentrations of weak acids or bases. Specific ion electrodes are readily adapted to the determination of solubility product constants. For example, a chloride ion electrode can be used to find $[Cl^-]$ in equilibrium with $AgCl(s)$ and a known $[Ag^+]$. From that information, K_{sp} of AgCl can be calculated.

17-6 Electrolytic Cells

In an **electrolytic cell,** a nonspontaneous redox reaction is made to occur by pumping electrical energy into the system. A general diagram for such a cell is shown in Figure 17.10. The storage battery at the left provides a source of direct electric current. From the terminals of the battery, two wires lead to the electrolytic cell. This consists of two electrodes, A and C, dipping into a solution containing ions M^+ and X^-.

The battery acts as an electron pump, pushing electrons into the *cathode,* C, and removing them from the *anode,* A. ◂ To maintain electrical neutrality, some process within the cell must consume electrons at C and liberate them at A. This process is an oxidation-reduction reaction; when carried out in an electrolytic cell, it is called **electrolysis.** At the cathode, an ion or molecule undergoes reduction by accepting electrons. At the anode, electrons are produced by the oxidation of an ion or molecule.

Oxidation occurs at the anode, reduction at the cathode, in both voltaic and electrolytic cells.

Quantitative Relationships

There is a simple relationship between the amount of electricity passed through an electrolytic cell and the amounts of substances produced by oxidation or reduction at the electrodes. From the balanced half-equations

$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$
$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$
$$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$$

you can deduce that

1 mol of e^- ⟶ 1 mol of Ag (107.9 g of Ag)
2 mol of e^- ⟶ 1 mol of Cu (63.55 g of Cu)
3 mol of e^- ⟶ 1 mol of Au (197.0 g of Au)

Relations of this type, obtained from balanced half-equations, can be used in many practical calculations involving electrolytic cells. You will also need to become familiar with certain electrical units, including those of

quantity of electrical charge. The common unit here is the **coulomb** (C). The coulomb is related to the charge carried by a mole of electrons through the Faraday constant:

$$1 \text{ mol electrons} = 9.648 \times 10^4 \text{ C}$$

rate of current flow. Here the common unit is the **ampere** (A). When a current of one ampere passes through an electrical circuit, one coulomb passes a given point in the circuit in one second. That is,

$$1 \text{ A} = 1 \text{ C/s}$$

amount of electrical energy. This can be expressed in joules, J. When a charge of one coulomb (C) moves through a potential difference of one volt (V), it acquires an energy of one joule:

$$1 \text{ J} = 1 \text{ C} \cdot \text{V}$$

Your electric bill deals with a different unit of electrical energy called the kilowatt-hour (kWh). The joule and the kilowatt-hour are related through a simple conversion factor:

$$1 \text{ kWh} = 3.600 \times 10^6 \text{ J} = 3.600 \times 10^3 \text{ kJ}$$

These relations and others appear in Table 17.3.

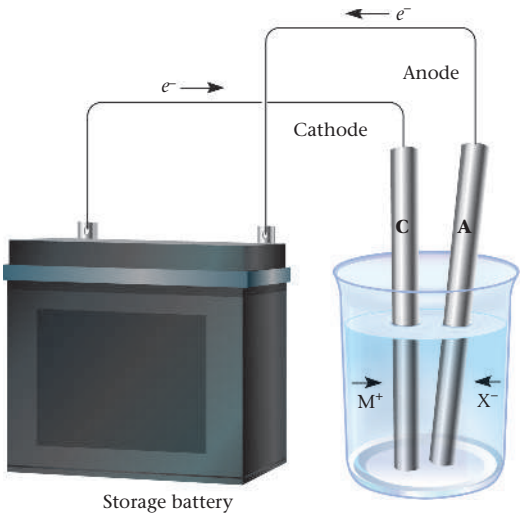

Figure 17.10 Diagram of an electrolytic cell. Electrons enter the cathode from an external source. Cations move to the cathode, where they are reduced, and anions move to the anode, where they are oxidized.

Table 17.3 Electrical Units

Quantity	Unit	Defining Relation	Conversion Factors
Charge	coulomb (C)	1 C = 1 A·s = 1 J/V	1 mol e^- = 9.648×10^4 C
Current	ampere (A)	1 A = 1 C/s	
Potential	volt (V)	1 V = 1 J/C	
Power	watt (W)	1 W = 1 J/s	
Energy	joule (J)	1 J = 1 V·C	1 kWh = 3.600×10^6 J

EXAMPLE 17.10

Chromium metal can be electroplated from an aqueous solution of potassium dichromate. The reduction half-reaction is

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 12e^- \longrightarrow 2Cr(s) + 7H_2O$$

A current of 6.00 A and a voltage of 4.5 V are used in the electroplating.

continued

a How many grams of chromium can be plated if the current is run for 48 minutes?

ANALYSIS

Information given:	reduction half-reaction: $(Cr_2O_7^{2-}(aq) + 14H^+(aq) + 12e^- \longrightarrow 2Cr(s) + 7H_2O)$ current (6.00 A); voltage (4.5 V); time in s (48 × 60)
Information implied:	1 C = 1 A · s; MM Cr
Asked for:	mass Cr plated

STRATEGY

1. Since mass is asked for, you may assume that you have all the information to convert the amount of electricity to moles of electrons. Moles of electrons provide the bridge that connects the amount of electricity to the stoichiometry of the chemical reaction. Use the following plan:

$$\text{amperes (A)} \xrightarrow{\times \text{ time (s)}} \text{coulomb (C)} \xrightarrow{1 \text{ mol } e^- = 9.648 \times 10^4 \text{ C}} \text{mol } e^-$$

2. Convert mol e^- to mass of Cr using the stoichiometry of the reaction.

$$\text{mol } e^- \xrightarrow{12 \text{ mol } e^-/2 \text{ mol Cr}} \text{mol Cr} \xrightarrow{\text{MM}} \text{mass Cr}$$

SOLUTION

1. mol e^-

$$6.00 \text{ A} = 6.00 \text{ C/s}$$

$$6.00 \frac{\text{C}}{\text{s}} \times (48 \times 60)\text{s} \times \frac{1 \text{ mol } e^-}{9.648 \times 10^4 \text{ C}} = 0.179 \text{ mol } e^-$$

2. Mass Cr

$$0.179 \text{ mol } e^- \times \frac{2 \text{ mol Cr}}{12 \text{ mol } e^-} \times \frac{52.00 \text{ g Cr}}{1 \text{ mol Cr}} = 1.55 \text{ g}$$

b How long will it take to completely convert 215 mL of 1.25 *M* $K_2Cr_2O_7$ to elemental chromium?

ANALYSIS

Information given:	reduction half-reaction: $(Cr_2O_7^{2-}(aq) + 14H^+(aq) + 12e^- \longrightarrow 2Cr(s) + 7H_2O)$ current (6.00 A); voltage (4.5 V) $K_2Cr_2O_7$: *V* (0.215 L); *M* (1.25)
Information implied:	1 C = 1 A · s
Asked for:	time

STRATEGY

1. Since *V* and *M* are given for $K_2Cr_2O_7$ (thus for $Cr_2O_7^{2-}$), you have enough information to convert to mole e^- using the stoichiometry of the reaction.

$$V \times M \longrightarrow \text{mol } Cr_2O_7^{2-} \xrightarrow{12 \text{ mol } e^-/1 \text{ mol } Cr_2O_7^{2-}} \text{mol } e^-$$

2. Convert mol e^- to coulombs.

$$\text{mol } e^- \xrightarrow{9.648 \times 10^4 \text{ C}/1 \text{ mol } e^-} \text{coulombs}$$

3. Convert coulomb to time. Recall 1 A = 1 C/s.

SOLUTION

1. mol e^-

$$(0.215 \text{ L})(1.25 \text{ mol/L})(12 \text{ mol } e^-/\text{mol } Cr_2O_7^{2-}) = 3.225 \text{ mol } e^-$$

2. C

$$3.225 \text{ mol } e^- \times \frac{9.648 \times 10^4 \text{ C}}{1 \text{ mol } e^-} = 3.11 \times 10^5 \text{ C}$$

3. Time

$$\text{time} = \frac{3.11 \times 10^5 \text{ C}}{6.00 \text{ C/s}} = 5.16 \times 10^4 \text{ s} = 14.4 \text{ h}$$

continued

C How many kilowatt-hours of electrical energy are required to plate 1.00 g of chromium?

ANALYSIS

Information given:	reduction half-reaction: $(Cr_2O_7^{2-}(aq) + 14H^+(aq) + 12e^- \longrightarrow 2Cr(s) + 7H_2O)$ current (6.00 A); voltage (4.5 V) mass Cr (1.00 g)
Information implied:	1 A = 1 C/s; 1 kWh = 3.600×10^6 J; 1 J = 1 C · V MM for Cr
Asked for:	kilowatt-hours

STRATEGY

1. Convert the mass of Cr to mol e^- using stoichiometry

$$\text{mass Cr} \xrightarrow{\text{MM}} \text{mol Cr} \xrightarrow{\text{2 mol Cr/12 mol } e^-} \text{mol } e^-$$

2. Find kWh by finding the energy in joules (C × V) and then convert to kWh (3.600×10^6 J = 1 kWh)

$$\text{mol } e^- \xrightarrow{1\text{ mol } e^- = 9.648 \times 10^4\text{ C}} \text{coulomb (C)} \xrightarrow{\text{V}} \text{C} \cdot \text{V} \longrightarrow \text{J} \longrightarrow \text{kWh}$$

SOLUTION

1. mol e^-

$$1.00\text{ g Cr} \times \frac{1\text{ mol Cr}}{52.00\text{ g}} \times \frac{12\text{ mol } e^-}{2\text{ mol Cr}} = 0.115\text{ mol } e^-$$

2. kWh

$$0.115\text{ mol } e^- \times \frac{9.468 \times 10^4\text{ C}}{1\text{ mol } e^-} \times 4.5\text{ V} \times \frac{1\text{ J}}{1\text{ C} \cdot \text{V}} \times \frac{1\text{ kWh}}{3.600 \times 10^6\text{ J}} = 0.014\text{ kWh}$$

END POINTS

1. Note that whether you are given data to determine the moles of a species in a reaction or the coulombs of electricity, you can get to moles of electrons.
2. The value given for the voltage used is irrelevant for parts (a) and (b). You only need it to find the number of kilowatt hours.

In working Example 17.11, we have in effect assumed that the electrolyses were 100% efficient in converting electrical energy into chemical energy. In practice, this is almost never the case. Some electrical energy is wasted in side reactions at the electrodes and in the form of heat. This means that the actual yield of products is less than the theoretical yield.

Nobody is 100% efficient.

Cell Reactions (Water Solution)

As is always the case, a reduction half-reaction occurs at the cathode of an electrolytic cell. This half-reaction in aqueous solution may be

- *the reduction of a cation to the corresponding metal.* This commonly occurs with transition metal cations, which are relatively easy to reduce. Examples include

$$Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad E^\circ_{red} = +0.799\text{ V}$$
$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \qquad E^\circ_{red} = +0.339\text{ V}$$

  This type of half-reaction is characteristic of electroplating processes, in which a metal object serves as the cathode (Figure 17.11).
- *the reduction of a water molecule to hydrogen gas*

$$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad E^\circ_{red} = -0.828\text{ V}$$

  This half-reaction commonly occurs when the cation in solution is very difficult to reduce. For example, electrolysis of a solution containing K^+ ions

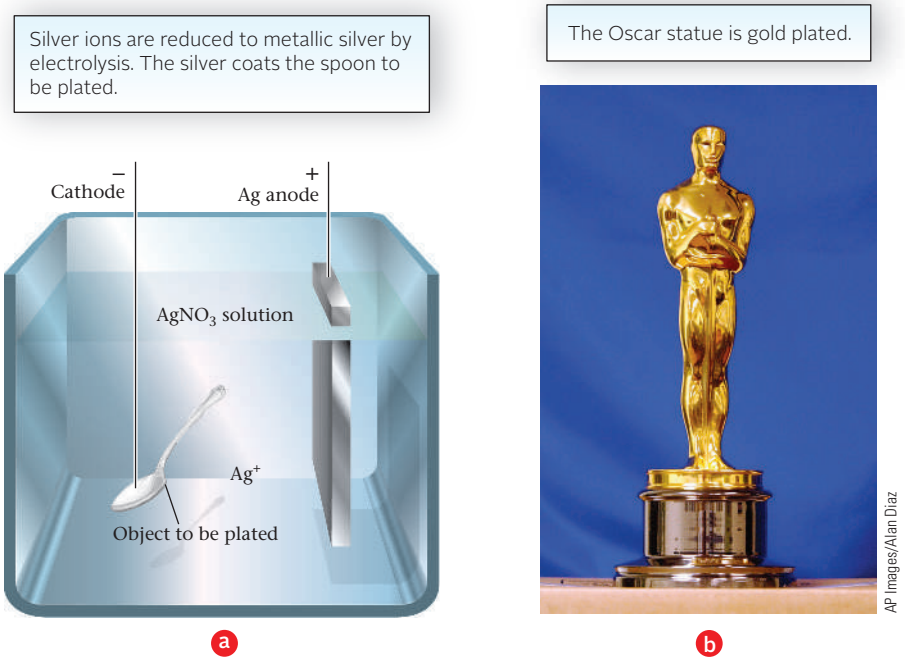

Figure 17.11 Electroplating.

Table 17.4 Electrolysis of Water Solutions

Solution	Cathode Product	Anode Product
$CuBr_2(aq)$	$Cu(s)$	$Br_2(l)$
$AgNO_3(aq)$	$Ag(s)$	$O_2(g)$
$KI(aq)$	$H_2(g)$	$I_2(s)$
$Na_2SO_4(aq)$	$H_2(g)$	$O_2(g)$

Figure 17.12 Electrolysis of potassium iodide (KI) solution. The electrolysis of aqueous KI is similar to that of aqueous NaCl. The cathode reaction *(left)* is the reduction of water to $H_2(g)$ and OH^-, as shown by the pink color of phenolphthalein indicator in the water. The anode reaction *(right)* is the oxidation of $I^-(aq)$ to $I_2(aq)$, as shown by the brown color of the solution.

($E^\circ_{red} = -2.936$ V) or Na^+ ions ($E^\circ_{red} = -2.714$ V) yields hydrogen gas at the cathode (Table 17.4).

At the anode of an electrolytic cell, the half-reaction may be

- *the oxidation of an anion to the corresponding nonmetal*

$$2I^-(aq) \longrightarrow I_2(s) + 2e^- \qquad E^\circ_{ox} = -0.534 \text{ V}$$

Electrolysis of a water solution of KI gives a saturated solution of iodine at the anode (Figure 17.12).

- *the oxidation of a water molecule to oxygen gas*

$$2H_2O \longrightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E^\circ_{ox} = -1.229 \text{ V}$$

This half-reaction occurs when the anion cannot be oxidized. Examples include nitrate and sulfate anions, where the nonmetal present is already in its highest oxidation state (+5 for N, +6 for S).

17-7 Commercial Cells

To a chemist, electrochemical cells are of interest primarily for the information they yield concerning the spontaneity of redox reactions, the strengths of oxidizing and reducing agents, and the concentrations of trace species in solution. The

viewpoint of an engineer is somewhat different; applications of electrolytic cells in electroplating and electrosynthesis are of particular importance. To the nonscientist, electrochemistry is important primarily because of commercial voltaic cells, which supply the electrical energy for instruments ranging in size from pacemakers to automobiles.

Electrolysis of Aqueous NaCl

From a commercial standpoint, the most important electrolysis carried out in water solution is that of sodium chloride (Figure 17.13). At the anode, Cl^- ions are oxidized to chlorine gas:

$$\text{anode:} \qquad 2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$$

At the cathode, the half-reaction involves H_2O molecules, which are easier to reduce ($E^\circ_{red} = -0.828$ V) than Na^+ ions ($E^\circ_{red} = -2.714$ V).

$$\text{cathode:} \qquad 2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$$

To obtain the overall cell reaction, add the half-reactions:

$$2Cl^-(aq) + 2H_2O \longrightarrow Cl_2(g) + H_2(g) + 2OH^-(aq)$$

Chlorine gas bubbles out of solution at the anode. At the cathode, hydrogen gas is formed, and the solution around the electrode becomes strongly basic.

The products of this electrolysis have a variety of uses. Chlorine is used to purify drinking water; large quantities of it are consumed in making plastics such as polyvinyl chloride (PVC). Hydrogen, prepared in this and many other industrial processes, is used chiefly in the synthesis of ammonia (Chapter 12). Sodium hydroxide (lye), obtained on evaporation of the electrolyte, is used in processing pulp and paper, in the purification of aluminum ore, in the manufacture of glass and textiles, and for many other purposes.

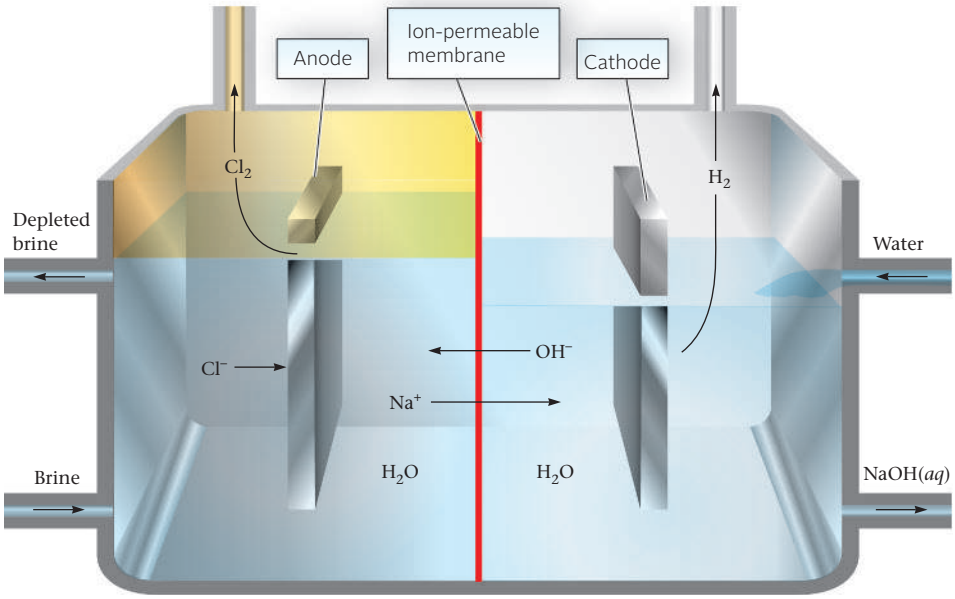

Figure 17.13 Electrolysis of aqueous NaCl (brine). The anode and cathode half-cells are separated by a membrane that is permeable to ions. Thus the flow of ions maintains charge balance. The products, NaOH(*aq*), Cl_2, and H_2, are all valuable industrial chemicals.

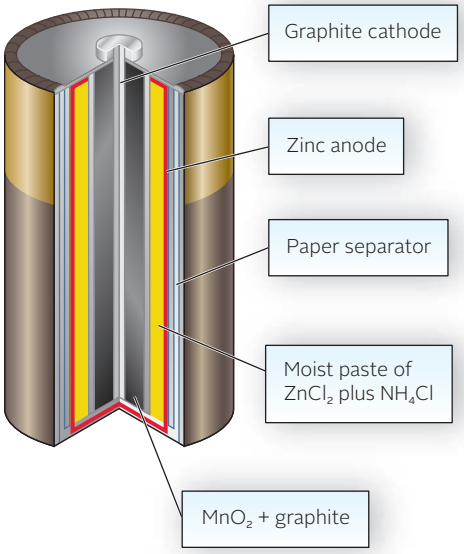

Figure 17.14 Zn-MnO_2 dry cell. This cell produces 1.5 V and will deliver a current of about half an ampere for six hours.

Primary (Nonrechargeable) Voltaic Cells

The construction of the ordinary dry cell (Leclanché cell) used in flashlights is shown in Figure 17.14. The zinc wall of the cell is the anode. The graphite rod through the center of the cell is the cathode. The space between the electrodes is filled with a moist paste. This contains MnO_2, $ZnCl_2$, and NH_4Cl. When the cell operates, the half-reaction at the anode is

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

At the cathode, manganese dioxide is reduced to species in which Mn is in the +3 oxidation state, such as Mn_2O_3:

$$2MnO_2(s) + 2NH_4^+(aq) + 2e^- \longrightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O$$

The overall reaction occurring in this voltaic cell is

$$Zn(s) + 2MnO_2(s) + 2NH_4^+(aq) \longrightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2NH_3(aq) + H_2O$$

If too large a current is drawn from a Leclanché cell, the ammonia forms a gaseous insulating layer around the carbon cathode. When this

CHEMISTRY THE **HUMAN** SIDE

The laws of electrolysis were discovered by Michael Faraday, perhaps the most talented experimental scientist of the nineteenth century. Faraday lived his entire life in what is now greater London. The son of a blacksmith, he had no formal education beyond the rudiments of reading, writing, and arithmetic. Apprenticed to a bookbinder at the age of 13, Faraday educated himself by reading virtually every book that came into the shop. One that particularly impressed him was a textbook, *Conversations in Chemistry,* written by Mrs. Jane Marcet. Anxious to escape a life of drudgery as a tradesman, Faraday wrote to Sir Humphry Davy at the Royal Institution, requesting employment. Shortly afterward, a vacancy arose, and Faraday was hired as a laboratory assistant.

Davy quickly recognized Faraday's talents and as time passed allowed him to work more and more independently. In his years with Davy, Faraday published papers covering almost every field of chemistry. They included studies on the condensation of gases (he was the first to liquefy ammonia), the reaction of silver compounds with ammonia, and the isolation of several organic compounds, the most important of which was benzene. In 1825, Faraday began a series of lectures at the Royal Institution that were brilliantly successful. That same year he succeeded Davy as director of the laboratory. As Faraday's reputation grew, it was said that "Humphrey Davy's greatest discovery was Michael Faraday." Perhaps it was witticisms of this sort that led to an estrangement between master and protégé. Late in his life, Davy opposed Faraday's nomination as a Fellow of the Royal Society and is reputed to have cast the only vote against him.

To Michael Faraday, science was an obsession; one of his biographers described him as a "work maniac." An observer (Faraday had no students) said of him,

> *. . . if he had to cross the laboratory for anything, he did not walk, he ran; the quickness of his perception was equalled by the calm rapidity of his movements.*

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Michael Faraday
(1791–1867)

In 1839, he suffered a nervous breakdown, the result of overwork. For much of the rest of his life, Faraday was in poor health. He gradually gave up more and more of his social engagements but continued to do research at the same pace as before.

Faraday developed the laws of electrolysis between 1831 and 1834. In mid-December of 1833, he began a quantitative study of the electrolysis of several metal cations, including Sn^{2+}, Pb^{2+}, and Zn^{2+}. Despite taking a whole day off for Christmas, he managed to complete these experiments, write up the results of three years' work, and get his paper published in the *Philosophic Transactions of the Royal Society* on January 9, 1834. In this paper, Faraday introduced the basic vocabulary of electrochemistry, using for the first time the terms "anode," "cathode," "ion," "electrolyte," and "electrolysis."

happens, the voltage drops sharply and then returns slowly to its normal value of 1.5 V. This problem can be avoided by using an alkaline dry cell, in which the paste between the electrodes contains KOH rather than NH_4Cl. In this case the overall cell reaction is simply

A flashlight draws about 1 A and runs for about an hour before "dying."

$$Zn(s) + 2MnO_2(s) \longrightarrow ZnO(s) + Mn_2O_3(s)$$

No gas is produced. The alkaline dry cell, although more expensive than the Leclanché cell, has a longer shelf life and provides more current.

Another important primary battery is the mercury cell. It usually comes in very small sizes and is used in hearing aids, watches, cameras, and some calculators. The anode of this cell is a zinc-mercury amalgam; the reacting species is zinc. The cathode is a plate made up of mercury(II) oxide, HgO. The electrolyte is a paste containing HgO and sodium or potassium hydroxide. The electrode reactions are

Mercury cells are no longer sold, because of mercury's toxicity.

$$\begin{array}{rr} \text{anode:} & Zn(s) + 2OH^-(aq) \longrightarrow Zn(OH)_2(s) + 2e^- \\ \text{cathode:} & HgO(s) + H_2O + 2e^- \longrightarrow Hg(l) + 2\,OH^-(aq) \\ \hline & Zn(s) + HgO(s) + H_2O \longrightarrow Zn(OH)_2(s) + Hg(l) \end{array}$$

Notice that the overall reaction does not involve any ions in solution, so there are no concentration changes when current is drawn. As a result, the battery maintains a constant voltage of about 1.3 V throughout its life.

Storage (Rechargeable) Voltaic Cells

A storage cell, unlike an ordinary dry cell, can be recharged repeatedly. This can be accomplished because the products of the reaction are deposited directly on the electrodes. By passing a current through a storage cell, it is possible to reverse the electrode reactions and restore the cell to its original condition.

A 12-V storage battery can deliver 300 A for a minute or so.

Lead Storage Battery

The rechargeable 12-V lead storage battery used in automobiles consists of six voltaic cells of the type shown in Figure 17.15. A group of lead plates, the grids of which are filled with spongy gray lead, forms the anode of the cell. The multiple cathode consists of another group of plates of similar design filled with lead(IV) oxide, PbO_2. These two sets of plates alternate through the cell. They are immersed in a water solution of sulfuric acid, H_2SO_4, which acts as the electrolyte.

When a lead storage battery is supplying current, the lead in the anode grids is oxidized to Pb^{2+} ions, which precipitate as $PbSO_4$. At the cathode, lead dioxide is reduced to Pb^{2+} ions, which also precipitate as $PbSO_4$.

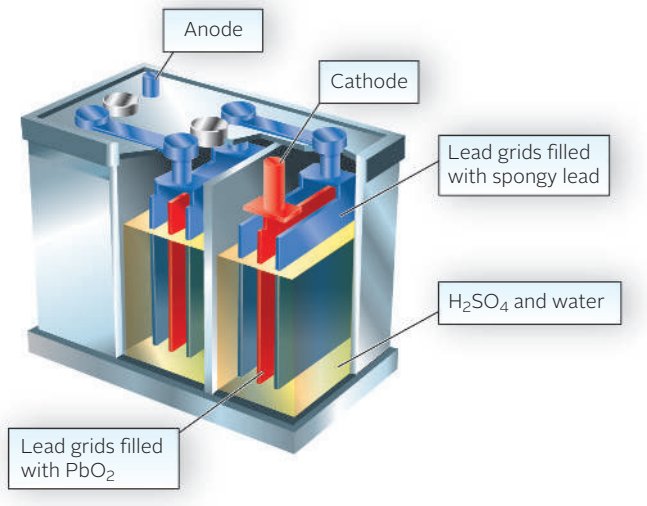


Figure 17.15 Lead storage battery. Three advantages of the lead storage battery are its ability to deliver large amounts of energy for a short time, the ease of recharging, and a nearly constant voltage from full charge to discharge. A disadvantage is its high mass-to-energy ratio.

$$\begin{array}{rr} \text{Anode:} & Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2e^- \\ \text{Cathode:} & PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O \\ \hline & Pb(s) + PbO_2(s) + 2H^+(aq) + 2HSO_4^-(aq) \longrightarrow 2PbSO_4(s) + 2H_2O \end{array}$$

$$\Delta G^\circ = -371.4 \text{ kJ } (25^\circ C)$$

Deposits of lead sulfate slowly build up on the plates, partially covering and replacing the lead and lead dioxide.

To recharge a lead storage battery, a direct current is passed through it in the proper direction so as to reverse the above reaction. In an automobile, the energy required to carry out the recharging comes from the engine.

When the battery is charged, some water may be electrolyzed:

$$2H_2O \longrightarrow 2H_2(g) + O_2(g) \qquad \Delta G° \text{ at } 25°C = 474.4 \text{ kJ}$$

The hydrogen and oxygen produced create a safety hazard. Beyond that, they can cause Pb, PbO_2, and $PbSO_4$ to flake off the plates. In a modern "maintenance-free" battery, the lead plates are alloyed with small amounts of calcium, which inhibits the electrolysis reaction.

One of the advantages of the lead storage battery is that its voltage stays constant at 2 V per cell over a wide range of sulfuric acid concentrations. Only when the battery is nearly completely discharged does the voltage drop. It is also true that the cell voltage is virtually independent of temperature. You have trouble starting your car on a cold morning because the conductivity of the electrolyte drops off sharply with temperature; the voltage is still 2 V per cell at −40°C.

Nickel-Based Batteries

Nickel-cadmium (Nicad) batteries have an anode of solid cadmium and a cathode of solid nickeloxy hydroxide, NiO(OH). Aqueous potassium hydroxide is often used as an electrolyte. The reaction taking place in the cell is

$$\text{anode:} \quad Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^-$$
$$\text{cathode:} \quad 2NiO(OH)(s) + 2H_2O + 2e^- \longrightarrow 2Ni(OH)_2(s) + 2OH^-(aq)$$

The battery produces about 1.3 V. As the battery is used, solid hydroxides of nickel and cadmium are deposited on the electrode. When the battery is recharged by a current it runs in the opposite direction, where the hydroxides of nickel and cadmium regenerate Cd and NiO(OH). Nicad batteries are a popular choice for emergency medical equipment and power tools.

Nicad batteries have been popular for many years but are being replaced by the nickel-metal **hydride**, NiMH, battery. This is because of the toxicity of cadmium and the difficulty of disposal for Nicad batteries.

In nickel-metal hydride batteries, the cathode is also nickeloxy hydroxide. The anode is a metal hydride, MH, where the "metal" is not a single element but an alloy of several metals. The half-reactions for this battery are

$$\text{anode:} \quad MH(s) + OH^-(aq) \longrightarrow M(s) + H_2O + e^-$$
$$\text{cathode:} \quad NiO(OH)(s) + H_2O + e^- \longrightarrow Ni(OH)_2(s) + OH^-(aq)$$

Besides being environmentally friendlier than Nicad batteries, nickel-metal hydride batteries have a higher energy content per unit mass. This is called the battery's energy density with units expressed in watt-hour/kg. These batteries are commonly used in hybrid electric cars and buses.

Lithium-Ion (Li-Ion) Batteries

The latest type of rechargeable battery is the lithium-ion battery. The reaction taking place in the cell is more complicated than in either the lead storage battery or the nickel-based batteries. Suffice it to say that lithium ions move from the anode to the cathode. The anode is made up of carbon layers in which lithium ions are embedded. The cathode is a lithium metal oxide like $LiCoO_2$. The electrolyte is a lithium salt in an organic solvent.

These batteries have a number of advantages. Lithium is the lightest metal (d = 0.53 g/cm^3) and extremely reactive. These characteristics translate into a high-energy density. A typical Li-ion battery can store 150 watt-hours in 1 kg of battery. In comparison, NiMH batteries can store 80 Wh/kg while a lead storage battery can store 2.5 Wh/kg. Li-ion batteries hold their charge, losing only about 5% a month,

whereas NiMH batteries lose about 20% per month. Li-ion batteries also have no memory effect, which means that you do not have to completely discharge them before recharging. However, if you completely discharge a Li-ion battery, it is ruined. The biggest disadvantage to the consumer is its cost and limited life span.

Li-ion batteries are used when light weight and high energy density are required. They are commonly used in cell phones, laptops, and digital cameras.

Fuel Cells

A fuel cell (Figure 17.16) is a voltaic cell in which a fuel, usually hydrogen, is oxidized at the anode. At the cathode, oxygen is reduced. The reaction taking place in the alkaline fuel cells used in the space program since the 1960s is

$$\text{anode:} \quad 2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O + 4e^-$$

$$\text{cathode:} \quad O_2(g) + 2H_2O + 4e^- \longrightarrow 4\,OH^-(aq)$$

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O \qquad \Delta G^\circ \text{ at } 25^\circ C = -474.4 \text{ kJ}$$

Using a platinum catalyst, this reaction can now be carried out at temperatures as low as 40°C. The hydrogen used must be very pure; traces of carbon monoxide can poison the catalyst.

Current research on fuel cells is directed toward the replacement of the internal combustion engine. To do this, hydrogen must be stored in the vehicle and replenished from time to time at "filling stations." Three kilograms of hydrogen should be enough to drive a small car 500 km (300 miles) between fill-ups.

The rationale for using a hydrogen fuel cell is that the cell reaction produces only water. In contrast, your car's engine produces small amounts of air pollutants such as NO and copious amounts of CO_2, which contributes to global warming. On the other hand, there are a couple of deterrents to the use of fuel cells, i.e.,

- the cost per kilojoule of energy is higher than with a gasoline- or diesel-powered engine.
- the storage of hydrogen in a vehicle is a serious problem. To carry three kilograms of hydrogen as a compressed gas at 200 atm (~3000 psi) requires a heavy tank with a volume of 200 L (50 gallons). Liquid hydrogen requires a smaller tank, but its extremely low critical temperature (−240°C) creates all sorts of problems. Another possibility is to convert hydrogen reversibly to a transition metal hydride (e.g., TiH_2). It's hard to say at this point how well that would work. All in all, it is almost certain that your next car will *not* use hydrogen as a fuel.

AP Images/Koji Sasahara

Figure 17.16 Fuel cell under Honda Clarity hood.

Fuel cells have been around for about 50 years.

CHEMISTRY **BEYOND** THE CLASSROOM

Fuel Cells: The Next Step in Chemical-to-Electrical-Energy Conversion?

Steven R. Shaw, Montana State University

Fuel cells have attracted considerable interest because of their potential for efficient conversion of the energy (ΔG) from a chemical reaction to electrical energy (ΔE). This efficiency is achieved by directly converting chemical energy to electricity. Conventional systems burn fuel in an engine and convert the resulting mechanical output to electrical power. Potential applications include stationary multi-megawatt power plants, battery replacements for personal electronics, and even fuel-cell-powered unmanned autonomous vehicles (UAVs).

The different types of fuel cells depend on the electrolytes used and the temperatures at which the electrolytes operate. One popular fuel cell that operates at low temperatures (80°C) used a polymer-electrolyte membrane, also known as a proton-exchange membrane (PEM). This membrane is made of a fluorinated polymer, like Teflon, that is highly conductive to electrons. It allows an energetically favorable reaction ($\Delta G < 0$) between the fuel gas and oxidant to be spatially confined, so that the electrons evolving from and consumed by the half-cell reactions can do work in an external circuit. Figure A shows a schematic of a hydrogen/oxygen fuel cell with a proton-exchange membrane.

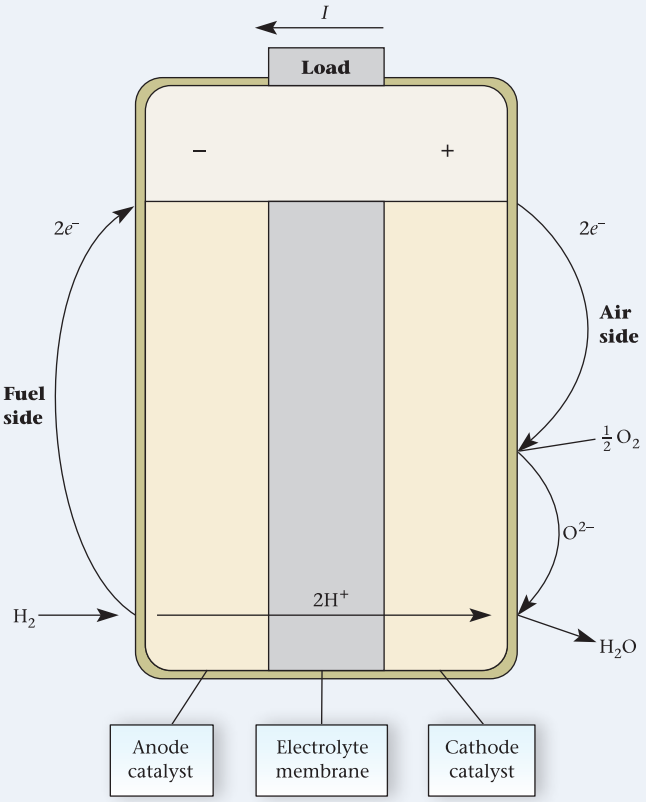


Figure A

The half-cell reactions supported by this structure are

$$H_2 \longrightarrow 2e^- + 2H^+$$

$$2H^+ + 2e^- + \tfrac{1}{2}O_2 \longrightarrow H_2O$$

Taken together, the overall reaction is simply the energetically favorable oxidation of hydrogen.

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O$$

Unlike burning hydrogen in air, in a fuel cell the electrolyte partitions the overall reaction into half-cell reactions on either side of the cell. Hydrogen ions flow through the membrane, but since the electrolyte is nonconductive to electrons, it forces the electrons to flow through an external electrical circuit to complete the reaction. This flow of electrons can be harnessed to do useful work, such as illuminating a light bulb or running a laptop. The voltage at the terminals of a single cell is rather small, on the order of a volt, so in applications a number of cells are usually connected in series to form a fuel cell "stack."

Although it is attractive to directly convert chemical energy to electricity, PEM fuel cells face significant practical obstacles. Expensive heavy metals like platinum are typically used as catalysts to reduce energy barriers associated with the half-cell reactions. PEM fuel cells also cannot use practical hydrocarbon fuels like diesel without complicated preprocessing steps. Those significantly increase the complexity of the overall system. At this time, it appears likely that PEM fuel cells will be confined to niche applications where high cost and special fuel requirements are tolerable.

On the other hand, high-temperature fuel cells, which work at 800°C, offer some significant advantages over low-temperature cells like PEMs. One of their principal advantages is the potential to use more practical hydrocarbon fuels such as methane, or even mixtures of gasoline and diesel. This feature avoids the need for the "new energy infrastructure" sometimes associated with hydrogen fuel cells. Another advantage is the lower cost of the catalysts needed for the operation of a high-temperature fuel cell. As an added benefit, the exhaust gases are hot enough for secondary energy recovery. For example, "waste heat" from a high-temperature fuel cell can supply energy needed to convert conventional hydrocarbon fuels into simpler components (like carbon monoxide and hydrogen) that work efficiently in the fuel cell. The exhaust of a high-temperature fuel cell can also be used to drive a conventional turbine and generator in what is called a combined cycle or hybrid system. Some high-temperature fuel-cell test installations use the exhaust to heat nearby buildings.

One leading prototype of a high-temperature fuel cell is the solid oxide fuel cell, or SOFC. The basic principle of the SOFC, like the PEM, is to use an electrolyte layer with high ionic conductivity but very small electronic conductivity. Figure B shows a schematic illustration of a SOFC fuel cell using carbon monoxide as fuel.

Unlike the PEM, the ionic conduction occurs for the oxygen ion instead of the hydrogen ion. SOFCs are made of ceramic materials like zirconium ($Z = 40$) stabilized by yttrium ($Z = 39$). High-temperature oxygen conductivity is achieved by creating oxygen vacancies in the lattice

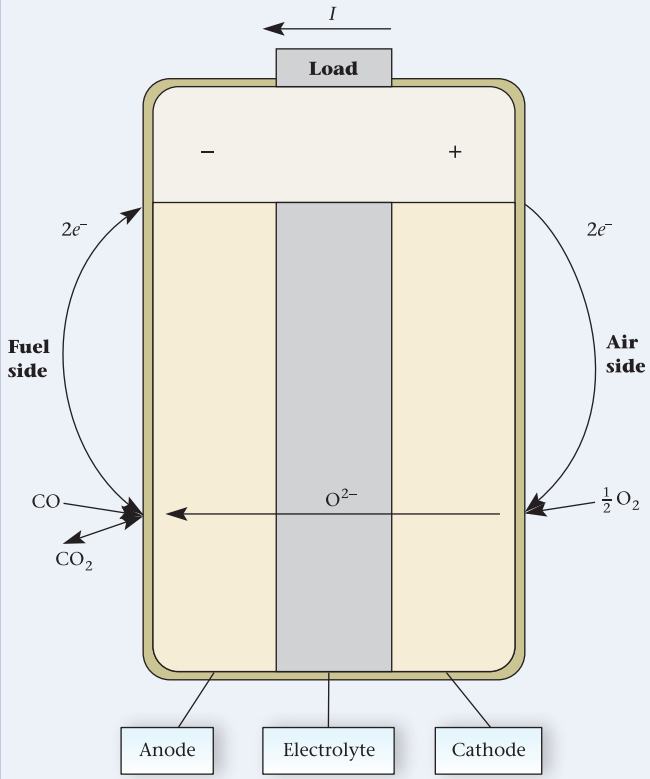


Figure B

structure of the electrolyte material. The half-cell reactions in this case are

$$\tfrac{1}{2}O_2 + 2e^- \longrightarrow O^{2-}$$

$$O^{2-} + CO \longrightarrow CO_2 + 2e^-$$

Note that the overall reaction

$$\tfrac{1}{2}O_2(g) + CO(g) \longrightarrow CO_2(g)$$

is the oxidation of CO, but the fuel cell's materials partition the reaction so that the electrons flow through an external circuit and perform useful work.

Figure C shows an electron photomicrograph of a broken planar SOFC. The thick portion on the left is the porous anode structure. This is an anode-supported cell, meaning that in addition to collecting current and supporting the anode reaction, the anode layer stiffens the whole cell. The layer on the right is the cathode, and the interface between the two is the thin electrolyte. One of the challenges of this design is to ensure that the rates of expansion of the cathode and the anode match. If the anode expands faster than the cathode, the planar cell tends to curl like a potato chip when the temperature changes.

Note that fuel cells do not provide a new source of energy. They are designed to use conventional, currently available fuels. Their main advantage lies in the efficiency of their operation, which creates fewer byproducts to threaten the environment.

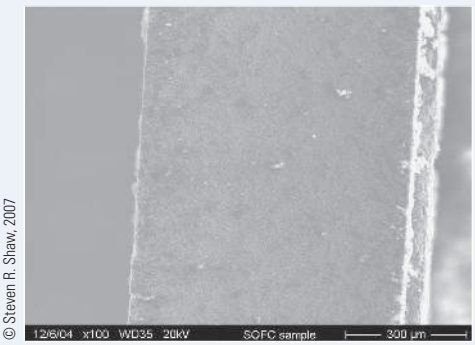


Figure C

Key Concepts

1. Balance redox half-equations and overall equation. **(Examples 17.1, 17.2, Problems 1–10)**
2. Draw a diagram for a voltaic cell, labeling electrodes and direction of current flow. **(Example 17.3; Problems 11–18)**
3. Use standard potentials (Table 17.1) to
   - compare the relative strengths of different oxidizing agents; different reducing agents. **(Example 17.4; Problems 19–28)**
   - calculate $E°$ and/or reaction spontaneity. **(Examples 17.5, 17.6; Problems 29–48)**
4. Relate $E°$ to $\Delta G°$ and K. **(Example 17.7; Problems 49–62)**
5. Use the Nernst equation to relate voltage to concentration. **(Examples 17.8, 17.9; Problems 63–76)**
6. Relate mass of product to amount of electricity (coulombs) or amount of energy (joules) used in electrolysis reactions. **(Example 17.10; Problems 77–84)**

Key Equations

Standard voltage $\quad E° = E°_{red} + E°_{ox}$

$E°, \Delta G°, K \quad E° = \dfrac{-\Delta G°}{nF} = \dfrac{RT \ln K}{nF} = \dfrac{0.0257\ \text{V}}{n} \ln K \qquad (\text{at } 25°\text{C})$

Nernst equation $\quad E = E° - \dfrac{RT}{nF} \ln Q = E° - \dfrac{0.0257\ \text{V}}{n} \ln Q \qquad (\text{at } 25°\text{C})$

Key Terms

ampere
anode
cathode
coulomb
electrodes
electrolysis
electrolytic cell
Faraday constant
half-cell
half-equations
oxidation
oxidizing agent
reducing agent
reduction
salt bridge
standard oxidation voltage ($E°_{ox}$)
standard potential ($E°$)
standard reduction voltage ($E°_{red}$)
voltaic (galvanic) cell

Summary Problem

A voltaic cell consists of two half-cells. One of the half-cells contains a platinum electrode dipped in an aqueous solution of permanganate and manganese(II) ions. The other half-cell has a platinum electrode dipped in an aqueous solution of chlorate ions. Chlorine gas is bubbled into the half-cell solution. Assume that the cell reaction, which produces a positive voltage, involves permanganate ions and chlorine gas in acidic solution. The temperature of the cells is kept constant at 25°C.

(a) Write a balanced oxidation half-reaction. Where does it occur?

(b) Write a balanced reduction half-reaction. Where does it occur?

(c) Write a balanced overall equation for the redox reaction taking place.

(d) Write the cell notation.

(e) Calculate $E°$ for the cell.

(f) For the redox reaction in (c), calculate K and $\Delta G°$.

(g) Calculate the pH of the cell, when the cell voltage is 0.023 V, all ionic species except H^+ are at 0.200 M, and P_{Cl_2} is 0.873 atm.

An electrolytic cell contains a solution of manganese(II) nitrate. Assume that in this cell, manganese plates out at one electrode and that oxygen gas is evolved at the other electrode.

(h) Write the anode half-reaction, the cathode half-reaction, and a balanced overall equation for the electrolysis.

(i) How long will it take to deposit 5.00 g of manganese using a current of 6.20 A?

(j) A current of 5.00 A is passed through the cell for 1.00 h. Starting out with 175 mL of 1.25 M $Mn(NO_3)_2$, what is $[Mn^{2+}]$ after electrolysis? What is the pH of the solution? (Assume that the H^+ present before electrolysis is negligible.) What is the volume of oxygen gas produced at 757 mm Hg and 25°C? Assume 100% efficiency and no change in volume during electrolysis.

Answers

(a) oxidation half-reaction at the anode:
$Cl_2(g) + 6H_2O \longrightarrow 2ClO_3^-(aq) + 12H^+(aq) + 10e^-$

(b) reduction half-reaction at the cathode:
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$

(c) $Cl_2(g) + 2MnO_4^-(aq) + 4H^+(aq) \longrightarrow 2ClO_3^-(aq) + 2Mn^{2+}(aq) + 2H_2O$

(d) $Pt \mid Cl_2 \mid ClO_3^- \parallel MnO_4^-, Mn^{2+} \mid Pt$

(e) 0.054 V

(f) $\Delta G° = -52$ kJ; $K = 1 \times 10^9$

(g) 1.65

(h) anode: $2H_2O \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$
cathode: $Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$
overall: $2Mn^{2+}(aq) + 2H_2O \longrightarrow 2Mn(s) + O_2(g) + 4H^+(aq)$

(i) 47.2 min

(j) 0.717 M; −0.028; 1.15 L

Questions and Problems

Even-numbered questions and Challenge Problems have answers in Appendix 5 and fully worked solutions in the *Student Solutions Manual*.

17-1 Oxidation-Reduction Reactions Revisited

1. Balance the following half-equations. Balance (a) and (b) in basic medium, (c) and (d) in acidic medium.
(a) $O_2(g) \longrightarrow O^{2-}(aq)$
(b) $MnO_4^-(aq) \longrightarrow MnO_2(s)$
(c) $Cr_2O_7^{2-}(aq) \longrightarrow Cr^{3+}(aq)$
(d) $Cl^-(aq) \longrightarrow Cl_2(g)$

2. Balance the following half-equations. Balance (a) and (b) in acidic medium, (c) and (d) in basic medium.
(a) $CH_3OH(aq) \longrightarrow CO_2(g)$
(b) $NO_3^-(aq) \longrightarrow NH_4^+(aq)$
(c) $Fe^{3+}(aq) \longrightarrow Fe(s)$
(d) $V^{2+}(aq) \longrightarrow VO_3^-(aq)$

3. Balance the following reactions in base:
(a) $Ag(s) + NO_3^-(aq) \longrightarrow Ag^+(aq) + NO(g)$
(b) $CO_2(g) + H_2O(l) \longrightarrow C_2H_4(g) + O_2(g)$

4. Balance the following reactions in acid:
(a) $H_2O_2(aq) + Ni^{2+}(aq) \longrightarrow Ni^{3+}(aq) + H_2O$
(b) $Cr_2O_7^{2-}(aq) + Sn^{2+}(aq) \longrightarrow Cr^{3+}(aq) + Sn^{4+}(aq)$

5. Write balanced equations for the following reactions in acid solution.
(a) $Ni^{2+}(aq) + IO_4^-(aq) \longrightarrow Ni^{3+}(aq) + I^-(aq)$
(b) $O_2(g) + Br^-(aq) \longrightarrow H_2O + Br_2(l)$
(c) $Ca(s) + Cr_2O_7^{2-}(aq) \longrightarrow Ca^{2+}(aq) + Cr^{3+}(aq)$
(d) $IO_3^-(aq) + Mn^{2+}(aq) \longrightarrow I^-(aq) + MnO_2(s)$

6. Write balanced equations for the following reactions in acid solution.
(a) $P_4(s) + Cl^-(aq) \longrightarrow PH_3(g) + Cl_2(g)$
(b) $MnO_4^-(aq) + NO_2^-(aq) \longrightarrow Mn^{2+}(aq) + NO_3^-(aq)$
(c) $HBrO_3(aq) + Bi(s) \longrightarrow HBrO_2(aq) + Bi_2O_3(s)$
(d) $CrO_4^{2-}(aq) + SO_3^{2-}(aq) \longrightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$

7. Write balanced equations for the following reactions in basic solution.

(**a**) $SO_2(g) + I_2(aq) \longrightarrow SO_3(g) + I^-(aq)$

(**b**) $Zn(s) + NO_3^-(aq) \longrightarrow NH_3(aq) + Zn^{2+}(aq)$

(**c**) $ClO^-(aq) + CrO_2^-(aq) \longrightarrow Cl^-(aq) + CrO_4^{2-}(aq)$

(**d**) $K(s) + H_2O \longrightarrow K^+(aq) + H_2(g)$

8. Write balanced net ionic equations for the following reactions in basic medium.

(**a**) $Ca(s) + VO_4^{3-}(aq) \longrightarrow Ca^{2+}(aq) + V^{2+}(aq)$

(**b**) $C_2H_4(g) + BiO_3^-(aq) \longrightarrow CO_2(g) + Bi^{3+}(aq)$

(**c**) $PbO_2(s) + H_2O \longrightarrow O_2(g) + Pb^{2+}$

(**b**) $IO_3^-(aq) + Cl^-(aq) \longrightarrow Cl_2(g) + I_3^-(aq)$

9. Write balanced net ionic equations for the following reactions in acid solution.

(**a**) Liquid hydrazine reacts with an aqueous solution of sodium bromate. Nitrogen gas and bromide ions are formed.

(**b**) Solid phosphorus (P_4) reacts with an aqueous solution of nitrate to form nitrogen oxide gas and dihydrogen phosphate ($H_2PO_4^-$) ions.

(**c**) Aqueous solutions of potassium sulfite and potassium permanganate react. Sulfate and manganese(II) ions are formed.

10. Write balanced net ionic equations for the following reactions in acid solution.

(**a**) Nitrogen oxide and hydrogen gases react to form ammonia gas and steam.

(**b**) Hydrogen peroxide reacts with an aqueous solution of sodium hypochlorite to form oxygen and chlorine gases.

(**c**) Zinc metal reduces the vanadyl ion (VO^{2+}) to vanadium(III) ions. Zinc ions are also formed.

17-2 Voltaic Cells

11. Write a balanced chemical equation for the overall cell reaction represented as

(**a**) $Ag \mid Ag^+ \parallel Sn^{4+}, Sn^{2+} \mid Pt$.

(**b**) $Al \mid Al^{3+} \parallel Cu^{2+} \mid Cu$.

(**c**) $Pt \mid Fe^{2+}, Fe^{3+} \parallel MnO_4^-, Mn^{2+} \mid Pt$.

12. Write a balanced net ionic equation for the overall cell reaction represented by

(**a**) $Cd \mid Cd^{2+} \parallel Sb^{3+} \mid Sb$

(**b**) $Pt \mid Cu^+, Cu^{2+} \parallel Mg^{2+} \mid Mg$

(**c**) $Pt \mid Cr^{3+}, Cr_2O_7^{2-} \parallel ClO_3^-, Cl^- \mid Pt$ (acid)

13. Draw a diagram for a salt bridge cell for each of the following reactions. Label the anode and cathode, and indicate the direction of current flow throughout the circuit.

(**a**) $Zn(s) + Cd^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cd(s)$

(**b**) $2AuCl_4^-(aq) + 3Cu(s) \longrightarrow 2Au(s) + 8Cl^-(aq) + 3Cu^{2+}(aq)$

(**c**) $Fe(s) + Cu(OH)_2(s) \longrightarrow Cu(s) + Fe(OH)_2(s)$

14. Follow the directions in Question 13 for the following reactions:

(**a**) $Sn(s) + 2Ag^+(aq) \longrightarrow Sn^{2+}(aq) + 2Ag(s)$

(**b**) $H_2(g) + Hg_2Cl_2(s) \longrightarrow 2H^+(aq) + 2Cl^-(aq) + 2Hg(l)$

(**c**) $Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \longrightarrow 2PbSO_4(s) + 2H_2O$

15. Consider a voltaic salt bridge cell represented by the following reaction:

$$Ca(s) + 2H^+(aq) \longrightarrow Ca^{2+}(aq) + H_2(g)$$

(**a**) What is the direction of the electrons in the external circuit?

(**b**) What electrode can be used at the cathode?

(**c**) What is the reaction occurring at the anode?

16. Consider a salt bridge voltaic cell represented by the following reaction

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O$$

(**a**) What is the direction of the electrons in the external circuit?

(**b**) What electrode can be used at the anode?

(**c**) What is the reaction occurring at the cathode?

17. Consider a salt bridge cell in which the anode is a manganese rod immersed in an aqueous solution of manganese(II) sulfate. The cathode is a chromium strip immersed in an aqueous solution of chromium(III) sulfate. Sketch a diagram of the cell, indicating the flow of the current throughout. Write the half-equations for the electrode reactions, the overall equation, and the abbreviated notation for the cell.

18. Follow the directions in Question 17 for a salt bridge cell in which the anode is a platinum rod immersed in an aqueous solution of sodium iodide containing solid iodine crystals. The cathode is another platinum rod immersed in an aqueous solution of sodium bromide with bromine liquid.

17-3 Standard Voltages

Strength of Oxidizing and Reducing Species

19. Which species in the pair is the stronger oxidizing agent?

(**a**) Cr or Cd

(**b**) I^- or Br^-

(**c**) OH^- or NO_2^- (basic solution)

(**d**) NO in acidic solution or NO in basic solution

20. Which species in each pair is the stronger reducing agent?

(**a**) Cl^- or Br^- (**b**) Cu or Ni (**c**) Hg_2^{2+} or $NO(g)$

21. Using Table 17.1, arrange the following reducing agents in order of increasing strength.

Br^- Zn Co $PbSO_4$ H_2S (acidic)

22. Use Table 17.1 to arrange the following oxidizing agents in order of increasing strength:

Mn^{2+} S Co^{3+} Cl_2 K^+

23. Consider the following species.

Cr^{3+} $Hg(l)$ H_2 (acidic) Sn^{2+} Br_2 (acidic)

Classify each species as oxidizing agent, reducing agent, or both. Arrange the oxidizing agents in order of increasing strength. Do the same for the reducing agents.

24. Follow the directions of Question 23 for the following species:

Cu^+ Zn Ni^{2+} Fe^{2+} H^+(acidic)

25. For the following half-reactions, answer these questions.

$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$ $E° = +1.61$ V

$Ag^+(aq) + e^- \longrightarrow Ag(s)$ $E° = +0.80$ V

$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$ $E° = +0.80$ V

$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$ $E° = -0.14$ V
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$ $E° = -0.24$ V
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$ $E° = -1.68$ V

(a) Which is the weakest oxidizing agent?
(b) Which is the strongest oxidizing agent?
(c) Which is the strongest reducing agent?
(d) Which is the weakest reducing agent?
(e) Will $Sn(s)$ reduce $Ag^+(aq)$ to $Ag(s)$?
(f) Will $Hg(l)$ reduce $Sn^{2+}(aq)$ to $Sn(s)$?
(g) Which ion(s) can be reduced by $Sn(s)$?
(h) Which metal(s) can be oxidized by $Ag^+(aq)$?

26. For the following half-reactions, answer the questions below.

$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$ $E° = +1.953$ V
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$ $E° = +0.769$ V
$I_2(aq) + 2e^- \longrightarrow 2I^-(aq)$ $E° = +0.534$ V
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$ $E° = -0.127$ V
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$ $E° = -0.402$ V
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$ $E° = -1.182$ V

(a) Which is the weakest reducing agent?
(b) Which is the strongest reducing agent?
(c) Which is the strongest oxidizing agent?
(d) Which is the weakest oxidizing agent?
(e) Will $Pb(s)$ reduce $Fe^{3+}(aq)$ to $Fe^{2+}(aq)$?
(f) Will $I^-(aq)$ reduce $Pb^{2+}(aq)$ to $Pb(s)$?
(g) Which ion(s) can be reduced by $Pb(s)$?
(h) Which if any metal(s) can be oxidized by $Fe^{3+}(aq)$?

27. Use Table 17.1 to select
(a) a reducing agent in acidic solution that converts ClO_3^- to Cl_2 but not $Cr_2O_7^{2-}$ to Cr^{3+}.
(b) an oxidizing agent that converts Mg to Mg^{2+} but not Mn to Mn^{2+}.
(c) a reducing agent in basic solution that converts NO_2^- to NO_3^- but not OH^- to O_2.

28. Use Table 17.1 to select
(a) an oxidizing agent in basic solution that converts ClO_3^- to ClO_4^- but not Cl^- to ClO_3^-.
(b) a reducing agent that converts Mg^{2+} to Mg but not Ba^{2+} to Ba.
(c) a reducing agent that converts Na^+ to Na but not Li^+ to Li.

Calculation of $E°$

29. Calculate $E°$ for the following voltaic cells:
(a) $MnO_2(s) + 4H^+(aq) + 2I^-(aq) \longrightarrow Mn^{2+}(aq) + 2H_2O + I_2(s)$
(b) $H_2(g) + 2OH^-(aq) + S(s) \longrightarrow 2H_2O + S^{2-}(aq)$
(c) an Ag-Ag^+ half-cell and an Au-$AuCl_4^-$ half-cell

30. Calculate $E°$ for the following voltaic cells:
(a) $2Na(s) + Fe^{2+}(aq) \longrightarrow 2Na^+(aq) + Fe(s)$
(b) $3SO_4^{2-}(aq) + 12H^+(aq) + 2Al(s) \longrightarrow 3SO_2(g) + 2Al^{3+}(aq) + 6H_2O$
(c) $2S(s) + 4OH^-(aq) \longrightarrow O_2(g) + 2S^{2-}(aq) + 2H_2O$ (basic)

31. Using Table 17.1, calculate $E°$ for the reaction between
(a) lead and silver nitrate ion to produce lead(II) nitrate.
(b) oxygen and iron(II) ions to produce water and iron(III) ions.
(c) sulfur and nitrogen oxide gas in basic solution to form nitrate and sulfide ions.

32. Using Table 17.1, calculate $E°$ for the reaction between
(a) chromium(II) ions and tin(IV) ions to produce chromium(III) ions and tin(II) ions.
(b) manganese(II) ions and hydrogen peroxide to produce solid manganese dioxide (MnO_2).

33. Calculate $E°$ for the following cells:
(a) $Pb \mid PbSO_4 \parallel Pb^{2+} \mid Pb$
(b) $Pt \mid Cl_2 \mid ClO_3^- \parallel O_2 \mid H_2O \mid Pt$
(c) $Pt \mid OH^- \mid O_2 \parallel ClO_3^-, Cl^- \mid Pt$ (basic medium)

34. Calculate $E°$ for the following cells:
(a) $Ag \mid Ag^+ \parallel Sn^{4+}, Sn^{2+} \mid Pt$
(b) $Al \mid Al^{3+} \parallel Cu^{2+} \mid Cu$
(c) $Pt \mid Fe^{2+}, Fe^{3+} \parallel MnO_4^-, Mn^{2+} \mid Pt$

35. Suppose $E°_{red}$ for $Ag^+ \longrightarrow Ag$ were set equal to zero instead of that of $H^+ \longrightarrow H_2$. What would be
(a) $E°_{red}$ for $H^+ \longrightarrow H_2$?
(b) $E°_{ox}$ for $Ca \longrightarrow Ca^{2+}$?
(c) $E°$ for the cell in 33(c)? Compare your answer with that obtained in 33(c).

36. Suppose $E°_{red}$ for $H^+ \longrightarrow H_2$ were taken to be 0.300 V instead of 0.000 V. What would be
(a) $E°_{ox}$ for $H_2 \longrightarrow H^+$?
(b) $E°_{red}$ for $Br_2 \longrightarrow Br^-$?
(c) $E°$ for the cell in 34(c)? Compare your answer with that obtained in 34(c).

Spontaneity and $E°$

37. Which of the following reactions is/are spontaneous at standard conditions?
(a) $Zn(s) + 2Fe^{3+} \longrightarrow Zn^{2+}(aq) + 2Fe^{2+}(aq)$
(b) $Cu(s) + 2H^+(aq) \longrightarrow Cu^{2+}(aq) + H_2(g)$
(c) $2Br^-(aq) + I_2(s) \longrightarrow Br_2(l) + 2I^-(aq)$

38. Which of the following reactions is(are) spontaneous at standard conditions?
(a) $Ba(s) + 2Cr^{3+}(aq) \longrightarrow 2Cr^{2+}(aq) + Ba^{2+}(aq)$
(b) $Co^{2+}(aq) + Cu(s) \longrightarrow Co(s) + Cu^{2+}(aq)$
(c) $2S(s) + 4OH^-(aq) \longrightarrow O_2(g) + 2S^{2-}(aq) + 2H_2O$ (basic)

39. Use the following half-equations to write three spontaneous reactions. Justify your answers by calculating $E°$ for the cells.
1. $MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$ $E° = +1.512$ V
2. $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$ $E° = +1.229$ V
3. $Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$ $E° = -0.282$ V

40. Follow the directions of Question 39 for the following half-reactions:
1. $I_2(s) + 2e^- \longrightarrow 2I^-(aq)$
2. $Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$
3. $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$

41. Use Table 17.1 to answer the following questions:
(a) Will chlorate ions in acidic solution oxidize Cl^- to Cl_2 or F^- to F_2?
(b) What is the product when Fe reduces Cr^{3+}?

(c) Oxygen is reduced to water in acidic medium and to OH^- in basic medium. If ClO_3^- (oxidized to ClO_4^-) is the reducing agent, in which medium will oxygen be reduced spontaneously? ($E°_{red}$ for ClO_4^- in acidic medium is 1.19 V.)

42. Use Table 17.1 to answer the following questions.

(a) Will nitrate ions in acidic solution oxidize copper to copper(II) ions or gold to gold(III) ions?

(b) What is the product of the oxidation of copper by iron(II) ions? copper(I) ions or copper(II) ions?

(c) Oxygen is reduced to water in acidic medium and to OH^- in basic medium. If ClO_3^- (oxidized to ClO_4^-) is the reducing agent, in which medium will oxygen be reduced spontaneously? (The standard reduction potential for ClO_4^- in acidic medium is 1.19 V.)

43. Write the equation for the reaction, if any, that occurs when each of the following experiments is performed under standard conditions.

(a) Crystals of iodine are added to an aqueous solution of potassium bromide.

(b) Liquid bromine is added to an aqueous solution of sodium chloride.

(c) A chromium wire is dipped into a solution of nickel(II) chloride.

44. Write the equation for the reaction, if any, that occurs when each of the following experiments is performed under standard conditions.

(a) Sulfur is added to mercury.

(b) Manganese dioxide in acidic solution is added to liquid mercury.

(c) Aluminum metal is added to a solution of potassium ions.

45. Which of the following species will be oxidized by 1 *M* HCl?

(a) Au (b) Mg (c) Cu (d) F^-

46. Which of the following species will be oxidized by 1 *M* HBr?

(a) Na (b) Hg (c) Pb (d) Mn^{2+}

47. Use Table 17.1 to predict what reaction, if any, will occur when the following species are mixed in acidic solution at standard conditions.

(a) Cr, Ni^{2+}, Cl^- (b) F_2, Na^+, Br^- (c) SO_2, Fe^{3+}, NO_3^-

48. Use Table 17.1 to predict what reaction, if any, will occur if sulfur is added to acidic aqueous solutions of the following species at standard conditions.

(a) $MgBr_2$ (b) $Sn(NO_3)_2$ (c) $Cr(ClO_3)_2$

17-4 Relations between $E°$, $\Delta G°$, and K

49. Consider a cell reaction at 25°C where $n = 2$. Fill in the following table.

	$\Delta G°$	$E°$	K
(a)	19 kJ	_____	_____
(b)	_____	0.035 V	_____
(c)	_____	_____	0.095

50. Consider a cell reaction at 25°C where $n = 4$. Fill in the following table.

	$\Delta G°$	$E°$	K
(a)	_____	_____	1.6×10^{-3}
(b)	_____	0.117 V	_____
(c)	−5.8 kJ	_____	_____

51. For a certain cell, $\Delta G° = 25.0$ kJ. Calculate $E°$ if n is

(a) 1 (b) 2 (c) 4

Comment on the effect that the number of electrons exchanged has on the voltage of a cell.

52. For a certain cell, $E° = 1.08$ V. Calculate $\Delta G°$ if n is

(a) 1 (b) 2 (c) 3

53. Calculate $E°$, $\Delta G°$, and K at 25°C for the reaction

$$3Mn^{2+}(aq) + 2MnO_4^-(aq) + 2H_2O \longrightarrow 5MnO_2(s) + 4H^+(aq)$$

54. Calculate $E°$, $\Delta G°$, and K at 25°C for the reaction

$$2MnO_4^-(aq) + 4H^+(aq) + Cl_2(g) \longrightarrow 2Mn^{2+}(aq) + 2ClO_3^-(aq) + 2H_2O$$

55. Calculate $\Delta G°$ at 25°C for each of the reactions referred to in Question 29. Assume smallest whole-number coefficients.

56. Calculate $\Delta G°$ at 25°C for each of the reactions referred to in Question 30. Assume smallest whole-number coefficients.

57. Calculate K at 25°C for each of the reactions referred to in Question 31.

58. Calculate K at 25°C for each of the reactions referred to in Question 32. Assume smallest whole-number coefficients.

59. Consider the reaction for the formation of the complex ion $CuCl_2^-$.

$$Cu^+(s) + 2Cl^-(aq) \rightarrow CuCl_2^-(aq)$$

The formation constant K_f for this reaction is 3.0×10^5.

(a) Write the two half-reactions that give rise to the formation of the complex ion.

(b) Find the standard reduction potential at 25°C for the reaction.

60. Use Table 17.1 to find K_f for $AuCl_4^-(aq)$ at 25°C.

61. Given the following information:

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq) \qquad K_{sp} = 1 \times 10^{-12}$$

$$Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad E° = +0.799 \text{ V}$$

find the standard reduction potential at 25°C for the half-reaction

$$Ag_2CrO_4(s) + 2e^- \longrightarrow 2Ag(s) + CrO_4^{2-}(aq)$$

62. What is $E°$ at 25°C for the following reaction?

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$$

K_{sp} for $BaSO_4$ is 1.1×10^{-10}.

17-5 Effect of Concentration on Voltage

63. Consider a voltaic cell at 25°C in which the following reaction takes place.

$$3H_2O_2(aq) + 6H^+(aq) + 2Au(s) \longrightarrow 2Au^{3+}(aq) + 6H_2O$$

(a) Calculate $E°$.
(b) Write the Nernst equation for the cell.
(c) Calculate E when $[Au^{3+}] = 0.250\ M$, $[H^+] = 1.25\ M$, $[H_2O_2] = 1.50\ M$.

64. Consider the voltaic cell at 25°C in which the following reaction takes place:

$$MnO_2(s) + 4H^+(aq) + 2Br^-(aq) \longrightarrow Br_2(l) + Mn^{2+}(aq) + 2H_2O$$

(a) Calculate $E°$.
(b) Write the Nernst equation for the cell.
(c) Find E under the following conditions: $[Mn^{2+}] = 0.60\ M$, $[Br^-] = 0.83\ M$, pH = 3.17

65. Consider a voltaic cell in which the following reaction takes place.

$$2Fe^{2+}(aq) + H_2O_2(aq) + 2H^+(aq) \longrightarrow 2Fe^{3+}(aq) + 2H_2O$$

(a) Calculate $E°$.
(b) Write the Nernst equation for the cell.
(c) Calculate E at 25°C under the following conditions: $[Fe^{2+}] = 0.00813\ M$, $[H_2O_2] = 0.914\ M$, $[Fe^{3+}] = 0.199\ M$, pH = 2.88.

66. Consider a voltaic cell in which the following reaction takes place in basic medium at 25°C.

$$2NO_3^-(aq) + 3S^{2-}(aq) + 4H_2O \longrightarrow 3S(s) + 2NO(g) + 8OH^-(aq)$$

(a) Calculate $E°$.
(b) Write the Nernst equation for the cell voltage E.
(c) Calculate E under the following conditions: $P_{NO} = 0.994$ atm, pH = 13.7, $[S^{2-}] = 0.154\ M$, $[NO_3^-] = 0.472\ M$

67. Calculate the voltages of the following cells at 25°C and under the following conditions:
(a) $Cu \mid Cu^+(0.80\ M) \parallel Hg_2^{2+}\ (0.10\ M) \mid Hg \mid Pt$
(b) $Cr \mid Cr^{3+}(0.615\ M) \parallel Ni^{2+}\ (0.228\ M) \mid Ni$

68. Calculate voltages of the following cells at 25°C and under the following conditions.
(a) $Zn \mid Zn^{2+}\ (0.50\ M) \parallel Cd^{2+}\ (0.020\ M) \mid Cd$
(b) $Cu \mid Cu^{2+}\ (0.0010\ M) \parallel H^+\ (0.010\ M) \mid H_2\ (1.00\ atm) \mid Pt$

69. Consider the reaction

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

At what concentration of Cu^{2+} is the voltage zero, if all other species are at $0.200\ M$?

70. Consider the reaction at 25°C:

$$S(s) + 2H^+(aq) + 2Ag(s) + 2Br^-(aq) \longrightarrow 2AgBr(s) + H_2S(aq)$$

At what pH is the voltage zero if all the species are at standard conditions?

71. Complete the following cell notation.

$$Ag \mid Br^-\ (3.73\ M) \mid AgBr \parallel H^+\ (?) \mid H_2\ (1.0\ atm) \mid Pt \qquad E = -0.030\ V$$

72. Complete the following cell notation.

$$Zn \mid Zn^{2+}(1.00\ M) \parallel H^+\ (?) \mid H_2(1.0\ atm) \mid Pt \qquad E = +0.40\ V$$

73. Consider the reaction below at 25°C:

$$2MnO_4^-(aq) + 16H^+(aq) + 10Br^-(aq) \longrightarrow 2Mn^{2+}(aq) + 5Br_2(l) + 8H_2O$$

Use Table 17.1 to answer the following questions. Support your answers with calculations.
(a) Is the reaction spontaneous at standard conditions?
(b) Is the reaction spontaneous at a pH of 2.00 with all other ionic species at $0.100\ M$?
(c) Is the reaction spontaneous at a pH of 5.00 with all other ionic species at $0.100\ M$?
(d) At what pH is the reaction at equilibrium with all other ionic species at $0.100\ M$?

74. Consider the reaction below at 25°C:

$$3SO_4^{2-}(aq) + 12H^+(aq) + 2Cr(s) \longrightarrow 3SO_2(g) + 2Cr^{3+}(aq) + 6H_2O$$

Use Table 17.1 to answer the following questions. Support your answers with calculations.
(a) Is the reaction spontaneous at standard conditions?
(b) Is the reaction spontaneous at a pH of 3.00 with all other ionic species at $0.100\ M$ and all gases at 1.00 atm?
(c) Is the reaction spontaneous at a pH of 8.00 with all other ionic species at $0.100\ M$ and all gases at 1.00 atm?
(d) At what pH is the reaction at equilibrium with all other ionic species at $0.100\ M$ and all gases at 1.00 atm?

75. Consider a cell in which the reaction is

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

(a) Calculate $E°$ for this cell.
(b) Chloride ions are added to the $Ag \mid Ag^+$ half-cell to precipitate AgCl. The measured voltage is +0.060 V. Taking $[Cu^{2+}] = 1.0\ M$, calculate $[Ag^+]$.
(c) Taking $[Cl^-]$ in (b) to be $0.10\ M$, calculate K_{sp} of AgCl.

76. Consider a cell in which the reaction is

$$Pb(s) + 2H^+(aq) \longrightarrow Pb^{2+}(aq) + H_2(g)$$

(a) Calculate $E°$ for this cell.
(b) Chloride ions are added to the $Pb \mid Pb^{2+}$ half-cell to precipitate $PbCl_2$. The voltage is measured to be +0.210 V. Taking $[H^+] = 1.0\ M$ and $P_{H_2} = 1.0$ atm, calculate $[Pb^{2+}]$.
(c) Taking $[Cl^-]$ in (b) to be $0.10\ M$, calculate K_{sp} of $PbCl_2$.

17-6 Electrolytic Cells

77. An electrolytic cell produces aluminum from Al_2O_3 at the rate of ten kilograms a day. Assuming a yield of 100%,
(a) how many moles of electrons must pass through the cell in one day?
(b) how many amperes are passing through the cell?
(c) how many moles of oxygen (O_2) are being produced simultaneously?

78. The electrolysis of an aqueous solution of NaCl has the overall equation

$$2H_2O + 2Cl^- \longrightarrow H_2(g) + Cl_2(g) + 2OH^-(ag)$$

During the electrolysis, 0.228 mol of electrons pass through the cell.
(a) How many electrons does this represent?
(b) How many coulombs does this represent?

(c) Assuming 100% yield, what masses of H_2 and Cl_2 are produced?

79. A solution containing a metal ion ($M^{2+}(aq)$) is electrolyzed by a current of 5.00 A. After 15.3 minutes, 2.83 g of the metal plated out.

(a) How many coulombs are supplied by the battery?

(b) What is the metal? (Assume 100% efficiency.)

80. A solution containing a metal ion ($M^{2+}(aq)$) is electrolyzed by a current of 7.8 A. After 15.5 minutes, 2.39 g of the metal is plated out.

(a) How many coulombs are supplied by the battery?

(b) What is the metal? (Assume 100% efficiency.)

81. A baby's spoon with an area of 6.25 cm^2 is plated with silver from $AgNO_3$ using a current of 2.00 A for two hours and 25 minutes.

(a) If the current efficiency is 82.0%, how many grams of silver are plated?

(b) What is the thickness of the silver plate formed (d = 10.5 g/cm^3)?

82. A metallurgist wants to gold-plate an object with a surface area of 17.21 in^2. The gold plating must be 0.00200 in. thick (assume uniform thickness).

(a) How many grams of gold (d = 10.5 g/cm^3) are required?

(b) How many minutes will it take to plate the object from a solution of AuCN using a current of 7.00 A? Assume 100% efficiency.

83. A lead storage battery delivers a current of 6.00 A for one hour and 22 minutes at a voltage of 12.0 V.

(a) How many grams of lead are converted to $PbSO_4$?

(b) How much electrical energy is produced in kilowatt hours?

84. Calcium metal can be obtained by the direct electrolysis of molten $CaCl_2$, at a voltage of 3.2 V.

(a) How many joules of electrical energy are required to obtain 12.0 lb of calcium?

(b) What is the cost of the electrical energy obtained in (a) if electrical energy is sold at the rate of nine cents per kilowatt hour?

Unclassified

85. Given the following data:

$$PtCl_4^{2-}(aq) + 2e^- \longrightarrow Pt(s) + 4Cl^-(aq) \qquad E^\circ_{red} = 0.73\ V$$

$$Pt^{2+}(aq) + 2e^- \longrightarrow Pt(s) \qquad E^\circ_{red} = 1.20\ V$$

Find K_f for $PtCl_4^{2-}$ at 25°C.

86. In a nickel-cadmium battery (Nicad), cadmium is oxidized to $Cd(OH)_2$ at the anode, while Ni_2O_3 is reduced to $Ni(OH)_2$ at the cathode. A portable CD player uses 0.175 amp of current. How many grams of Cd and Ni_2O_3 are consumed when the CD player is used for an hour and a half?

87. Hydrogen gas is produced when water is electrolyzed.

$$2H_2O(g) \longrightarrow 2H_2(g) + O_2(g)$$

A balloonist wants to fill a balloon with hydrogen gas. How long must a current of 12.0 A be used in the electrolysis of water to fill the balloon to a volume of 10.00 L and a pressure of 0.924 atm at 22°C?

88. Consider the electrolysis of $NiCl_2$ to Ni(s) and $Cl_2(g)$.

(a) What is the minimum voltage required to carry out this reaction at standard conditions?

(b) If a voltage of 3.0 V is actually used, and 10.00 kJ of energy are consumed, how many grams of Ni(s) are obtained? (1 J = 1 volt-coulomb)

89. An electrolysis experiment is performed to determine the value of the Faraday constant (number of coulombs per mole of electrons). In this experiment, 28.8 g of gold is plated out from a AuCN solution by running an electrolytic cell for two hours with a current of 2.00 A. What is the experimental value obtained for the Faraday constant?

90. An electrolytic cell consists of a 100.0-g strip of copper in 0.200 M $Cu(NO_3)_2$ and a 100.0-g strip of Cr in 0.200 M $Cr(NO_3)_3$. The overall reaction is:

$$3Cu(s) + 2Cr^{3+}(aq) \longrightarrow 3Cu^{2+}(aq) + 2Cr(s) \quad E^\circ = -1.083\ V$$

An external battery provides 3 amperes for 70 minutes and 20 seconds with 100% efficiency. What is the mass of the copper strip after the battery has been disconnected?

91. After use, a nickel-cadmium battery (Nicad) has 0.133 g of $Cd(OH)_2$ deposited on the anode. The battery is inserted into a recharger to convert all the $Cd(OH)_2$ back to Cd. It takes the recharger 18.3 minutes to complete the process. How many amperes did the recharger supply? Assume 100% efficiency. (See Problem 86 for a description of a Nicad battery.)

92. Consider the following reaction carried out at 1000°C.

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g)$$

Assuming that all gases are at 1.00 atm, calculate the voltage produced at the given conditions. (Use Appendix 1 and assume that ΔH° and ΔS° do not change with an increase in temperature.)

93. Atomic masses can be determined by electrolysis. In one hour, a current of 0.600 A deposits 2.42 g of a certain metal, M, which is present in solution as M^+ ions. What is the atomic mass of the metal?

94. Consider the following reaction at 25°C:

$$O_2(g) + 4H^+(aq) + 4Cl^-(aq) \longrightarrow 2H_2O + 2Cl_2(g)$$

The $[H^+]$ is adjusted by adding a buffer that is 0.125 M in lactic acid (HLac) and 0.125 M in sodium lactate (NaLac). The pressure of both gases is 1.00 atm and $[Cl^-]$ is 0.200 M. (K_a for HLac is 1.4×10^{-4}.) Will the cell function as a voltaic cell?

95. Given the standard reduction potential for $Zn(OH)_4^{2-}$:

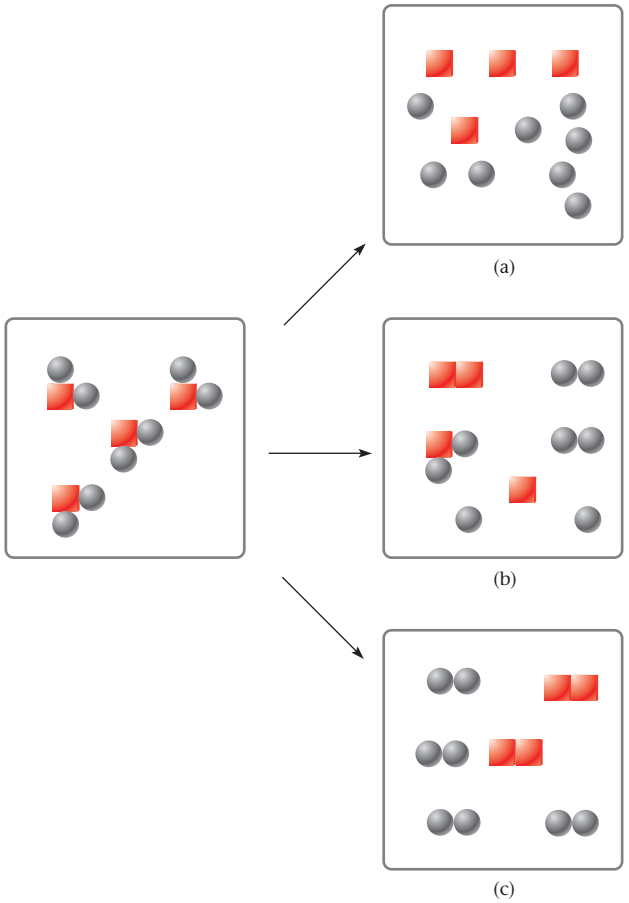
$$Zn(OH)_4^{2-}(aq) + 2e^- \longrightarrow Zn(s) + 4\,OH^-(aq) \qquad E^\circ_{red} = -1.19\ V$$

Calculate the formation constant (K_f) for the reaction

$$Zn^{2+}(aq) + 4OH^-(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq)$$

Conceptual Problems

96. Choose the figure that best represents the results after the electrolysis of water. (Circles represent hydrogen atoms and squares represent oxygen atoms.)



97. For the cell:

$$\text{Cr} \mid \text{Cr}^{3+} \parallel \text{Co}^{2+} \mid \text{Co}$$

$E°$ is 0.46 V. The same cell was prepared in the laboratory at standard conditions. The voltage obtained was 0.40 V. A possible explanation for the difference is

(a) the surface area of the chromium electrode was smaller than the cobalt electrode.
(b) the mass of the chromium electrode was larger than the mass of the cobalt electrode.
(c) the concentration of $Co(NO_3)_2$ solution used was less than 1.0 *M*.
(d) the concentration of $Cr(NO_3)_2$ solution used was less than 1.0 *M*.
(e) the volume of $Co(NO_3)_2$ solution used was larger than the volume of $Cr(NO_3)_2$ solution used.

98. Which of the changes below will increase the voltage of the following cell?

$$\text{Co} \mid \text{Co}^{2+}\ (0.010\ M) \parallel \text{H}^{+}\ (0.010\ M) \mid \text{H}_2\ (0.500\ \text{atm}) \mid \text{Pt}$$

(a) Increase the volume of $CoCl_2$ solution from 100 mL to 300 mL.
(b) Increase $[H^+]$ from 0.010 *M* to 0.500 *M*.
(c) Increase the pressure of H_2 from 0.500 atm to 1 atm.
(d) Increase the mass of the Co electrode from 15 g to 25 g.
(e) Increase $[Co^{2+}]$ from 0.010 *M* to 0.500 *M*.

99. The standard potential for the reduction of AgSCN is 0.0895 V.

$$\text{AgSCN}(s) + e^- \longrightarrow \text{Ag}(s) + \text{SCN}^-(aq)$$

Find another electrode potential to use together with the above value and calculate K_{sp} for AgSCN.

100. Consider the following standard reduction potentials:

$$\text{Tl}^+(aq) + e^- \longrightarrow \text{Tl}(s) \qquad E°_{red} = -0.34\ \text{V}$$
$$\text{Tl}^{3+}(aq) + 3e^- \longrightarrow \text{Tl}(s) \qquad E°_{red} = 0.74\ \text{V}$$
$$\text{Tl}^{3+}(aq) + 2e^- \longrightarrow \text{Tl}^+(aq) \qquad E°_{red} = 1.28\ \text{V}$$

and the following abbreviated cell notations:

(1) $\text{Tl} \mid \text{Tl}^+ \parallel \text{Tl}^{3+}, \text{Tl}^+ \mid \text{Pt}$
(2) $\text{Tl} \mid \text{Tl}^{3+} \parallel \text{Tl}^{3+}, \text{Tl}^+ \mid \text{Pt}$
(3) $\text{Tl} \mid \text{Tl}^+ \parallel \text{Tl}^{3+} \mid \text{Tl}$

(a) Write the overall equation for each cell.
(b) Calculate $E°$ for each cell.
(c) Calculate $\Delta G°$ for each overall equation.
(d) Comment on whether $\Delta G°$ and/or $E°$ are state properties. (*Hint:* A state property is path-independent.)

101. Use Table 17.1 to answer the following questions. Use **LT** (for *is less than*), **GT** (for *is greater than*), **EQ** (for *is equal to*), or **MI** (for *more information required*).

(a) For the half reaction

$$\tfrac{1}{2}\text{Br}_2(l) + e^- \longrightarrow \text{Br}^-(aq)$$

$E°_{red}$ _____ 1.077 V.

(b) For the reaction

$$2\text{Br}^-(aq) + \text{Co}^{2+}(aq) \longrightarrow \text{Br}_2(l) + \text{Co}(s)$$

$E°$ _____ 0.

(c) If the half reaction

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

is designated as the new standard where $E°_{red}$ is 0.00, then $E°_{red}$ for

$$2\text{H}^+(aq) + 2e^- \longrightarrow \text{H}_2(g)$$

is _____ 0.

(d) For the reaction

$$2\text{Cr}^{3+}(aq) + 3\text{Co}(s) \longrightarrow 2\text{Cr}(s) + 3\text{Co}^{2+}(aq)$$

the number of electrons exchanged is _____ 6.

(e) For the reaction described in (d), the number of coulombs that passes through the cell is _____ 9.648×10^4.

102. Consider three metals, X, Y, and Z, and their salts, XA, YA, and ZA. Three experiments take place with the following results:

- X + hot $H_2O \longrightarrow H_2$ bubbles
- X + YA $\longrightarrow$ no reaction
- X + ZA $\longrightarrow$ X discolored + Z

Rank metals X, Y, and Z, in order of decreasing strength as reducing agents.

Challenge Problems

103. An alloy made up of tin and copper is prepared by simultaneously electroplating the two metals from a solution containing $Sn(NO_3)_2$ and $Cu(NO_3)_2$. If 20.0% of the total current is used to plate tin, while 80.0% is used to plate copper, what is the percent composition of the alloy?

104. In a fully charged lead storage battery, the electrolyte consists of 38% sulfuric acid by mass. The solution has a density of 1.286 g/cm^3. Calculate E for the cell. Assume all the H^+ ions come from the first dissociation of H_2SO_4, which is complete.

105. Consider a voltaic cell in which the following reaction occurs.

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

(**a**) Calculate $E°$ for the cell.

(**b**) When the cell operates, what happens to the concentration of Zn^{2+}? The concentration of Sn^{2+}?

(**c**) When the cell voltage drops to zero, what is the ratio of the concentration of Zn^{2+} to that of Sn^{2+}?

(**d**) If the concentration of both cations is 1.0 M originally, what are the concentrations when the voltage drops to zero?

106. In biological systems, acetate ion is converted to ethyl alcohol in a two-step process:

$$CH_3COO^-(aq) + 3H^+(aq) + 2e^- \longrightarrow CH_3CHO(aq) + H_2O \qquad E°' = -0.581\ V$$

$$CH_3CHO(aq) + 2H^+(aq) + 2e^- \longrightarrow C_2H_5OH(aq) \qquad E°' = -0.197\ V$$

($E°'$ is the standard reduction voltage at 25°C and pH of 7.00.)

(**a**) Calculate $\Delta G°'$ for each step and for the overall conversion.

(**b**) Calculate $E°'$ for the overall conversion.

107. Consider the cell

$$Pt \mid H_2 \mid H^+ \parallel H^+ \mid H_2 \mid Pt$$

In the anode half-cell, hydrogen gas at 1.0 atm is bubbled over a platinum electrode dipping into a solution that has a pH of 7.0. The other half-cell is identical to the first except that the solution around the platinum electrode has a pH of 0.0. What is the cell voltage?

108. A hydrogen-oxygen fuel cell operates on the reaction:

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l)$$

If the cell is designed to produce 1.5 amp of current and if the hydrogen is contained in a 1.0-L tank at 200 atm pressure and 25°C, how long can the fuel cell operate before the hydrogen runs out? Assume that oxygen gas is in excess.

109. An alloy is made up of 68% zinc and 32% tin. It is prepared by simultaneously electroplating the two metals from a solution containing both $Zn(NO_3)_2$ and $Sn(NO_3)_2$. What percent of the total current is used to plate each metal?