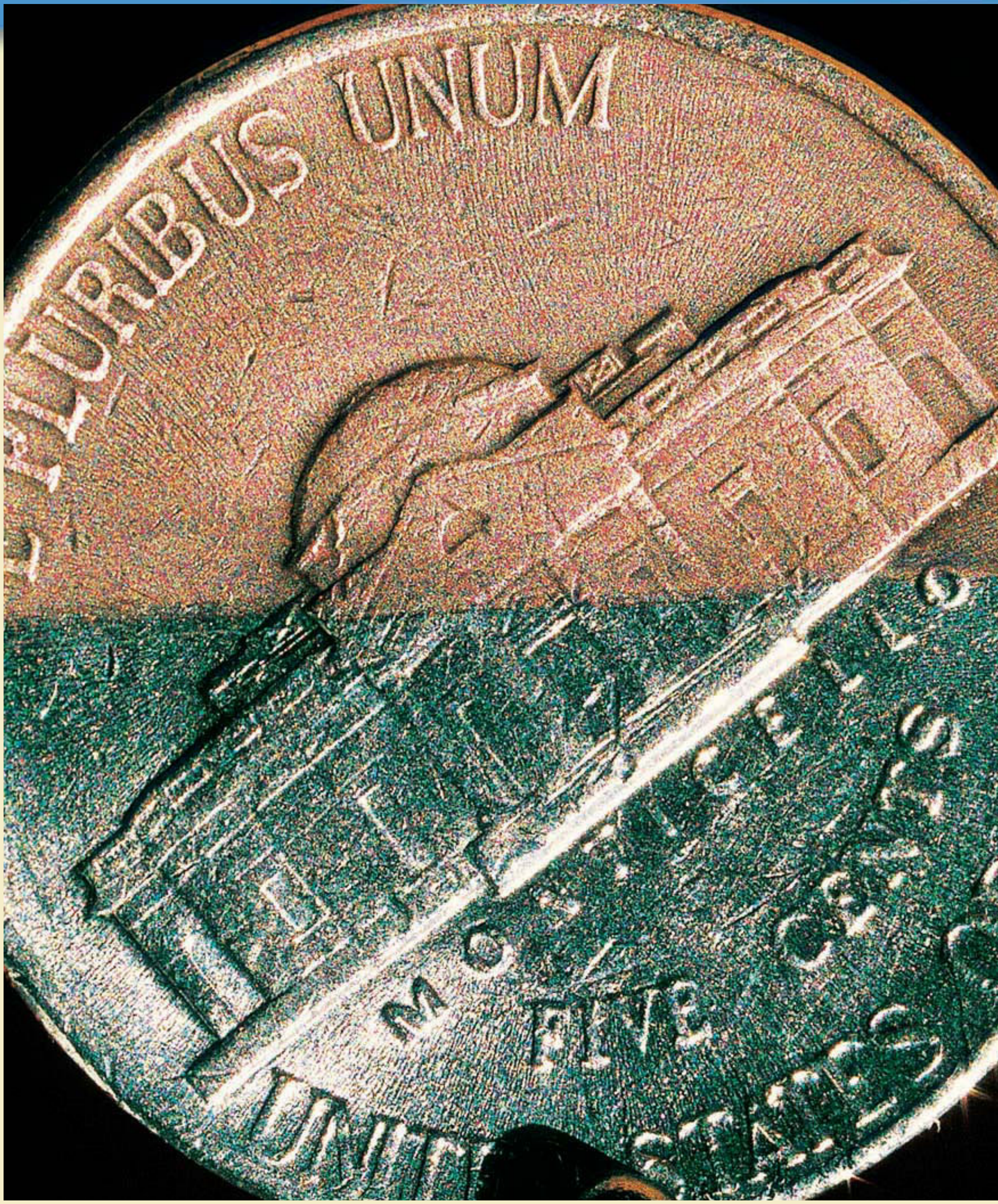
17 Electrochemistry

Contents



A nickel half-electroplated with copper.

Electrochemistry constitutes one of the most important interfaces between chemistry and everyday life. Every time you start your car, turn on your calculator, look at your digital watch, or listen to a radio at the beach, you are depending on electrochemical reactions. Our society sometimes seems to run almost entirely on batteries. Certainly the advent of small, dependable batteries along with silicon-chip technology has made possible the tiny calculators, tape recorders, and clocks that we take for granted.

Electrochemistry is important in other less obvious ways. For example, the corrosion of iron, which has tremendous economic implications, is an electrochemical process. In addition, many important industrial materials such as aluminum, chlorine, and sodium hydroxide are prepared by electrolytic processes. In analytical chemistry, electrochemical techniques employ electrodes that are specific for a given molecule or ion, such as H^+ (pH meters), F^-, Cl^-, and many others. These increasingly important methods are used to analyze for trace pollutants in natural waters or for the tiny quantities of chemicals in human blood that may signal the development of a specific disease.

Electrochemistry is best defined as *the study of the interchange of chemical and electrical energy.* It is primarily concerned with two processes that involve oxidation–reduction reactions: the generation of an electric current from a spontaneous chemical reaction and the opposite process, the use of a current to produce chemical change.

17.1 Galvanic Cells

As we discussed in detail in Section 4.9, an **oxidation–reduction (redox) reaction** involves a transfer of electrons from the **reducing agent** to the **oxidizing agent.** Recall that **oxidation** involves a *loss of electrons* (an increase in oxidation number) and that **reduction** involves a *gain of electrons* (a decrease in oxidation number).

To understand how a redox reaction can be used to generate a current, let's consider the reaction between MnO_4^- and Fe^{2+}:

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

In this reaction, Fe^{2+} is oxidized and MnO_4^- is reduced; electrons are transferred from Fe^{2+} (the reducing agent) to MnO_4^- (the oxidizing agent).

Balancing half-reactions is discussed in Section 4.10.

It is useful to break a redox reaction into **half-reactions,** one involving oxidation and one involving reduction. For the reaction above, the half-reactions are

$$\text{Reduction:}\quad 8H^+ + MnO_4^- + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$
$$\text{Oxidation:}\quad 5(Fe^{2+} \longrightarrow Fe^{3+} + e^-)$$

The multiplication of the second half-reaction by 5 indicates that this reaction must occur five times for each time the first reaction occurs. The balanced overall reaction is the sum of the half-reactions.

When MnO_4^- and Fe^{2+} are present in the same solution, the electrons are transferred directly when the reactants collide. Under these conditions, no useful work is obtained from the chemical energy involved in the reaction, which instead is released as heat. How can we harness this energy? The key is to separate the oxidizing agent from the reducing agent, thus requiring the electron transfer to occur through a wire. The current produced in the wire by the electron flow can then be directed through a device, such as an electric motor, to provide useful work.

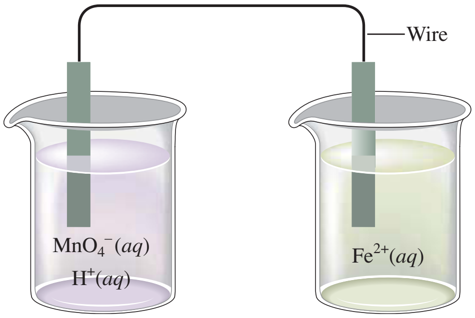


FIGURE 17.1
Schematic of a method to separate the oxidizing and reducing agents of a redox reaction. (The solutions also contain counterions to balance the charge.)

For example, consider the system illustrated in Fig. 17.1. If our reasoning has been correct, electrons should flow through the wire from Fe^{2+} to MnO_4^-. However, when we construct the apparatus as shown, no flow of electrons is apparent. Why? Careful observation shows that when we connect the wires from the two compartments, current flows for an instant and then ceases. The current stops flowing because of charge buildups in the two compartments. If electrons flowed from the right to the left compartment in the apparatus as shown, the left compartment (receiving electrons) would become negatively charged, and the right compartment (losing electrons) would become positively charged. Creating a charge separation of this type requires a large amount of energy. Thus sustained electron flow cannot occur under these conditions.

However, we can solve this problem very simply. The solutions must be connected so that ions can flow to keep the net charge in each compartment zero. This connection might involve a **salt bridge** (a U-tube filled with an electrolyte) or a **porous disk** in a tube connecting the two solutions (see Fig. 17.2). Either of these devices allows ions to flow without extensive mixing of the solutions. When we make the provision for ion flow, the circuit is complete. Electrons flow through the wire from reducing agent to oxidizing agent, and ions flow from one compartment to the other to keep the net charge zero.

A galvanic cell uses a spontaneous redox reaction to produce a current that can be used to do work.

We now have covered all the essential characteristics of a **galvanic cell,** *a device in which chemical energy is changed to electrical energy.* (The opposite process is called *electrolysis* and will be considered in Section 17.7.)

Oxidation occurs at the anode. Reduction occurs at the cathode.

The reaction in an electrochemical cell occurs at the interface between the electrode and the solution where the electron transfer occurs. The electrode compartment in which *oxidation* occurs is called the **anode;** the electrode compartment in which *reduction* occurs is called the **cathode** (see Fig. 17.3).

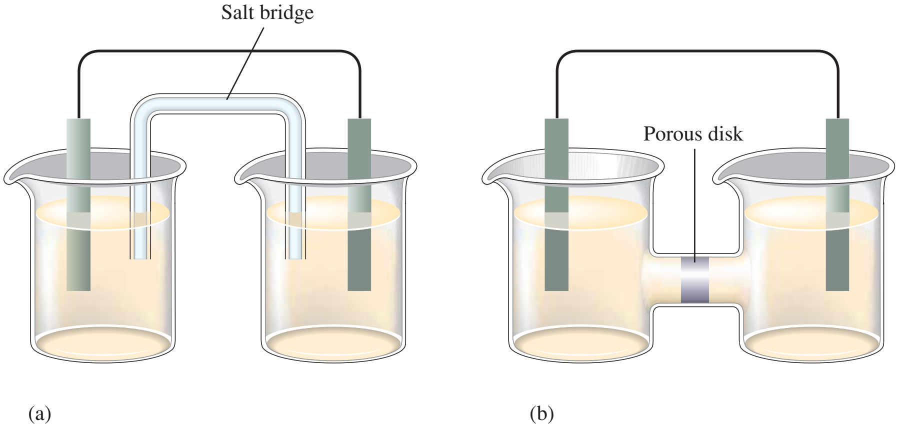


FIGURE 17.2
Galvanic cells can contain a salt bridge as in (a) or a porous-disk connection as in (b). A salt bridge contains a strong electrolyte held in a Jello-like matrix. A porous disk contains tiny passages that allow hindered flow of ions.

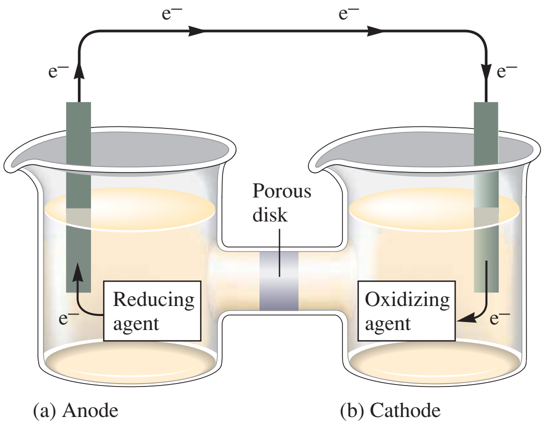


FIGURE 17.3
An electrochemical process involves electron transfer at the interface between the electrode and the solution. (a) The species in the solution acting as the reducing agent supplies electrons to the anode. (b) The species in the solution acting as the oxidizing agent receives electrons from the cathode.

Cell Potential

Visualization: Voltaic Cell: Cathode Reaction

Visualization: Voltaic Cell: Anode Reaction

A volt is 1 joule of work per coulomb of charge transferred: 1 V = 1 J/C.

A galvanic cell consists of an oxidizing agent in one compartment that pulls electrons through a wire from a reducing agent in the other compartment. The "pull," or driving force, on the electrons is called the **cell potential** ($\mathscr{E}_{\text{cell}}$), or the **electromotive force** (emf) of the cell. The unit of electrical potential is the **volt** (abbreviated V), which is defined as 1 joule of work per coulomb of charge transferred.

How can we measure the cell potential? One possible instrument is a crude **voltmeter,** which works by drawing current through a known resistance. However, when current flows through a wire, the frictional heating that occurs wastes some of the potentially useful energy of the cell. A traditional voltmeter will therefore measure a potential that is less than the maximum cell potential. The key to determining the maximum potential is to do the measurement under conditions of zero current so that no energy is wasted. Traditionally, this has been accomplished by inserting a variable-voltage device (powered from an external source) in *opposition* to the cell potential. The voltage on this instrument (called a **potentiometer**) is adjusted until no current flows in the cell circuit. Under such conditions, the cell potential is equal in magnitude and opposite in sign to the voltage setting of the potentiometer. This value represents the *maximum* cell potential, since no energy is wasted heating the wire. More recently, advances in electronic technology have allowed the design of *digital voltmeters* that draw only a negligible amount of current (see Fig. 17.4). Since these instruments are more convenient to use, they have replaced potentiometers in the modern laboratory.

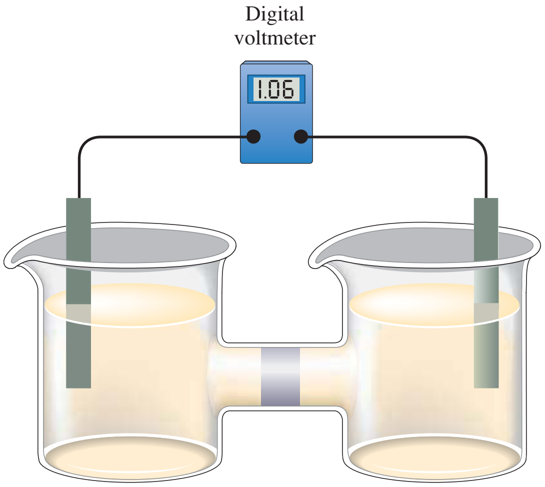


FIGURE 17.4
Digital voltmeters draw only a negligible current and are convenient to use.

17.2 Standard Reduction Potentials

The reaction in a galvanic cell is always an oxidation–reduction reaction that can be broken down into two half-reactions. It would be convenient to assign a potential to *each* half-reaction so that when we construct a cell from a given pair of half-reactions we can obtain the cell potential by summing the half-cell potentials. For example, the observed potential for the cell shown in Fig. 17.5(a) is 0.76 V, and the cell reaction* is

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

The name *galvanic cell* honors Luigi Galvani (1737–1798), an Italian scientist generally credited with the discovery of electricity. These cells are sometimes called *voltaic cells* after Alessandro Volta (1745–1827), another Italian, who first constructed cells of this type around 1800.

For this cell, the anode compartment contains a zinc metal electrode with Zn^{2+} and SO_4^{2-} ions in aqueous solution. The anode reaction is the oxidation half-reaction:

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

The zinc metal, in producing Zn^{2+} ions that go into solution, is giving up electrons, which flow through the wire. For now, we will assume that all cell components are in their standard states, so in this case the solution in the anode compartment will contain 1 *M* Zn^{2+}. The cathode reaction of this cell is the reduction half-reaction:

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

The cathode consists of a platinum electrode (used because it is a chemically inert conductor) in contact with 1 *M* H^+ ions and bathed by hydrogen gas at 1 atm. Such an electrode, called the **standard hydrogen electrode,** is shown in Fig. 17.5(b).

Although we can measure the *total* potential of this cell (0.76 V), there is no way to measure the potentials of the individual electrode processes. Thus, if we want potentials for the half-reactions (half-cells), we must arbitrarily divide the total cell potential. For example, if we assign the reaction

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

An electrochemical cell with a measured potential of 1.10 V.

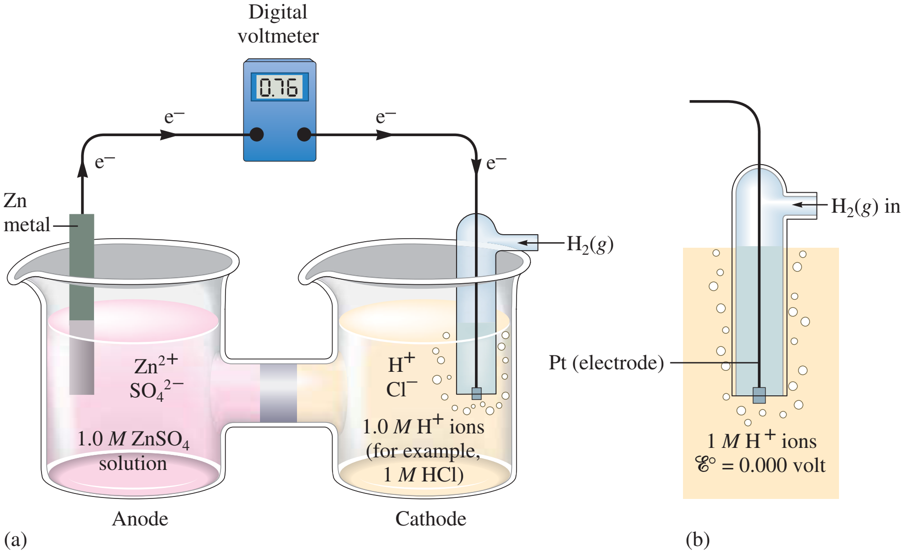


FIGURE 17.5
(a) A galvanic cell involving the reactions $Zn \rightarrow Zn^{2+} + 2e^-$ (at the anode) and $2H^+ + 2e^- \rightarrow H_2$ (at the cathode) has a potential of 0.76 V. (b) The standard hydrogen electrode where $H_2(g)$ at 1 atm is passed over a platinum electrode in contact with 1 *M* H^+ ions. This electrode process (assuming ideal behavior) is arbitrarily assigned a value of exactly zero volts.

---

*In this text we will follow the convention of indicating the physical states of the reactants and products only in the overall redox reaction. For simplicity, half-reactions will *not* include the physical states.

where $$[\mathrm{H}^+] = 1\,M \quad \text{and} \quad P_{\mathrm{H}_2} = 1\text{ atm}$$

a potential of exactly zero volts, then the reaction

$$\mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+} + 2\mathrm{e}^-$$

will have a potential of 0.76 V because

$$\underset{\underset{0.76\text{ V}}{\uparrow}}{\mathscr{E}^\circ_{\text{cell}}} = \underset{\underset{0\text{ V}}{\uparrow}}{\mathscr{E}^\circ_{\mathrm{H}^+ \rightarrow \mathrm{H}_2}} + \underset{\underset{0.76\text{ V}}{\uparrow}}{\mathscr{E}^\circ_{\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+}}}$$

Visualization: Electrochemical Half-Reactions in a Galvanic Cell

Standard states were discussed in Section 6.4.

where the superscript ° indicates that *standard states* are employed. In fact, by setting the standard potential for the half-reaction $2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{H}_2$ equal to zero, we can assign values to all other half-reactions.

For example, the measured potential for the cell shown in Fig. 17.6 is 1.10 V. The cell reaction is

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

Visualization: Zinc/Copper Cells with Lemons

which can be divided into the half-reactions

$$\begin{aligned} &\text{Anode:} && \mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+} + 2\mathrm{e}^- \\ &\text{Cathode:} && \mathrm{Cu}^{2+} + 2\mathrm{e}^- \longrightarrow \mathrm{Cu} \end{aligned}$$

Then $$\mathscr{E}^\circ_{\text{cell}} = \mathscr{E}^\circ_{\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+}} + \mathscr{E}^\circ_{\mathrm{Cu}^{2+} \rightarrow \mathrm{Cu}}$$

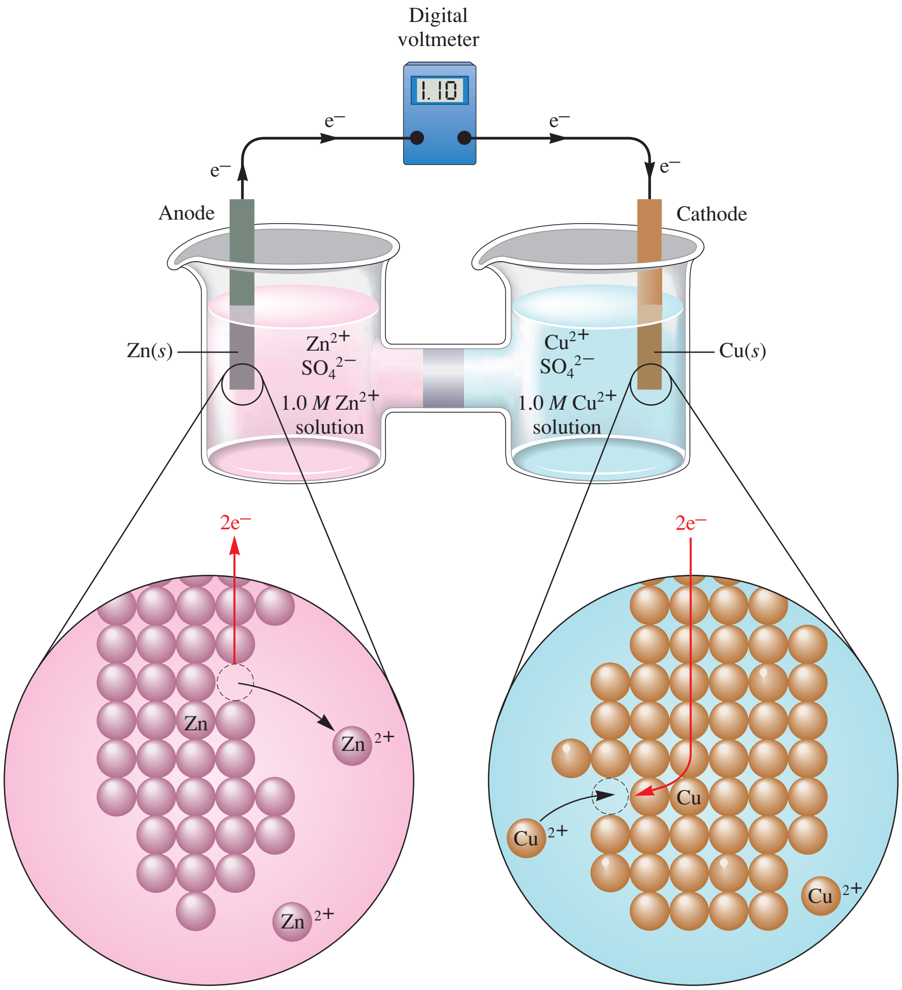


FIGURE 17.6
A galvanic cell involving the half-reactions $\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+} + 2\mathrm{e}^-$ (anode) and $\mathrm{Cu}^{2+} + 2\mathrm{e}^- \rightarrow \mathrm{Cu}$ (cathode), with $\mathscr{E}^\circ_{\text{cell}} = 1.10$ V.

Since $\mathscr{E}^\circ_{\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+}}$ was earlier assigned a value of 0.76 V, the value of $\mathscr{E}^\circ_{\mathrm{Cu}^{2+} \rightarrow \mathrm{Cu}}$ must be 0.34 V because

$$1.10 \text{ V} = 0.76 \text{ V} + 0.34 \text{ V}$$

The standard hydrogen potential is the reference potential against which all half-reaction potentials are assigned.

The scientific community has universally accepted the half-reaction potentials based on the assignment of zero volts to the process $2H^+ + 2e^- \rightarrow H_2$ (under standard conditions where ideal behavior is assumed). However, before we can use these values to calculate cell potentials, we need to understand several essential characteristics of half-cell potentials.

The accepted convention is to give the potentials of half-reactions as *reduction* processes. For example:

Visualization: Galvanic (Voltaic) Cells

$$\begin{aligned} 2H^+ + 2e^- &\longrightarrow H_2 \\ Cu^{2+} + 2e^- &\longrightarrow Cu \\ Zn^{2+} + 2e^- &\longrightarrow Zn \end{aligned}$$

All half-reactions are given as reduction processes in standard tables.

The $\mathscr{E}^\circ$ values corresponding to reduction half-reactions with all solutes at 1 *M* and all gases at 1 atm are called **standard reduction potentials.** Standard reduction potentials for the most common half-reactions are given in Table 17.1 and Appendix 5.5.

Combining two half-reactions to obtain a balanced oxidation–reduction reaction often requires two manipulations:

1. One of the reduction half-reactions must be reversed (since redox reactions must involve a substance being oxidized and a substance being reduced). The half-reaction with the largest positive potential will run as written (as a reduction), and the other

TABLE 17.1 Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions

Half-Reaction	$\mathscr{E}^\circ$ (V)	Half-Reaction	$\mathscr{E}^\circ$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3-} + e^- \rightarrow Co^{2-}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^- + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

When a half-reaction is reversed, the sign of $\mathscr{E}^\circ$ is reversed.

half-reaction will be forced to run in reverse (will be the oxidation reaction). The net potential of the cell will be the *difference* between the two. Since the reduction process occurs at the cathode and the oxidation process occurs at the anode, we can write

$$\mathscr{E}^\circ_{\text{cell}} = \mathscr{E}^\circ\,(\text{cathode}) - \mathscr{E}^\circ\,(\text{anode})$$

Because subtraction means "change the sign and add," in the examples done here we will change the sign of the oxidation (anode) reaction when we reverse it and add it to the reduction (cathode) reaction.

When a half-reaction is multiplied by an integer, $\mathscr{E}^\circ$ remains the same.

2. Since the number of electrons lost must equal the number gained, the half-reactions must be multiplied by integers as necessary to achieve the balanced equation. However, the *value of* $\mathscr{E}^\circ$ *is not changed* when a half-reaction is multiplied by an integer. Since a standard reduction potential is an *intensive property* (it does not depend on how many times the reaction occurs), the potential is *not* multiplied by the integer required to balance the cell reaction.

   Consider a galvanic cell based on the redox reaction

$$\text{Fe}^{3+}(aq) + \text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq) + \text{Fe}^{2+}(aq)$$

The pertinent half-reactions are

$$\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+} \qquad \mathscr{E}^\circ = 0.77\ \text{V} \qquad (1)$$

$$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu} \qquad \mathscr{E}^\circ = 0.34\ \text{V} \qquad (2)$$

Visualization: Copper Metal in Water
Visualization: Copper Metal in Sulfuric Acid
Visualization: Copper Metal in Hydrochloric Acid
Visualization: Copper Metal in Nitric Acid

To balance the cell reaction and calculate the standard cell potential, reaction (2) must be reversed:

$$\text{Cu} \longrightarrow \text{Cu}^{2+} + 2\text{e}^- \qquad -\mathscr{E}^\circ = -0.34\ \text{V}$$

Note the change in sign for the $\mathscr{E}^\circ$ value. Now, since each Cu atom produces two electrons but each Fe^{3+} ion accepts only one electron, reaction (1) must be multiplied by 2:

$$2\text{Fe}^{3+} + 2\text{e}^- \longrightarrow 2\text{Fe}^{2+} \qquad \mathscr{E}^\circ = 0.77\ \text{V}$$

Note that $\mathscr{E}^\circ$ is not changed in this case.

Now we can obtain the balanced cell reaction by summing the appropriately modified half-reactions:

$$\begin{array}{lll}
 & 2\text{Fe}^{3+} + 2\text{e}^- \longrightarrow 2\text{Fe}^{2+} & \mathscr{E}\,(\text{cathode}) = 0.77\ \text{V} \\
 & \text{Cu} \longrightarrow \text{Cu}^{2+} + 2\text{e}^- & -\mathscr{E}\,(\text{anode}) = -0.34\ \text{V} \\
\hline
\text{Cell reaction:} & \text{Cu}(s) + 2\text{Fe}^{3+}(aq) \longrightarrow \text{Cu}^{2+}(aq) + 2\text{Fe}^{2+}(aq) & \mathscr{E}^\circ_{\text{cell}} = \mathscr{E}^\circ\,(\text{cathode}) - \mathscr{E}^\circ\,(\text{anode}) \\
 & & = 0.77\ \text{V} - 0.34\ \text{V} = 0.43\ \text{V}
\end{array}$$

Sample Exercise 17.1 Galvanic Cells

a. Consider a galvanic cell based on the reaction

$$\text{Al}^{3+}(aq) + \text{Mg}(s) \longrightarrow \text{Al}(s) + \text{Mg}^{2+}(aq)$$

The half-reactions are

$$\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al} \qquad \mathscr{E}^\circ = -1.66\ \text{V} \qquad (1)$$

$$\text{Mg}^{2+} + 2\text{e}^- \longrightarrow \text{Mg} \qquad \mathscr{E}^\circ = -2.37\ \text{V} \qquad (2)$$

Give the balanced cell reaction and calculate $\mathscr{E}^\circ$ for the cell.

b. A galvanic cell is based on the reaction

$$\text{MnO}_4^-(aq) + \text{H}^+(aq) + \text{ClO}_3^-(aq) \longrightarrow \text{ClO}_4^-(aq) + \text{Mn}^{2+}(aq) + \text{H}_2\text{O}(l)$$

The half-reactions are

$$MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O \qquad \mathscr{E}° = 1.51\text{ V} \qquad (1)$$
$$ClO_4^- + 2H^+ + 2e^- \longrightarrow ClO_3^- + H_2O \qquad \mathscr{E}° = 1.19\text{ V} \qquad (2)$$

Give the balanced cell reaction and calculate $\mathscr{E}°$ for the cell.

Solution

a. The half-reaction involving magnesium must be reversed and since this is the oxidation process, it is the anode:

$$Mg \longrightarrow Mg^{2+} + 2e^- \qquad -\mathscr{E}°\text{ (anode)} = -(-2.37\text{ V}) = 2.37\text{ V}$$

Also, since the two half-reactions involve different numbers of electrons, they must be multiplied by integers as follows:

$$\begin{array}{rlr} 2(Al^{3+} + 3e^- \longrightarrow Al) & & \mathscr{E}°\text{ (cathode)} = -1.66\text{ V} \\ 3(Mg \longrightarrow Mg^{2+} + 2e^-) & & -\mathscr{E}°\text{ (anode)} = 2.37\text{ V} \\ \hline 2Al^{3+}(aq) + 3Mg(s) \longrightarrow 2Al(s) + 3Mg^{2+}(aq) & & \mathscr{E}°_{cell} = \mathscr{E}°\text{ (cathode)} - \mathscr{E}°\text{ (anode)} \\ & & = -1.66\text{ V} + 2.37\text{ V} = 0.71\text{ V} \end{array}$$

b. Half-reaction (2) must be reversed (it is the anode), and both half-reactions must be multiplied by integers to make the number of electrons equal:

$$\begin{array}{rr} 2(MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O) & \mathscr{E}°\text{ (cathode)} = 1.51\text{ V} \\ 5(ClO_3^- + H_2O \longrightarrow ClO_4^- + 2H^+ + 2e^-) & -\mathscr{E}°\text{ (anode)} = -1.19\text{ V} \\ \hline 2MnO_4^-(aq) + 6H^+(aq) + 5ClO_3^-(aq) \longrightarrow & \mathscr{E}°_{cell} = \mathscr{E}°\text{ (cathode)} - \mathscr{E}°\text{ (anode)} \\ 2Mn^{2+}(aq) + 3H_2O(l) + 5ClO_4^-(aq) & = 1.51\text{ V} - 1.19\text{ V} = 0.32\text{ V} \end{array}$$

See Exercises 17.27 and 17.28.

Line Notation

We now will introduce a handy line notation used to describe electrochemical cells. In this notation the anode components are listed on the left and the cathode components are listed on the right, separated by double vertical lines (indicating the salt bridge or porous disk). For example, the line notation for the cell described in Sample Exercise 17.1(a) is

$$Mg(s)|Mg^{2+}(aq)||Al^{3+}(aq)|Al(s)$$

In this notation a phase difference (boundary) is indicated by a single vertical line. Thus, in this case, vertical lines occur between the solid Mg metal and the Mg^{2+} in aqueous solution and between solid Al and Al^{3+} in aqueous solution. Also note that the substance constituting the anode is listed at the far left and the substance constituting the cathode is listed at the far right.

For the cell described in Sample Exercise 17.1(b), all the components involved in the oxidation–reduction reaction are ions. Since none of these dissolved ions can serve as an electrode, a nonreacting (inert) conductor must be used. The usual choice is platinum. Thus, for the cell described in Sample Exercise 17.1(b), the line notation is

$$Pt(s)|ClO_3^-(aq), ClO_4^-(aq), H^+(aq)||H^+(aq), MnO_4^-(aq), Mn^{2+}(aq)|Pt(s)$$

Complete Description of a Galvanic Cell

Next we want to consider how to describe a galvanic cell fully, given just its half-reactions. This description will include the cell reaction, the cell potential, and the physical setup of the cell. Let's consider a galvanic cell based on the following half-reactions:

$$\begin{array}{lr} Fe^{2+} + 2e^- \longrightarrow Fe & \mathscr{E}^\circ = -0.44\ V \\ MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O & \mathscr{E}^\circ = 1.51\ V \end{array}$$

In a working galvanic cell, one of these reactions must run in reverse. Which one?

A galvanic cell runs spontaneously in the direction that gives a positive value for $\mathscr{E}_{cell}$.

We can answer this question by considering the sign of the potential of a working cell: *A cell will always run spontaneously in the direction that produces a positive cell potential.* Thus, in the present case, it is clear that the half-reaction involving iron must be reversed, since this choice leads to a positive cell potential:

$$\begin{array}{rlr} Fe \longrightarrow Fe^{2+} + 2e^- & -\mathscr{E}^\circ = 0.44\ V & \text{Anode reaction} \\ MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O & \mathscr{E}^\circ = 1.51\ V & \text{Cathode reaction} \end{array}$$

where $\mathscr{E}^\circ_{cell} = \mathscr{E}^\circ\,(\text{cathode}) - \mathscr{E}^\circ\,(\text{anode}) = 1.51\ V + 0.44\ V = 1.95\ V$

The balanced cell reaction is obtained as follows:

$$\begin{array}{r} 5(Fe \longrightarrow Fe^{2+} + 2e^-) \\ 2(MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O) \\ \hline 2MnO_4^-(aq) + 5Fe(s) + 16H^+(aq) \longrightarrow 5Fe^{2+}(aq) + 2Mn^{2+}(aq) + 8H_2O(l) \end{array}$$

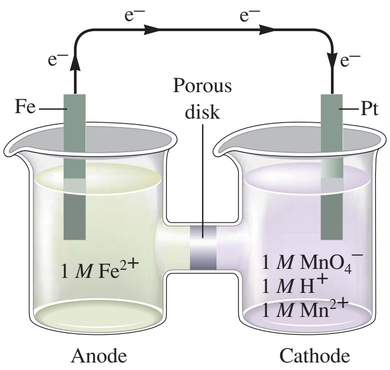


FIGURE 17.7
The schematic of a galvanic cell based on the half-reactions:

$$\begin{array}{r} Fe \longrightarrow Fe^{2+} + 2e^- \\ MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O \end{array}$$

Now consider the physical setup of the cell, shown schematically in Fig. 17.7. In the left compartment the active components in their standard states are pure metallic iron (Fe) and 1.0 *M* Fe^{2+}. The anion present depends on the iron salt used. In this compartment the anion does not participate in the reaction but simply balances the charge. The half-reaction that takes place at this electrode is

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

which is an oxidation reaction, so this compartment is the anode. The electrode consists of pure iron metal.

In the right compartment the active components in their standard states are 1.0 *M* MnO_4^-, 1.0 *M* H^+, and 1.0 *M* Mn^{2+}, with appropriate unreacting ions (often called *counterions*) to balance the charge. The half-reaction in this compartment is

$$MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$

which is a reduction reaction, so this compartment is the cathode. Since neither MnO_4^- nor Mn^{2+} ions can serve as the electrode, a nonreacting conductor such as platinum must be employed.

The next step is to determine the direction of electron flow. In the left compartment the half-reaction involves the oxidation of iron:

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

In the right compartment the half-reaction is the reduction of MnO_4^-:

$$MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$

Thus the electrons flow from Fe to MnO_4^- in this cell, or from the anode to the cathode, as is always the case. The line notation for this cell is

$$Fe(s)|Fe^{2+}(aq)||MnO_4^-(aq), Mn^{2+}(aq)|Pt(s)$$

A complete description of a galvanic cell usually includes four items:

- The cell potential (always positive for a galvanic cell where $\mathscr{E}^\circ_{cell} = \mathscr{E}^\circ\,(\text{cathode}) - \mathscr{E}^\circ\,(\text{anode})$ and the balanced cell reaction.
- The direction of electron flow, obtained by inspecting the half-reactions and using the direction that gives a positive $\mathscr{E}_{cell}$.

- Designation of the anode and cathode.
- The nature of each electrode and the ions present in each compartment. A chemically inert conductor is required if none of the substances participating in the half-reaction is a conducting solid.

Sample Exercise 17.2 Description of a Galvanic Cell

Describe completely the galvanic cell based on the following half-reactions under standard conditions:

$$\begin{aligned} &Ag^+ + e^- \longrightarrow Ag && \mathscr{E}^\circ = 0.80\ V && (1) \\ &Fe^{3+} + e^- \longrightarrow Fe^{2+} && \mathscr{E}^\circ = 0.77\ V && (2) \end{aligned}$$

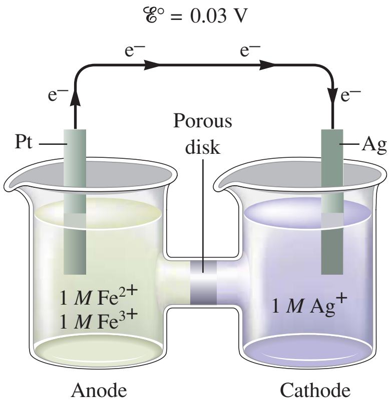


FIGURE 17.8
Schematic diagram for the galvanic cell based on the half-reactions

$$\begin{aligned} Ag^+ + e^- &\longrightarrow Ag \\ Fe^{2+} &\longrightarrow Fe^{3+} + e^- \end{aligned}$$

Solution

Item 1 Since a positive $\mathscr{E}^\circ_{cell}$ value is required, reaction (2) must run in reverse:

$$\begin{aligned} Ag^+ + e^- &\longrightarrow Ag & \mathscr{E}^\circ\ (\text{cathode}) &= 0.80\ V \\ Fe^{2+} &\longrightarrow Fe^{3+} + e^- & -\mathscr{E}^\circ\ (\text{anode}) &= -0.77\ V \\ \hline \text{Cell reaction:}\quad Ag^+(aq) + Fe^{2+}(aq) &\longrightarrow Fe^{3+}(aq) + Ag(s) & \mathscr{E}^\circ_{cell} &= 0.03\ V \end{aligned}$$

Item 2 Since Ag^+ receives electrons and Fe^{2+} loses electrons in the cell reaction, the electrons will flow from the compartment containing Fe^{2+} to the compartment containing Ag^+.

Item 3 Oxidation occurs in the compartment containing Fe^{2+} (electrons flow from Fe^{2+} to Ag^+). Hence this compartment functions as the anode. Reduction occurs in the compartment containing Ag^+, so this compartment functions as the cathode.

Item 4 The electrode in the Ag/Ag^+ compartment is silver metal, and an inert conductor, such as platinum, must be used in the Fe^{2+}/Fe^{3+} compartment. Appropriate counterions are assumed to be present. The diagram for this cell is shown in Fig. 17.8. The line notation for this cell is

$$Pt(s)|Fe^{2+}(aq), Fe^{3+}(aq)||Ag^+(aq)|Ag(s)$$

See Exercises 17.29 and 17.30.

Using a battery-powered drill to insert a screw.

17.3 Cell Potential, Electrical Work, and Free Energy

So far we have considered electrochemical cells in a very practical fashion without much theoretical background. The next step will be to explore the relationship between thermodynamics and electrochemistry.

The work that can be accomplished when electrons are transferred through a wire depends on the "push" (the thermodynamic driving force) behind the electrons. This driving force (the emf) is defined in terms of a *potential difference* (in volts) between two points in the circuit. Recall that a volt represents a joule of work per coulomb of charge transferred:

$$\text{emf} = \text{potential difference (V)} = \frac{\text{work (J)}}{\text{charge (C)}}$$

Thus 1 joule of work is produced or required (depending on the direction) when 1 coulomb of charge is transferred between two points in the circuit that differ by a potential of 1 volt.

In this book, *work is viewed from the point of view of the system.* Thus work flowing out of the system is indicated by a minus sign. When a cell produces a current, the cell potential is positive, and the current can be used to do work—to run a motor, for instance. Thus the cell potential $\mathscr{E}$ and the work w have opposite signs:

$$\mathscr{E} = \frac{-w \leftarrow \text{Work}}{q \leftarrow \text{Charge}}$$

Therefore,

$$-w = q\mathscr{E}$$

From this equation it can be seen that the maximum work in a cell would be obtained at the maximum cell potential:

$$-w_{\text{max}} = q\mathscr{E}_{\text{max}} \quad \text{or} \quad w_{\text{max}} = -q\mathscr{E}_{\text{max}}$$

Work is never the maximum possible if any current is flowing.

However, there is a problem. To obtain electrical work, current must flow. When current flows, some energy is inevitably wasted through frictional heating, and the maximum work is not obtained. This reflects the important general principle introduced in Section 16.9: *In any real, spontaneous process some energy is always wasted—the actual work realized is always less than the calculated maximum.* This is a consequence of the fact that the entropy of the universe must increase in any spontaneous process. Recall from Section 16.9 that the only process from which maximum work could be realized is the hypothetical reversible process. For a galvanic cell this would involve an infinitesimally small current flow and thus an infinite amount of time to do the work. Even though we can never achieve the maximum work through the actual discharge of a galvanic cell, we can measure the maximum potential. There is negligible current flow when a cell potential is measured with a potentiometer or an efficient digital voltmeter. No current flow implies no waste of energy, so the potential measured is the maximum.

Although we can never actually realize the maximum work from a cell reaction, the value for it is still useful in evaluating the efficiency of a real process based on the cell reaction. For example, suppose a certain galvanic cell has a maximum potential (at zero current) of 2.50 V. In a particular experiment 1.33 moles of electrons were passed through this cell at an average actual potential of 2.10 V. The actual work done is

$$w = -q\mathscr{E}$$

where $\mathscr{E}$ represents the actual potential difference at which the current flowed (2.10 V or 2.10 J/C) and q is the quantity of charge in coulombs transferred. The charge on 1 mole of electrons is a constant called the **faraday** (abbreviated F), which has the value *96,485 coulombs of charge per mole of electrons.* Thus q equals the number of moles of electrons times the charge per mole of electrons:

$$q = nF = 1.33 \text{ mol e}^- \times 96{,}485 \text{ C/mol e}^-$$

Then, for the preceding experiment, the actual work is

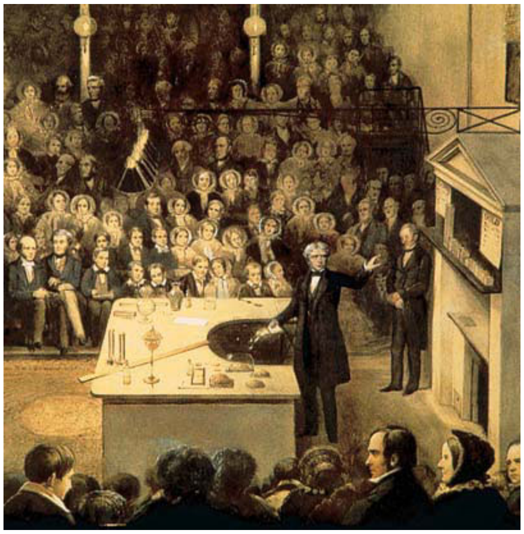
$$\begin{aligned} w &= -q\mathscr{E} = -(1.33 \text{ mol e}^- \times 96{,}485 \text{ C/mol e}^-) \times (2.10 \text{ J/C}) \\ &= -2.69 \times 10^5 \text{ J} \end{aligned}$$

For the maximum possible work, the calculation is similar, except that the maximum potential is used:

$$\begin{aligned} w_{\text{max}} &= -q\mathscr{E} \\ &= -\left(1.33 \text{ mol e}^- \times 96{,}485 \frac{\text{C}}{\text{mol e}^-}\right)\left(2.50 \frac{\text{J}}{\text{C}}\right) \\ &= -3.21 \times 10^5 \text{ J} \end{aligned}$$

Thus, in its actual operation, the efficiency of this cell is

$$\frac{w}{w_{\text{max}}} \times 100\% = \frac{-2.69 \times 10^5 \text{ J}}{-3.21 \times 10^5 \text{ J}} \times 100\% = 83.8\%$$



Michael Faraday lecturing at the Royal Institution before Prince Albert and others (1855). The faraday was named in honor of Michael Faraday (1791–1867), an Englishman who may have been the greatest experimental scientist of the nineteenth century. Among his many achievements were the invention of the electric motor and generator and the development of the principles of electrolysis.

Next we want to relate the potential of a galvanic cell to free energy. In Section 16.9 we saw that for a process carried out at constant temperature and pressure, the change in free energy equals the maximum useful work obtainable from that process:

$$w_{\max} = \Delta G$$

For a galvanic cell,

$$w_{\max} = -q\mathscr{E}_{\max} = \Delta G$$

Since $q = nF$

we have $\Delta G = -q\mathscr{E}_{\max} = -nF\mathscr{E}_{\max}$

From now on the subscript on $\mathscr{E}_{\max}$ will be deleted, with the understanding that any potential given in this book is the maximum potential. Thus

$$\Delta G = -nF\mathscr{E}$$

For standard conditions,

$$\Delta G^\circ = -nF\mathscr{E}^\circ$$

This equation states that *the maximum cell potential is directly related to the free energy difference between the reactants and the products in the cell.* This relationship is important because it provides an experimental means to obtain ΔG for a reaction. It also confirms that a galvanic cell will run in the direction that gives a positive value for $\mathscr{E}_{\text{cell}}$; a positive $\mathscr{E}_{\text{cell}}$ value corresponds to a negative ΔG value, which is the condition for spontaneity.

Sample Exercise 17.3

Calculating ΔG° for a Cell Reaction

Using the data in Table 17.1, calculate ΔG° for the reaction

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

Is this reaction spontaneous?

Solution

The half-reactions are

$$\begin{array}{rcll}
\text{Cu}^{2+} + 2\text{e}^- & \longrightarrow & \text{Cu} & \mathscr{E}^\circ\ (\text{cathode}) = 0.34\ \text{V} \\
\text{Fe} & \longrightarrow & \text{Fe}^{2+} + 2\text{e}^- & -\mathscr{E}^\circ\ (\text{anode}) = 0.44\ \text{V} \\
\hline
\text{Cu}^{2+} + \text{Fe} & \longrightarrow & \text{Fe}^{2+} + \text{Cu} & \mathscr{E}^\circ_{\text{cell}} = 0.78\ \text{V}
\end{array}$$

We can calculate ΔG° from the equation

$$\Delta G^\circ = -nF\mathscr{E}^\circ$$

Since two electrons are transferred per atom in the reaction, 2 moles of electrons are required per mole of reactants and products. Thus $n = 2$ mol e$^-$, $F = 96{,}485$ C/mol e$^-$, and $\mathscr{E}^\circ = 0.78\ \text{V} = 0.78\ \text{J/C}$. Therefore,

$$\begin{aligned}
\Delta G^\circ &= -(2\ \text{mol e}^-)\left(96{,}485\ \frac{\text{C}}{\text{mol e}^-}\right)\left(0.78\ \frac{\text{J}}{\text{C}}\right) \\
&= -1.5 \times 10^5\ \text{J}
\end{aligned}$$

The process is spontaneous, as indicated by both the negative sign of ΔG° and the positive sign of $\mathscr{E}^\circ_{\text{cell}}$.

This reaction is used industrially to deposit copper metal from solutions resulting from the dissolving of copper ores.

See Exercises 17.37 and 17.38.

Sample Exercise 17.4 Predicting Spontaneity

Using the data from Table 17.1, predict whether 1 *M* HNO_3 will dissolve gold metal to form a 1 *M* Au^{3+} solution.

A gold ring does not dissolve in nitric acid.

Solution

The half-reaction for HNO_3 acting as an oxidizing agent is

$$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O \qquad \mathscr{E}° \text{ (cathode)} = 0.96 \text{ V}$$

The reaction for the oxidation of solid gold to Au^{3+} ions is

$$Au \longrightarrow Au^{3+} + 3e^- \qquad -\mathscr{E}° \text{ (anode)} = -1.50 \text{ V}$$

The sum of these half-reactions gives the required reaction:

$$Au(s) + NO_3^-(aq) + 4H^+(aq) \longrightarrow Au^{3+}(aq) + NO(g) + 2H_2O(l)$$

and $$\mathscr{E}°_{cell} = \mathscr{E}° \text{ (cathode)} - \mathscr{E}° \text{ (anode)} = 0.96 \text{ V} - 1.50 \text{ V} = -0.54 \text{ V}$$

Since the $\mathscr{E}°$ value is negative, the process will *not* occur under standard conditions. That is, gold will not dissolve in 1 *M* HNO_3 to give 1 *M* Au^{3+}. In fact, a mixture (1:3 by volume) of concentrated nitric and hydrochloric acids, called *aqua regia,* is required to dissolve gold.

See Exercises 17.37 and 17.38.

17.4 Dependence of Cell Potential on Concentration

So far we have described cells under standard conditions. In this section we consider the dependence of the cell potential on concentration. Under standard conditions (all concentrations 1 *M*), the cell with the reaction

$$Cu(s) + 2Ce^{4+}(aq) \longrightarrow Cu^{2+}(aq) + 2Ce^{3+}(aq)$$

has a potential of 1.36 V. What will the cell potential be if $[Ce^{4+}]$ is greater than 1.0 *M*? This question can be answered qualitatively in terms of Le Châtelier's principle. An increase in the concentration of Ce^{4+} will favor the forward reaction and thus increase the driving force on the electrons. The cell potential will increase. On the other hand, an increase in the concentration of a product (Cu^{2+} or Ce^{3+}) will oppose the forward reaction, thus decreasing the cell potential.

These ideas are illustrated in Sample Exercise 17.5.

Sample Exercise 17.5 The Effects of Concentration on $\mathscr{E}$

For the cell reaction

$$2Al(s) + 3Mn^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Mn(s) \qquad \mathscr{E}°_{cell} = 0.48 \text{ V}$$

predict whether $\mathscr{E}_{cell}$ is larger or smaller than $\mathscr{E}°_{cell}$ for the following cases.

A concentration cell with 1.0 *M* Cu^{2+} on the right and 0.010 *M* Cu^{2+} on the left.

a. $[Al^{3+}] = 2.0\ M$, $[Mn^{2+}] = 1.0\ M$
b. $[Al^{3+}] = 1.0\ M$, $[Mn^{2+}] = 3.0\ M$

Solution

a. A product concentration has been raised above 1.0 *M*. This will oppose the cell reaction and will cause $\mathscr{E}_{cell}$ to be less than $\mathscr{E}°_{cell}$ ($\mathscr{E}_{cell} < 0.48$ V).
b. A reactant concentration has been increased above 1.0 *M*, and $\mathscr{E}_{cell}$ will be greater than $\mathscr{E}°_{cell}$ ($\mathscr{E}_{cell} > 0.48$ V).

See Exercise 17.51.

Concentration Cells

Because cell potentials depend on concentration, we can construct galvanic cells where both compartments contain the same components but at different concentrations. For example, in the cell in Fig. 17.9, both compartments contain aqueous $AgNO_3$, but with different molarities. Let's consider the potential of this cell and the direction of electron flow. The half-reaction relevant to both compartments of this cell is

$$Ag^+ + e^- \longrightarrow Ag \qquad \mathscr{E}° = 0.80\ V$$

If the cell had 1 M Ag^+ in both compartments,

$$\mathscr{E}°_{cell} = 0.80\ V - 0.80\ V = 0\ V$$

However, in the cell described here, the concentrations of Ag^+ in the two compartments are 1 M and 0.1 M. Because the concentrations of Ag^+ are unequal, the half-cell potentials will not be identical, and the cell will exhibit a positive voltage. In which direction will the electrons flow in this cell? The best way to think about this question is to recognize that nature will try to equalize the concentrations of Ag^+ in the two compartments. This can be done by transferring electrons from the compartment containing 0.1 M Ag^+ to the one containing 1 M Ag^+ (left to right in Fig. 17.9). This electron transfer will produce more Ag^+ in the left compartment and consume Ag^+ (to form Ag) in the right compartment.

A cell in which both compartments have the same components but at different concentrations is called a **concentration cell.** The difference in concentration is the only factor that produces a cell potential in this case, and the voltages are typically small.

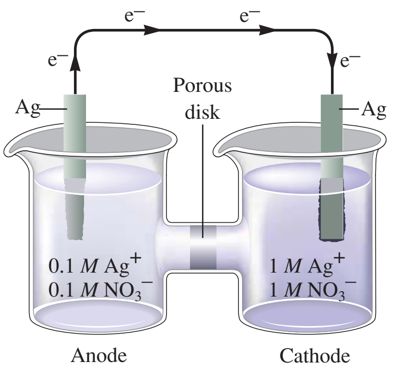


FIGURE 17.9
A concentration cell that contains a silver electrode and aqueous silver nitrate in both compartments. Because the right compartment contains 1 M Ag^+ and the left compartment contains 0.1 M Ag^+, there will be a driving force to transfer electrons from left to right. Silver will be deposited on the right electrode, thus lowering the concentration of Ag^+ in the right compartment. In the left compartment the silver electrode dissolves (producing Ag^+ ions) to raise the concentration of Ag^+ in solution.

Sample Exercise 17.6

Concentration Cells

Determine the direction of electron flow and designate the anode and cathode for the cell represented in Fig. 17.10.

Solution

The concentrations of Fe^{2+} ion in the two compartments can (eventually) be equalized by transferring electrons from the left compartment to the right. This will cause Fe^{2+} to be formed in the left compartment, and iron metal will be deposited (by reducing Fe^{2+} ions to Fe) on the right electrode. Since electron flow is from left to right, oxidation occurs in the left compartment (the anode) and reduction occurs in the right (the cathode).

See Exercise 17.52.

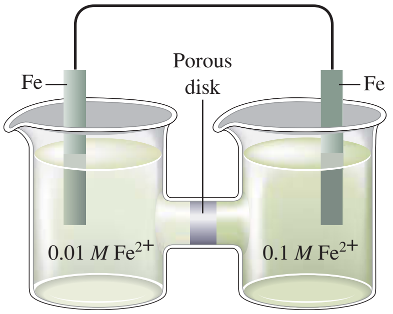


FIGURE 17.10
A concentration cell containing iron electrodes and different concentrations of Fe^{2+} ion in the two compartments.

The Nernst Equation

The dependence of the cell potential on concentration results directly from the dependence of free energy on concentration. Recall from Chapter 16 that the equation

$$\Delta G = \Delta G° + RT \ln(Q)$$

where Q is the reaction quotient, was used to calculate the effect of concentration on ΔG. Since $\Delta G = -nF\mathscr{E}$ and $\Delta G° = -nF\mathscr{E}°$, the equation becomes

$$-nF\mathscr{E} = -nF\mathscr{E}° + RT \ln(Q)$$

Dividing each side of the equation by $-nF$ gives

$$\mathscr{E} = \mathscr{E}° - \frac{RT}{nF} \ln(Q) \qquad (17.1)$$

Nernst was one of the pioneers in the development of electrochemical theory and is generally given credit for first stating the third law of thermodynamics. He won the Nobel Prize in chemistry in 1920.

Equation (17.1), which gives the relationship between the cell potential and the concentrations of the cell components, is commonly called the **Nernst equation,** after the German chemist Walther Hermann Nernst (1864–1941).

The Nernst equation is often given in a form that is valid at 25°C:

$$\mathscr{E} = \mathscr{E}^\circ - \frac{0.0591}{n}\log(Q)$$

Using this relationship, we can calculate the potential of a cell in which some or all of the components are not in their standard states.

For example, $\mathscr{E}^\circ_{\text{cell}}$ is 0.48 V for the galvanic cell based on the reaction

$$2\text{Al}(s) + 3\text{Mn}^{2+}(aq) \longrightarrow 2\text{Al}^{3+}(aq) + 3\text{Mn}(s)$$

Consider a cell in which

$$[\text{Mn}^{2+}] = 0.50\,M \quad \text{and} \quad [\text{Al}^{3+}] = 1.50\,M$$

The cell potential at 25°C for these concentrations can be calculated using the Nernst equation:

$$\mathscr{E}_{\text{cell}} = \mathscr{E}^\circ_{\text{cell}} - \frac{0.0591}{n}\log(Q)$$

We know that

$$\mathscr{E}^\circ_{\text{cell}} = 0.48\text{ V}$$

and

$$Q = \frac{[\text{Al}^{3+}]^2}{[\text{Mn}^{2+}]^3} = \frac{(1.50)^2}{(0.50)^3} = 18$$

Since the half-reactions are

$$\begin{aligned} &\text{Oxidation:} && 2\text{Al} \longrightarrow 2\text{Al}^{3+} + 6\text{e}^- \\ &\text{Reduction:} && 3\text{Mn}^{2+} + 6\text{e}^- \longrightarrow 3\text{Mn} \end{aligned}$$

we know that

$$n = 6$$

Thus

$$\begin{aligned} \mathscr{E}_{\text{cell}} &= 0.48 - \frac{0.0591}{6}\log(18) \\ &= 0.48 - \frac{0.0591}{6}(1.26) = 0.48 - 0.01 = 0.47\text{ V} \end{aligned}$$

Note that the cell voltage decreases slightly because of the nonstandard concentrations. This change is consistent with the predictions of Le Châtelier's principle (see Sample Exercise 17.5). In this case, since the reactant concentration is lower than 1.0 M and the product concentration is higher than 1.0 M, $\mathscr{E}_{\text{cell}}$ is less than $\mathscr{E}^\circ_{\text{cell}}$.

The potential calculated from the Nernst equation is the maximum potential before any current flow has occurred. As the cell discharges and current flows from anode to cathode, the concentrations will change, and as a result, $\mathscr{E}_{\text{cell}}$ will change. In fact, *the cell will spontaneously discharge until it reaches equilibrium,* at which point

$$Q = K\,(\text{the equilibrium constant}) \quad \text{and} \quad \mathscr{E}_{\text{cell}} = 0$$

A "dead" battery is one in which the cell reaction has reached equilibrium, and there is no longer any chemical driving force to push electrons through the wire. In other words, *at equilibrium, the components in the two cell compartments have the same free energy,* and $\Delta G = 0$ for the cell reaction at the equilibrium concentrations. The cell no longer has the ability to do work.

Sample Exercise 17.7 The Nernst Equation

Describe the cell based on the following half-reactions:

$$VO_2^+ + 2H^+ + e^- \longrightarrow VO^{2+} + H_2O \qquad \mathscr{E}^\circ = 1.00\ \text{V} \qquad (1)$$

$$Zn^{2+} + 2e^- \longrightarrow Zn \qquad \mathscr{E}^\circ = -0.76\ \text{V} \qquad (2)$$

where

$$T = 25^\circ\text{C}$$
$$[VO_2^+] = 2.0\ M$$
$$[H^+] = 0.50\ M$$
$$[VO^{2+}] = 1.0 \times 10^{-2}\ M$$
$$[Zn^{2+}] = 1.0 \times 10^{-1}\ M$$

Solution

The balanced cell reaction is obtained by reversing reaction (2) and multiplying reaction (1) by 2:

2 × reaction (1) $$2VO_2^+ + 4H^+ + 2e^- \longrightarrow 2VO^{2+} + 2H_2O \qquad \mathscr{E}^\circ\ (\text{cathode}) = 1.00\ \text{V}$$

Reaction (2) reversed $$Zn \longrightarrow Zn^{2+} + 2e^- \qquad -\mathscr{E}^\circ\ (\text{anode}) = 0.76\ \text{V}$$

Cell reaction: $$2VO_2^+(aq) + 4H^+(aq) + Zn(s) \longrightarrow 2VO^{2+}(aq) + 2H_2O(l) + Zn^{2+}(aq) \qquad \mathscr{E}^\circ_{\text{cell}} = 1.76\ \text{V}$$

Since the cell contains components at concentrations other than 1 M, we must use the Nernst equation, where $n = 2$ (since two electrons are transferred), to calculate the cell potential. At 25°C we can use the equation

$$\begin{aligned}
\mathscr{E} &= \mathscr{E}^\circ_{\text{cell}} - \frac{0.0591}{n}\log(Q) \\
&= 1.76 - \frac{0.0591}{2}\log\left(\frac{[Zn^{2+}][VO^{2+}]^2}{[VO_2^+]^2[H^+]^4}\right) \\
&= 1.76 - \frac{0.0591}{2}\log\left(\frac{(1.0 \times 10^{-1})(1.0 \times 10^{-2})^2}{(2.0)^2(0.50)^4}\right) \\
&= 1.76 - \frac{0.0591}{2}\log(4 \times 10^{-5}) = 1.76 + 0.13 = 1.89\ \text{V}
\end{aligned}$$

The cell diagram is given in Fig. 17.11.

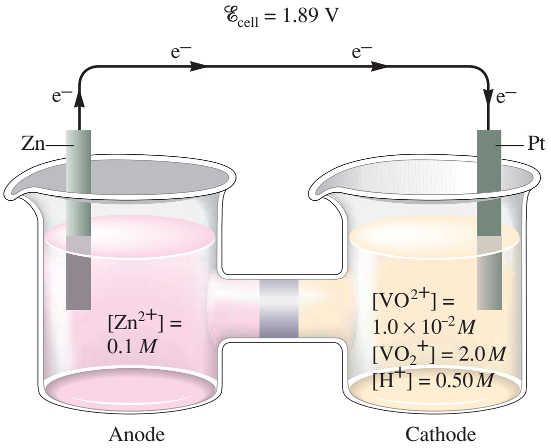


FIGURE 17.11
Schematic diagram of the cell described in Sample Exercise 17.7.

See Exercises 17.55 through 17.58.

FIGURE 17.12
A glass electrode contains a reference solution of dilute hydrochloric acid in contact with a thin glass membrane in which a silver wire coated with silver chloride has been embedded. When the electrode is dipped into a solution containing H^+ ions, the electrode potential is determined by the difference in $[H^+]$ between the two solutions.

Ion-Selective Electrodes

Because the cell potential is sensitive to the concentrations of the reactants and products involved in the cell reaction, measured potentials can be used to determine the concentration of an ion. A pH meter (see Fig. 14.9) is a familiar example of an instrument that measures concentration using an observed potential. The pH meter has three main components: a standard electrode of known potential, a special **glass electrode** that changes potential depending on the concentration of H^+ ions in the solution into which it is dipped, and a potentiometer that measures the potential between the electrodes. The potentiometer reading is automatically converted electronically to a direct reading of the pH of the solution being tested.

The glass electrode (see Fig. 17.12) contains a reference solution of dilute hydrochloric acid in contact with a thin glass membrane. The electrical potential of the glass electrode depends on the difference in $[H^+]$ between the reference solution and the solution into which the electrode is dipped. Thus the electrical potential varies with the pH of the solution being tested.

Electrodes that are sensitive to the concentration of a particular ion are called **ion-selective electrodes,** of which the glass electrode for pH measurement is just one example. Glass electrodes can be made sensitive to such ions as Na^+, K^+, or NH_4^+ by changing the composition of the glass. Other ions can be detected if an appropriate crystal replaces the glass membrane. For example, a crystal of lanthanum(III) fluoride (LaF_3) can be used in an electrode to measure $[F^-]$. Solid silver sulfide (Ag_2S) can be used to measure $[Ag^+]$ and $[S^{2-}]$. Some of the ions that can be detected by ion-selective electrodes are listed in Table 17.2.

TABLE 17.2 Some Ions Whose Concentrations Can Be Detected by Ion-Selective Electrodes

Cations	Anions
H^+	Br^-
Cd^{2+}	Cl^-
Ca^{2+}	CN^-
Cu^{2+}	F^-
K^+	NO_3^-
Ag^+	S^{2-}
Na^+	

Calculation of Equilibrium Constants for Redox Reactions

The quantitative relationship between $\mathcal{E}°$ and $\Delta G°$ allows calculation of equilibrium constants for redox reactions. For a cell at equilibrium,

$$\mathcal{E}_{\text{cell}} = 0 \quad \text{and} \quad Q = K$$

Applying these conditions to the Nernst equation valid at 25°C,

$$\mathcal{E} = \mathcal{E}° - \frac{0.0591}{n}\log(Q)$$

gives $$0 = \mathscr{E}° - \frac{0.0591}{n}\log(K)$$

or $$\log(K) = \frac{n\mathscr{E}°}{0.0591} \quad \text{at } 25°\text{C}$$

Sample Exercise 17.8 Equilibrium Constants from Cell Potentials

For the oxidation–reduction reaction

$$S_4O_6^{2-}(aq) + Cr^{2+}(aq) \longrightarrow Cr^{3+}(aq) + S_2O_3^{2-}(aq)$$

the appropriate half-reactions are

$$S_4O_6^{2-} + 2e^- \longrightarrow 2S_2O_3^{2-} \qquad \mathscr{E}° = 0.17\text{ V} \qquad (1)$$
$$Cr^{3+} + e^- \longrightarrow Cr^{2+} \qquad \mathscr{E}° = -0.50\text{ V} \qquad (2)$$

Balance the redox reaction, and calculate $\mathscr{E}°$ and K (at 25°C).

Solution

To obtain the balanced reaction, we must reverse reaction (2), multiply it by 2, and add it to reaction (1):

Reaction (1)	$S_4O_6^{2-} + 2e^- \longrightarrow 2S_2O_3^{2-}$	$\mathscr{E}°$ (cathode) = 0.17 V
2 × reaction (2) reversed	$2(Cr^{2+} \longrightarrow Cr^{3+} + e^-)$	$-\mathscr{E}°$ (anode) = −(−0.50) V
Cell reaction:	$2Cr^{2+}(aq) + S_4O_6^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 2S_2O_3^{2-}(aq)$	$\mathscr{E}°$ = 0.67 V


The blue solution contains Cr^{2+} ions, and the green solution contains Cr^{3+} ions.

In this reaction, 2 moles of electrons are transferred for every unit of reaction, that is, for every 2 mol Cr^{2+} reacting with 1 mol $S_4O_6^{2-}$ to form 2 mol Cr^{3+} and 2 mol $S_2O_3^{2-}$. Thus $n = 2$. Then

$$\log(K) = \frac{n\mathscr{E}°}{0.0591} = \frac{2(0.67)}{0.0591} = 22.6$$

The value of K is found by taking the antilog of 22.6:

$$K = 10^{22.6} = 4 \times 10^{22}$$

This very large equilibrium constant is not unusual for a redox reaction.

See Exercises 17.65, 17.66, 17.69, and 17.70.

17.5 Batteries

A **battery** is a galvanic cell or, more commonly, a group of galvanic cells connected in series, where the potentials of the individual cells add to give the total battery potential. Batteries are a source of direct current and have become an essential source of portable power in our society. In this section we examine the most common types of batteries. Some new batteries currently being developed are described at the end of the chapter.

Lead Storage Battery

Since about 1915 when self-starters were first used in automobiles, the **lead storage battery** has been a major factor in making the automobile a practical means of transportation. This type of battery can function for several years under temperature extremes from −30°F to 120°F and under incessant punishment from rough roads.

CHEMICAL IMPACT

Printed Batteries

Soon you may reach for a compact disc in your local record store and, as you touch it, the package will start playing one of the songs on the disc. Or you may stop to look at a product because the package begins to glow as you pass it in the store. These effects could happen soon thanks to the invention of a flexible, superthin battery that can actually be printed onto the package. This battery was developed by Power Paper, Ltd., a company founded by Baruch Levanon and several colleagues.

The battery developed by Power Paper consists of five layers of zinc (anode) and manganese dioxide (cathode) and is only 0.5 millimeter thick. The battery can be printed onto paper with a regular printing press and appears to present no environmental hazards.

The new battery has been licensed by International Paper Company, which intends to use it to bring light, sound, and other special effects to packaging to entice potential customers. You might see talking, singing, or glowing packages on the shelves within a year or two.

A CD case with an ultrathin battery that can be "printed" on packages like ink.

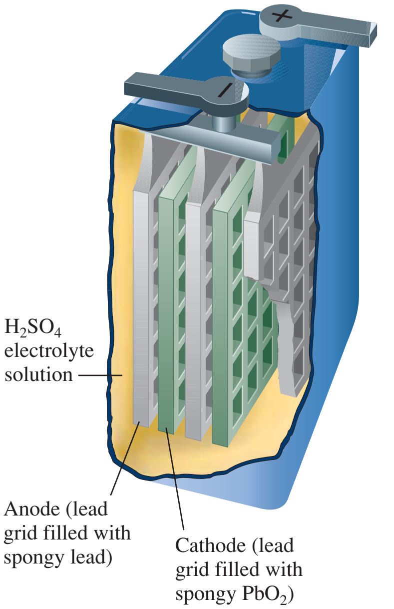


FIGURE 17.13
One of the six cells in a 12-V lead storage battery. The anode consists of a lead grid filled with spongy lead, and the cathode is a lead grid filled with lead dioxide. The cell also contains 38% (by mass) sulfuric acid.

In this battery, lead serves as the anode, and lead coated with lead dioxide serves as the cathode. Both electrodes dip into an electrolyte solution of sulfuric acid. The electrode reactions are

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

The typical automobile lead storage battery has six cells connected in series. Each cell contains multiple electrodes in the form of grids (Fig. 17.13) and produces approximately 2 V, to give a total battery potential of about 12 V. Note from the cell reaction that sulfuric acid is consumed as the battery discharges. This lowers the density of the electrolyte solution from its initial value of about 1.28 g/cm^3 in the fully charged battery. As a result, the condition of the battery can be monitored by measuring the density of the sulfuric acid solution. The solid lead sulfate formed in the cell reaction during discharge adheres to the grid surfaces of the electrodes. The battery is recharged by forcing current through it in the opposite direction to reverse the cell reaction. A car's battery is continuously charged by an alternator driven by the automobile engine.

An automobile with a dead battery can be "jump-started" by connecting its battery to the battery in a running automobile. This process can be dangerous, however, because the resulting flow of current causes electrolysis of water in the dead battery, producing hydrogen and oxygen gases (see Section 17.7 for details). Disconnecting the jumper cables after the disabled car starts causes an arc that can ignite the gaseous

CHEMICAL IMPACT

Thermophotovoltaics: Electricity from Heat

A photovoltaic cell transforms the energy of sunlight into an electric current. These devices are used to power calculators, electric signs in rural areas, experimental cars, and an increasing number of other devices. But what happens at night or on cloudy days? Usually photovoltaic power sources employ a battery as a reserve energy source when light levels are low.

Now there is an emerging technology, called *thermophotovoltaics* (TPV), that uses a heat source instead of the sun for energy. These devices can operate at night or on an overcast day without a battery. Although TPV devices could use many different sources of heat, the examples currently under development use a propane burner. To produce an electric current, the radiant heat from the burner is used to excite a "radiator," a device that emits infrared (IR) radiation when heated. The emitted IR radiation then falls on a "converter," which is a semiconductor that contains p–n junctions. The IR radiation excites electrons from valence bands to conduction bands in the semiconductor so that the electrons can flow as a current. A schematic of a TPV generator is illustrated in the diagram.

TPV technology has advanced recently because researchers have found that it is possible to use radiators such as silicon carbide, which can operate at relatively low temperatures (approximately 1000°C), with III–V semiconductor converters such as gallium antimonide (GSb) or gallium arsenide (GaAs). While development work continues on many fronts, the first commercial TPV product is being marketed by JX Crystals of Issaquah, Washington. The product—Midnight Sun—is a propane-powered TPV generator that can produce 30 watts of electricity and is intended for use on boats to charge the batteries that power navigation and other essential equipment. Although at $3000 the TPV generator is more expensive than a conventional diesel-powered generator, Midnight Sun is silent and more reliable because it has no moving parts.

Although TPV technology is still in its infancy, it has many possible uses. The utilization of industrial waste heat—generated by glass and steel manufacturing and other industries—could establish a huge market for TPV. For example, two-thirds of the energy used in the manufacture of glass ends up as waste heat. If a significant quantity of this

mixture. If this happens, the battery may explode, ejecting corrosive sulfuric acid. This problem can be avoided by connecting the ground jumper cable to a part of the engine remote from the battery. Any arc produced when this cable is disconnected will then be harmless.

Traditional types of storage batteries require periodic "topping off" because the water in the electrolyte solution is depleted by the electrolysis that accompanies the charging process. Recent types of batteries have electrodes made of an alloy of calcium and lead that inhibits the electrolysis of water. These batteries can be sealed, since they require no addition of water.

It is rather amazing that in the 85 years in which lead storage batteries have been used, no better system has been found. Although a lead storage battery does provide excellent service, it has a useful lifetime of 3 to 5 years in an automobile. While it might seem that the battery could undergo an indefinite number of discharge/charge cycles, physical damage from road shock and chemical side-reactions eventually cause it to fail.

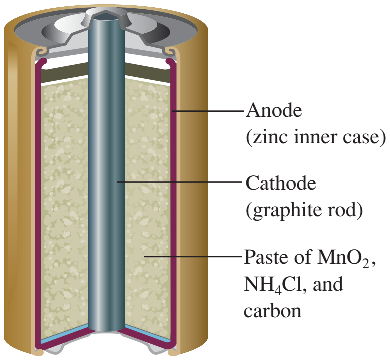
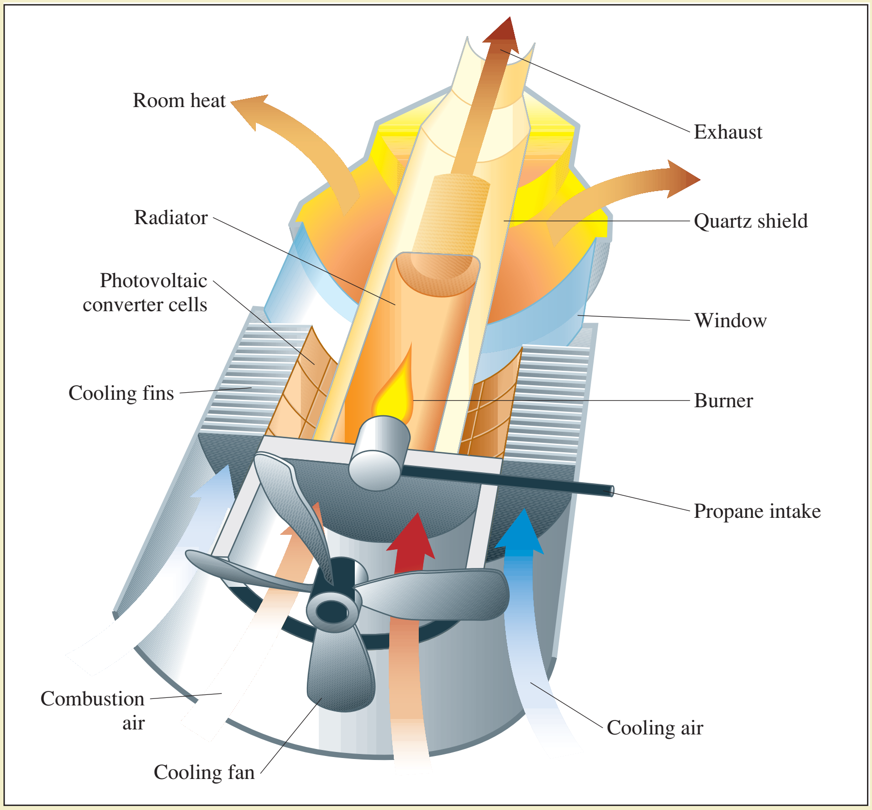


FIGURE 17.14
A common dry cell battery.

Other Batteries

The calculators, electronic games, digital watches, and portable CD players that are so familiar to us are all powered by small, efficient batteries. The common **dry cell battery** was invented more than 100 years ago by George Leclanché (1839–1882), a French chemist. In its *acid version,* the dry cell battery contains a zinc inner case that acts as the anode and a carbon rod in contact with a moist paste of solid MnO_2, solid NH_4Cl, and carbon that acts as the cathode (Fig. 17.14). The half-reactions are complex but can be



now wasted energy could be used to produce electricity, this would have tremendous fiscal implications.

Another promising application of TPV technology is for cars with hybrid energy sources. For example, an experimental electric car built at Western Washington University uses a 10-kW TPV generator to supplement the batteries that serve as the main power source.

Projections indicate that TPV devices could account for \$500 million in sales by 2005, mainly by substituting TPV generators for small diesel-powered generators used on boats and by the military in the field. It appears that this technology has a hot future.

Diagram of a TPV generator.

approximated as follows:

$$\begin{aligned} &\text{Anode reaction:} & Zn &\longrightarrow Zn^{2+} + 2e^- \\ &\text{Cathode reaction:} & 2NH_4^+ + 2MnO_2 + 2e^- &\longrightarrow Mn_2O_3 + 2NH_3 + H_2O \end{aligned}$$

This cell produces a potential of about 1.5 V.

In the *alkaline version* of the dry cell battery, the solid NH_4Cl is replaced with KOH or NaOH. In this case the half-reactions can be approximated as follows:

$$\begin{aligned} &\text{Anode reaction:} & Zn + 2OH^- &\longrightarrow ZnO + H_2O + 2e^- \\ &\text{Cathode reaction:} & 2MnO_2 + H_2O + 2e^- &\longrightarrow Mn_2O_3 + 2OH^- \end{aligned}$$

The alkaline dry cell lasts longer mainly because the zinc anode corrodes less rapidly under basic conditions than under acidic conditions.

Other types of useful batteries include the *silver cell,* which has a Zn anode and a cathode that employs Ag_2O as the oxidizing agent in a basic environment. *Mercury cells,* often used in calculators, have a Zn anode and a cathode involving HgO as the oxidizing agent in a basic medium (see Fig. 17.15).

An especially important type of battery is the *nickel–cadmium battery,* in which the electrode reactions are

$$\begin{aligned} &\text{Anode reaction:} & Cd + 2OH^- &\longrightarrow Cd(OH)_2 + 2e^- \\ &\text{Cathode reaction:} & NiO_2 + 2H_2O + 2e^- &\longrightarrow Ni(OH)_2 + 2OH^- \end{aligned}$$

As in the lead storage battery, the products adhere to the electrodes. Therefore, a nickel–cadmium battery can be recharged an indefinite number of times.

Batteries for electronic watches are, by necessity, very tiny.

CHEMICAL IMPACT

Fuel Cells for Cars

A gathering of several cars powered by fuel cells at Los Angeles Memorial Coliseum.

Your next car may be powered by a fuel cell. Until recently only affordable to NASA, fuel cells are now ready to become practical power plants in cars. Many car companies are testing vehicles that should be commercially available by 2004 or 2005. All of these vehicles are powered by hydrogen–oxygen fuel cells (see Fig. 17.16).

One of the most common types of fuel cells for automobiles uses a proton-exchange membrane (PEM). When H_2 releases electrons at the anode, H^+ ions form and then travel through the membrane to the cathode, where they combine with O_2 and electrons to form water. This cell generates about 0.7 V of power. To achieve the desired power level, several cells are stacked in series. Fuel cells of this type have appeared in several prototype vehicles, such as Nissan's Xterra FCV, Ford's Focus FCV, and DaimlerChrysler's Mercedes Benz NECAR 5 (see photo).

The main question yet to be answered deals with whether the fuel cells in these cars will be fueled by H_2 stored on board or by H_2 made from gasoline or methanol as it is needed. The latter systems include an onboard reformer that uses catalysts to produce H_2 from other fuels. The on-board storage of hydrogen could take place in a tank at high pressure (approximately 5000 psi) or it could utilize a metal-hydride–based solid. Energy Conversion Devices (ECD) of Troy, Michigan, is developing a storage system based on a magnesium alloy that absorbs H_2 to form a magnesium hydride. The H_2 gas can be released from this solid by heating it to 300°C. According to ECD, the alloy can be fully charged with H_2 in about 5 minutes, achieving a hydrogen density of 103 g/L. This density compares to 71 g/L for liquid hydrogen and 31 g/L for gaseous hydrogen at 5000 psi. ECD claims its storage system furnishes enough H_2 to power a fuel-cell car for 300 miles of driving.

Clearly, fuel-cell–powered cars are on the near horizon.

Fuel Cells

A **fuel cell** is *a galvanic cell for which the reactants are continuously supplied.* To illustrate the principles of fuel cells, let's consider the exothermic redox reaction of methane with oxygen:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) + \text{energy}$$

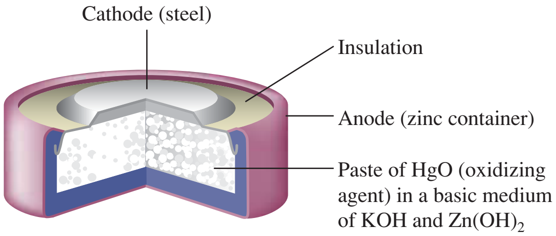


FIGURE 17.15
A mercury battery of the type used in calculators.

Usually the energy from this reaction is released as heat to warm homes and to run machines. However, in a fuel cell designed to use this reaction, the energy is used to produce an electric current: The electrons flow from the reducing agent (CH_4) to the oxidizing agent (O_2) through a conductor.

The U.S. space program has supported extensive research to develop fuel cells. The space shuttle uses a fuel cell based on the reaction of hydrogen and oxygen to form water:

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

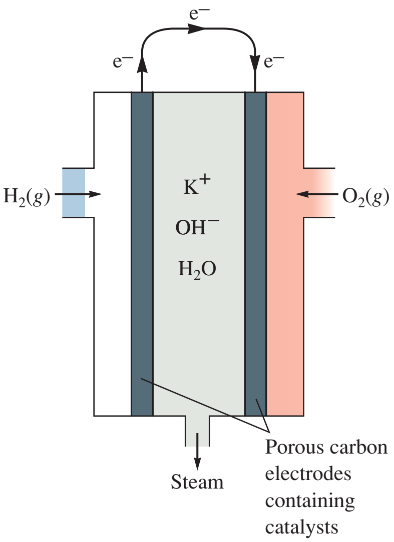


FIGURE 17.16
Schematic of the hydrogen–oxygen fuel cell.

A schematic of a fuel cell that employs this reaction is shown in Fig. 17.16. The half-reactions are

$$\text{Anode reaction:} \quad 2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$$

$$\text{Cathode reaction:} \quad 4e^- + O_2 + 2H_2O \longrightarrow 4OH^-$$

A cell of this type weighing about 500 pounds has been designed for space vehicles, but this fuel cell is not practical enough for general use as a source of portable power. However, current research on portable electrochemical power is now proceeding at a rapid pace. In fact, cars powered by fuel cells are now being tested on the streets.

Fuel cells are also finding use as permanent power sources. For example, a power plant built in New York City contains stacks of hydrogen–oxygen fuel cells, which can be rapidly put on-line in response to fluctuating power demands. The hydrogen gas is obtained by decomposing the methane in natural gas. A plant of this type also has been constructed in Tokyo.

In addition, new fuel cells are under development that can use fuels such as methane and diesel directly without having to produce hydrogen first.

17.6 Corrosion

Corrosion can be viewed as the process of returning metals to their natural state—the ores from which they were originally obtained. Corrosion involves oxidation of the metal. Since corroded metal often loses its structural integrity and attractiveness, this spontaneous process has great economic impact. Approximately one-fifth of the iron and steel produced annually is used to replace rusted metal.

Some metals, such as copper, gold, silver, and platinum, are relatively difficult to oxidize. These are often called *noble metals.*

Metals corrode because they oxidize easily. Table 17.1 shows that, with the exception of gold, those metals commonly used for structural and decorative purposes all have standard reduction potentials less positive than that of oxygen gas. When any of these half-reactions is reversed (to show oxidation of the metal) and combined with the reduction half-reaction for oxygen, the result is a positive $\mathscr{E}°$ value. Thus the oxidation of most metals by oxygen is spontaneous (although we cannot tell from the potential how fast it will occur).

In view of the large difference in reduction potentials between oxygen and most metals, it is surprising that the problem of corrosion does not completely prevent the use of metals in air. However, most metals develop a thin oxide coating, which tends to protect their internal atoms against further oxidation. The metal that best demonstrates this phenomenon is aluminum. With a reduction potential of -1.7 V, aluminum should be easily oxidized by O_2. According to the apparent thermodynamics of the reaction, an aluminum airplane could dissolve in a rainstorm. The fact that this very active metal can be used as a structural material is due to the formation of a thin, adherent layer of aluminum oxide (Al_2O_3), more properly represented as $Al_2(OH)_6$, which greatly inhibits further corrosion. The potential of the "passive," oxide-coated aluminum is -0.6 V, a value that causes it to behave much like a noble metal.

Iron also can form a protective oxide coating. This coating is not an infallible shield against corrosion, however; when steel is exposed to oxygen in moist air, the oxide that forms tends to scale off and expose new metal surfaces to corrosion.

CHEMICAL IMPACT

Paint That Stops Rust—Completely

Traditionally, paint has provided the most economical method for protecting steel against corrosion. However, as people who live in the Midwest know well, paint cannot prevent a car from rusting indefinitely. Eventually, flaws develop in the paint that allow the ravages of rusting to take place.

This situation may soon change. Chemists at Glidden Research Center in Ohio have developed a paint called Rustmaster Pro that worked so well to prevent rusting in its initial tests that the scientists did not believe their results. Steel coated with the new paint showed no signs of rusting after an astonishing 10,000 hours of exposure in a salt spray chamber at 38°C.

Rustmaster is a water-based polymer formulation that prevents corrosion in two different ways. First, the polymer layer that cures in air forms a barrier impenetrable to both oxygen and water vapor. Second, the chemicals in the coating react with the steel surface to produce an interlayer between the metal and the polymer coating. This interlayer is a complex mineral called *pyroaurite* that contains cations of the form $[M_{1-x}Z_x(OH)_2]^{x+}$, where M is a 2+ ion (Mg^{2+}, Fe^{2+}, Zn^{2+}, Co^{2+}, or Ni^{2+}), Z is a 3+ ion (Al^{3+}, Fe^{3+}, Mn^{3+}, Co^{3+}, or Ni^{3+}), and x is a number between 0 and 1. The anions in pyroaurite are typically CO_3^{2-}, Cl^-, and/or SO_4^{2-}.

This pyroaurite interlayer is the real secret of the paint's effectiveness. Because the corrosion of steel has an electrochemical mechanism, motion of ions must be possible between the cathodic and anodic areas on the surface of the steel for rusting to occur. However, the pyroaurite interlayer grows into the neighboring polymer layer, thus preventing this crucial movement of ions. In effect, this layer prevents corrosion in the same way that removing the salt bridge prevents current from flowing in a galvanic cell.

In addition to having an extraordinary corrosion-fighting ability, Rustmaster yields an unusually small quantity of volatile solvents as it dries. A typical paint can produce from 1 to 5 kg of volatiles per gallon; Rustmaster produces only 0.05 kg. This paint may signal a new era in corrosion prevention.

The corrosion products of noble metals such as copper and silver are complex and affect the use of these metals as decorative materials. Under normal atmospheric conditions, copper forms an external layer of greenish copper carbonate called *patina. Silver tarnish* is silver sulfide (Ag_2S), which in thin layers gives the silver surface a richer appearance. Gold, with a positive standard reduction potential of 1.50 V, significantly larger than that for oxygen (1.23 V), shows no appreciable corrosion in air.

Corrosion of Iron

Since steel is the main structural material for bridges, buildings, and automobiles, controlling its corrosion is extremely important. To do this, we must understand the corrosion mechanism. Instead of being a direct oxidation process as we might expect, the corrosion of iron is an electrochemical reaction, as shown in Fig. 17.17.

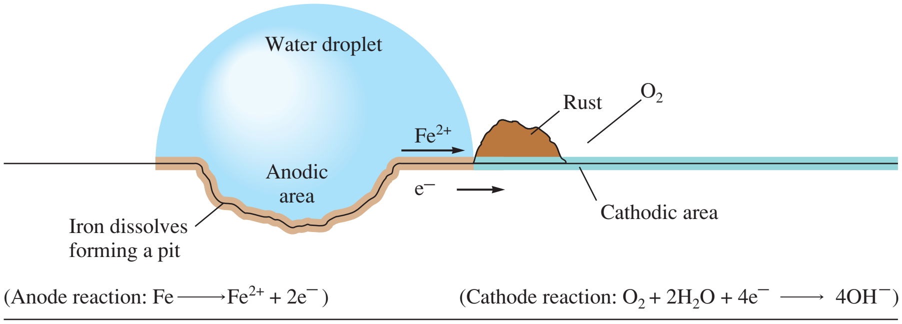


FIGURE 17.17
The electrochemical corrosion of iron.

Steel has a nonuniform surface because the chemical composition is not completely homogeneous. Also, physical strains leave stress points in the metal. These nonuniformities cause areas where the iron is more easily oxidized (*anodic regions*) than it is at others (*cathodic regions*). In the anodic regions each iron atom gives up two electrons to form the Fe^{2+} ion:

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

The electrons that are released flow through the steel, as they do through the wire of a galvanic cell, to a cathodic region, where they react with oxygen:

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

The Fe^{2+} ions formed in the anodic regions travel to the cathodic regions through the moisture on the surface of the steel, just as ions travel through a salt bridge in a galvanic cell. In the cathodic regions Fe^{2+} ions react with oxygen to form rust, which is hydrated iron(III) oxide of variable composition:

$$4Fe^{2+}(aq) + O_2(g) + (4 + 2n)H_2O(l) \longrightarrow \underset{\text{Rust}}{2Fe_2O_3 \cdot nH_2O(s)} + 8H^+(aq)$$

Because of the migration of ions and electrons, rust often forms at sites that are remote from those where the iron dissolved to form pits in the steel. The degree of hydration of the iron oxide affects the color of the rust, which may vary from black to yellow to the familiar reddish brown.

The electrochemical nature of the rusting of iron explains the importance of moisture in the corrosion process. Moisture must be present to act as a kind of salt bridge between anodic and cathodic regions. Steel does not rust in dry air, a fact that explains why cars last much longer in the arid Southwest than in the relatively humid Midwest. Salt also accelerates rusting, a fact all too easily recognized by car owners in the colder parts of the United States, where salt is used on roads to melt snow and ice. The severity of rusting is greatly increased because the dissolved salt on the moist steel surface increases the conductivity of the aqueous solution formed there and thus accelerates the electrochemical corrosion process. Chloride ions also form very stable complex ions with Fe^{3+}, and this factor tends to encourage the dissolving of the iron, again accelerating the corrosion.

Prevention of Corrosion

Prevention of corrosion is an important way of conserving our natural resources of energy and metals. The primary means of protection is the application of a coating, most commonly paint or metal plating, to protect the metal from oxygen and moisture. Chromium and tin are often used to plate steel (see Section 17.8) because they oxidize to form a durable, effective oxide coating. Zinc, also used to coat steel in a process called **galvanizing,** forms a mixed oxide–carbonate coating. Since zinc is a more active metal than iron, as the potentials for the oxidation half-reactions show,

$$Fe \longrightarrow Fe^{2+} + 2e^- \qquad -\mathscr{E}° = 0.44\text{ V}$$
$$Zn \longrightarrow Zn^{2+} + 2e^- \qquad -\mathscr{E}° = 0.76\text{ V}$$

any oxidation that occurs dissolves zinc rather than iron. Recall that the reaction with the most positive standard potential has the greatest thermodynamic tendency to occur. Thus zinc acts as a “sacrificial” coating on steel.

Alloying is also used to prevent corrosion. *Stainless steel* contains chromium and nickel, both of which form oxide coatings that change steel’s reduction potential to one characteristic of the noble metals. In addition, a new technology is now being developed

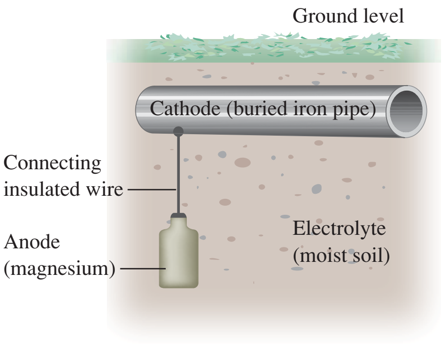


FIGURE 17.18
Cathodic protection of an underground pipe.

to create surface alloys. That is, instead of forming a metal alloy such as stainless steel, which has the same composition throughout, a cheaper carbon steel is treated by ion bombardment to produce a thin layer of stainless steel or other desirable alloy on the surface. In this process, a "plasma" or "ion gas" of the alloying ions is formed at high temperatures and is then directed onto the surface of the metal.

Cathodic protection is a method most often employed to protect steel in buried fuel tanks and pipelines. An active metal, such as magnesium, is connected by a wire to the pipeline or tank to be protected (Fig. 17.18). Because the magnesium is a better reducing agent than iron, electrons are furnished by the magnesium rather than by the iron, keeping the iron from being oxidized. As oxidation occurs, the magnesium anode dissolves, and so it must be replaced periodically. Ships' hulls are protected in a similar way by attaching bars of titanium metal to the steel hull (Fig. 17.18). In salt water the titanium acts as the anode and is oxidized instead of the steel hull (the cathode).

17.7 Electrolysis

An electrolytic cell uses electrical energy to produce a chemical change that would otherwise not occur spontaneously.

A galvanic cell produces current when an oxidation–reduction reaction proceeds spontaneously. A similar apparatus, an **electrolytic cell,** uses electrical energy to produce chemical change. The process of **electrolysis** involves *forcing a current through a cell to produce a chemical change for which the cell potential is negative;* that is, electrical work causes an otherwise nonspontaneous chemical reaction to occur. Electrolysis has great practical importance; for example, charging a battery, producing aluminum metal, and chrome plating an object are all done electrolytically.

To illustrate the difference between a galvanic cell and an electrolytic cell, consider the cell shown in Fig. 17.19(a) as it runs spontaneously to produce 1.10 V. In this *galvanic* cell the reaction at the anode is

$$\mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+} + 2e^-$$

whereas at the cathode the reaction is

$$\mathrm{Cu}^{2+} + 2e^- \longrightarrow \mathrm{Cu}$$

Figure 17.19(b) shows an external power source forcing electrons through the cell in the *opposite* direction to that in (a). This requires an external potential greater than 1.10 V, which must be applied in opposition to the natural cell potential. This device is an *electrolytic cell.* Notice that since electron flow is opposite in the two cases, the anode and cathode are reversed between (a) and (b). Also, ion flow through the salt bridge is opposite in the two cells.

Now we will consider the stoichiometry of electrolytic processes, that is, *how much chemical change occurs with the flow of a given current for a specified time.* Suppose we wish to determine the mass of copper that is plated out when a current of 10.0 amps

1 A = 1 C/s

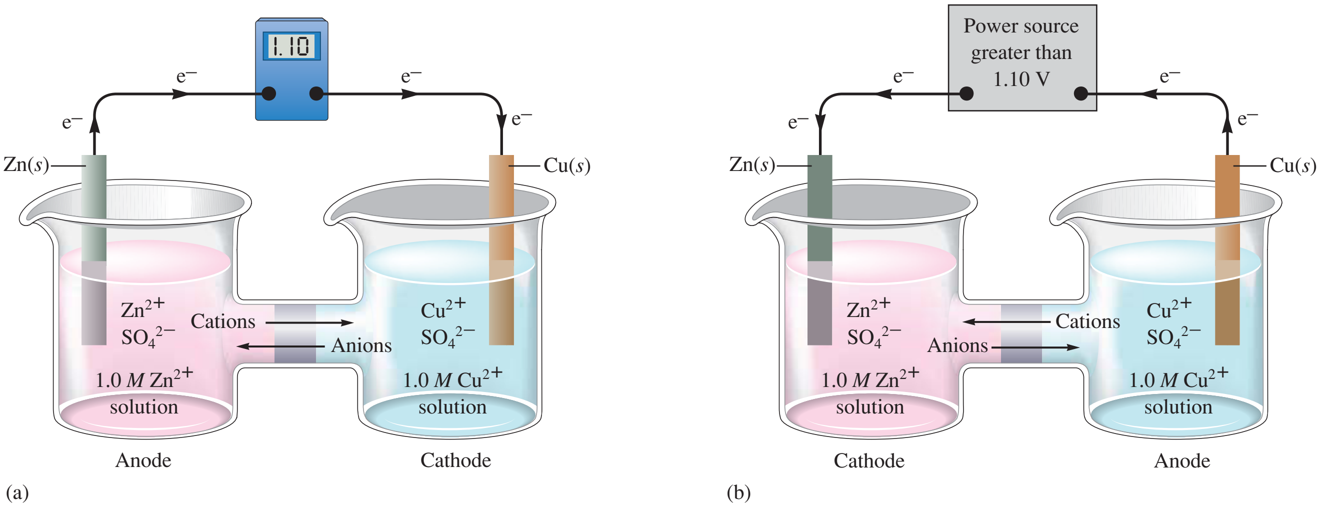


FIGURE 17.19
(a) A standard galvanic cell based on the spontaneous reaction

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

(b) A standard electrolytic cell. A power source forces the opposite reaction

$$Cu + Zn^{2+} \longrightarrow Cu^{2+} + Zn$$

(an **ampere** [amp], abbreviated A, is *1 coulomb of charge per second*) is passed for 30.0 minutes through a solution containing Cu^{2+}. *Plating* means depositing the neutral metal on the electrode by reducing the metal ions in solution. In this case each Cu^{2+} ion requires two electrons to become an atom of copper metal:

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

This reduction process will occur at the cathode of the electrolytic cell.

To solve this stoichiometry problem, we need the following steps:

$$\boxed{\text{current and time}} \xrightarrow{1} \boxed{\text{quantity of charge in coulombs}} \xrightarrow{2} \boxed{\text{moles of electrons}} \xrightarrow{3} \boxed{\text{moles of copper}} \xrightarrow{4} \boxed{\text{grams of copper}}$$

➥ 1 **Since an amp is a coulomb of charge per second, we multiply the current by the time in seconds to obtain the total coulombs of charge passed into the Cu^{2+} solution at the cathode:**

$$\text{Coulombs of charge} = \text{amps} \times \text{seconds} = \frac{C}{s} \times s$$

$$= 10.0\,\frac{C}{s} \times 30.0\text{ min} \times 60.0\,\frac{s}{\text{min}}$$

$$= 1.80 \times 10^{4}\text{ C}$$

➥ 2 **Since 1 mole of electrons carries a charge of 1 faraday, or 96,485 coulombs, we can calculate the number of moles of electrons required to carry 1.80×10^{4} coulombs of charge:**

$$1.80 \times 10^{4}\text{ C} \times \frac{1\text{ mol e}^{-}}{96{,}485\text{ C}} = 1.87 \times 10^{-1}\text{ mol e}^{-}$$

This means that 0.187 mole of electrons flowed into the Cu^{2+} solution.

➥ 3 **Each Cu^{2+} ion requires two electrons to become a copper atom. Thus each mole of electrons produces $\frac{1}{2}$ mole of copper metal:**

$$1.87 \times 10^{-1}\ \text{mol e}^- \times \frac{1\ \text{mol Cu}}{2\ \text{mol e}^-} = 9.35 \times 10^{-2}\ \text{mol Cu}$$

➥ 4 **We now know the moles of copper metal plated onto the cathode, and we can calculate the mass of copper formed:**

$$9.35 \times 10^{-2}\ \text{mol Cu} \times \frac{63.546\ \text{g}}{\text{mol Cu}} = 5.94\ \text{g Cu}$$

Sample Exercise 17.9

Electroplating

Sample Exercise 17.9 describes only the half-cell of interest. There also must be an anode at which oxidation is occurring.

How long must a current of 5.00 A be applied to a solution of Ag^+ to produce 10.5 g silver metal?

Solution

In this case, we must use the steps given earlier in reverse:

grams of silver → moles of silver → moles of electrons required → coulombs of charge required → time required for plating

$$10.5\ \text{g Ag} \times \frac{1\ \text{mol Ag}}{107.868\ \text{g Ag}} = 9.73 \times 10^{-2}\ \text{mol Ag}$$

Each Ag^+ ion requires one electron to become a silver atom:

$$Ag^+ + e^- \longrightarrow Ag$$

Thus 9.73×10^{-2} mol of electrons is required, and we can calculate the quantity of charge carried by these electrons:

$$9.73 \times 10^{-2}\ \text{mol e}^- \times \frac{96{,}485\ \text{C}}{\text{mol e}^-} = 9.39 \times 10^{3}\ \text{C}$$

The 5.00 A (5.00 C/s) of current must produce 9.39×10^3 C of charge. Thus

$$\left(5.00\ \frac{\text{C}}{\text{s}}\right) \times (\text{time, in s}) = 9.39 \times 10^{3}\ \text{C}$$

$$\text{Time} = \frac{9.39 \times 10^{3}}{5.00}\ \text{s} = 1.88 \times 10^{3}\ \text{s} = 31.3\ \text{min}$$

See Exercises 17.77 through 17.80.

Electrolysis of Water

We have seen that hydrogen and oxygen combine spontaneously to form water and that the accompanying decrease in free energy can be used to run a fuel cell to produce electricity. The reverse process, which is of course nonspontaneous, can be forced by electrolysis:

$$\begin{array}{llr}
\text{Anode reaction:} & 2H_2O \longrightarrow O_2 + 4H^+ + 4e^- & -\mathscr{E}° = -1.23\ \text{V} \\
\text{Cathode reaction:} & 4H_2O + 4e^- \longrightarrow 2H_2 + 4OH^- & \mathscr{E}° = -0.83\ \text{V} \\
\hline
\text{Net reaction:} & 6H_2O \longrightarrow 2H_2 + O_2 + \underbrace{4(H^+ + OH^-)}_{4H_2O} & \mathscr{E}° = -2.06\ \text{V}
\end{array}$$

or

$$2H_2O \longrightarrow 2H_2 + O_2$$

Note that these potentials assume an anode chamber with 1 M H^+ and a cathode chamber with 1 M OH^-. In pure water, where $[H^+] = [OH^-] = 10^{-7}$ M, the potential for the overall process is -1.23 V.

In practice, however, if platinum electrodes connected to a 6-V battery are dipped into pure water, no reaction is observed because pure water contains so few ions that only a negligible current can flow. However, addition of even a small amount of a soluble salt causes an immediate evolution of bubbles of hydrogen and oxygen, as illustrated in Fig. 17.20.

Visualization: Electrolysis of Water

FIGURE 17.20
The electrolysis of water produces hydrogen gas at the cathode (on the right) and oxygen gas at the anode (on the left).

Electrolysis of Mixtures of Ions

Suppose a solution in an electrolytic cell contains the ions Cu^{2+}, Ag^+, and Zn^{2+}. If the voltage is initially very low and is gradually turned up, in which order will the metals be plated out onto the cathode? This question can be answered by looking at the standard reduction potentials of these ions:

$$\begin{aligned} Ag^+ + e^- &\longrightarrow Ag & \mathscr{E}° &= 0.80 \text{ V} \\ Cu^{2+} + 2e^- &\longrightarrow Cu & \mathscr{E}° &= 0.34 \text{ V} \\ Zn^{2+} + 2e^- &\longrightarrow Zn & \mathscr{E}° &= -0.76 \text{ V} \end{aligned}$$

Remember that the more *positive* the $\mathscr{E}°$ value, the more the reaction has a tendency to proceed in the direction indicated. Of the three reactions listed, the reduction of Ag^+ occurs most easily, and the order of oxidizing ability is

$$Ag^+ > Cu^{2+} > Zn^{2+}$$

This means that silver will plate out first as the potential is increased, followed by copper, and finally zinc.

Sample Exercise 17.10

Relative Oxidizing Abilities

An acidic solution contains the ions Ce^{4+}, VO_2^+, and Fe^{3+}. Using the $\mathscr{E}°$ values listed in Table 17.1, give the order of oxidizing ability of these species and predict which one will be reduced at the cathode of an electrolytic cell at the lowest voltage.

Solution

The half-reactions and $\mathscr{E}°$ values are

$$\begin{aligned} Ce^{4+} + e^- &\longrightarrow Ce^{3+} & \mathscr{E}° &= 1.70 \text{ V} \\ VO_2^+ + 2H^+ + e^- &\longrightarrow VO^{2+} + H_2O & \mathscr{E}° &= 1.00 \text{ V} \\ Fe^{3+} + e^- &\longrightarrow Fe^{2+} & \mathscr{E}° &= 0.77 \text{ V} \end{aligned}$$

The order of oxidizing ability is therefore

$$Ce^{4+} > VO_2^+ > Fe^{3+}$$

The Ce^{4+} ion will be reduced at the lowest voltage in an electrolytic cell.

See Exercise 17.89.

The principle described in this section is very useful, but it must be applied with some caution. For example, in the electrolysis of an aqueous solution of sodium chloride, we should be able to use $\mathscr{E}°$ values to predict the products. Of the major species in the solution

CHEMICAL IMPACT

The Chemistry of Sunken Treasure

When the galleon *Atocha* was destroyed on a reef by a hurricane in 1622, it was bound for Spain carrying approximately 47 tons of copper, gold, and silver from the New World. The bulk of the treasure was silver bars and coins packed in wooden chests. When treasure hunter Mel Fisher salvaged the silver in 1985, corrosion and marine growth had transformed the shiny metal into something that looked like coral. Restoring the silver to its original condition required an understanding of the chemical changes that had occurred in 350 years of being submerged in the ocean. Much of this chemistry we have already considered at various places in this text.

As the wooden chests containing the silver decayed, the oxygen supply was depleted, favoring the growth of certain bacteria that use the sulfate ion rather than oxygen as an oxidizing agent to generate energy. As these bacteria consume sulfate ions, they release hydrogen sulfide gas that reacts with silver to form black silver sulfide:

$$2\mathrm{Ag}(s) + \mathrm{H_2S}(aq) \longrightarrow \mathrm{Ag_2S}(s) + \mathrm{H_2}(g)$$

Thus, over the years, the surface of the silver became covered with a tightly adhering layer of corrosion, which fortunately protected the silver underneath and thus prevented total conversion of the silver to silver sulfide.

Silver coins and tankards salvaged from the wreck of the *Atocha*.

(Na^+, Cl^-, and H_2O), only Cl^- and H_2O can be readily oxidized. The half-reactions (written as oxidization processes) are

$$2\mathrm{Cl^-} \longrightarrow \mathrm{Cl_2} + 2e^- \qquad -\mathscr{E}^\circ = -1.36\ \mathrm{V}$$

$$2\mathrm{H_2O} \longrightarrow \mathrm{O_2} + 4\mathrm{H^+} + 4e^- \qquad -\mathscr{E}^\circ = -1.23\ \mathrm{V}$$

Since water has the more positive potential, we would expect to see O_2 produced at the anode because it is easier (thermodynamically) to oxidize H_2O than Cl^-. Actually, this does not happen. As the voltage is increased in the cell, the Cl^- ion is the first to be oxidized. A much higher potential than expected is required to oxidize water. The voltage required in excess of the expected value (called the *overvoltage*) is much greater for the production of O_2 than for Cl_2, which explains why chlorine is produced first.

The causes of overvoltage are very complex. Basically, the phenomenon is caused by difficulties in transferring electrons from the species in the solution to the atoms on the electrode across the electrode–solution interface. Because of this situation, $\mathscr{E}^\circ$ values must be used cautiously in predicting the actual order of oxidation or reduction of species in an electrolytic cell.

Another change that took place as the wood decomposed was the formation of carbon dioxide. This shifted the equilibrium that is present in the ocean,

$$CO_2(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

to the right, producing higher concentrations of HCO_3^-. In turn, the HCO_3^- reacted with Ca^{2+} ions present in the seawater to form calcium carbonate:

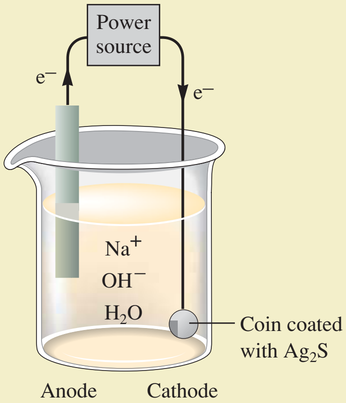
$$Ca^{2+}(aq) + HCO_3^-(aq) \rightleftharpoons CaCO_3(s) + H^+(aq)$$

Calcium carbonate is the main component of limestone. Thus, over time, the corroded silver coins and bars became encased in limestone.

Both the limestone formation and the corrosion had to be dealt with. Since $CaCO_3$ contains the basic anion CO_3^{2-}, acid dissolves limestone:

$$2H^+(aq) + CaCO_3(s) \longrightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(l)$$

Soaking the mass of coins in a buffered acidic bath for several hours allowed the individual pieces to be separated, and the black Ag_2S on the surfaces was revealed. An abrasive could not be used to remove this corrosion; it would have destroyed the details of the engraving—a very valuable feature of the coins to a historian or a collector—and it would have washed away some of the silver. Instead, the corrosion reaction was reversed through electrolytic reduction. The coins were connected to the cathode of an electrolytic cell in a dilute sodium hydroxide solution as represented in the figure.



As electrons flow, the Ag^+ ions in the silver sulfide are reduced to silver metal:

$$Ag_2S + 2e^- \longrightarrow Ag + S^{2-}$$

As a by-product, bubbles of hydrogen gas from the reduction of water form on the surface of the coins:

$$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-$$

The agitation caused by the bubbles loosens the flakes of metal sulfide and helps clean the coins.

These procedures have made it possible to restore the treasure to very nearly its condition when the *Atocha* sailed many years ago.

17.8 Commercial Electrolytic Processes

The chemistry of metals is characterized by their ability to donate electrons to form ions. Because metals are typically such good reducing agents, most are found in nature in *ores,* mixtures of ionic compounds often containing oxide, sulfide, and silicate anions. The noble metals, such as gold, silver, and platinum, are more difficult to oxidize and are often found as pure metals.

Production of Aluminum

Aluminum is one of the most abundant elements on earth, ranking third behind oxygen and silicon. Since aluminum is a very active metal, it is found in nature as its oxide in an ore called *bauxite* (named after Les Baux, France, where it was discovered in 1821). Production of aluminum metal from its ore proved to be more difficult than production of most other metals. In 1782 Lavoisier recognized aluminum to be a metal "whose affinity for oxygen is so strong that it cannot be overcome by any known reducing agent." As a result, pure aluminum metal remained unknown. Finally, in 1854 a process was found for producing metallic aluminum using sodium, but aluminum remained a very expensive rarity. In fact, it is said that Napoleon III served his most honored guests with aluminum forks and spoons, while the others had to settle for gold and silver utensils.

The breakthrough came in 1886 when two men, Charles M. Hall in the United States and Paul Heroult in France, almost simultaneously discovered a practical electrolytic process for producing aluminum (see Fig. 17.21). The key factor in the *Hall–Heroult process* is the use of molten cryolite (Na_3AlF_6) as the solvent for the aluminum oxide.

FIGURE 17.21
Charles Martin Hall (1863–1914) was a student at Oberlin College in Ohio when he first became interested in aluminum. One of his professors commented that anyone who could manufacture aluminum cheaply would make a fortune, and Hall decided to give it a try. The 21-year-old Hall worked in a wooden shed near his house with an iron frying pan as a container, a blacksmith's forge as a heat source, and galvanic cells constructed from fruit jars. Using these crude galvanic cells, Hall found that he could produce aluminum by passing a current through a molten Al_2O_3/Na_3AlF_6 mixture. By a strange coincidence, Paul Heroult, a Frenchman who was born and died in the same years as Hall, made the same discovery at about the same time.

Electrolysis is possible only if ions can move to the electrodes. A common method for producing ion mobility is dissolving the substance to be electrolyzed in water. This is not possible in the case of aluminum because water is more easily reduced than Al^{3+}, as the following standard reduction potentials show:

$$Al^{3+} + 3e^- \longrightarrow Al \qquad \mathscr{E}° = -1.66\ V$$
$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \qquad \mathscr{E}° = -0.83\ V$$

Thus aluminum metal cannot be plated out of an aqueous solution of Al^{3+}.

Ion mobility also can be produced by melting the salt. But the melting point of solid Al_2O_3 is much too high (2050°C) to allow practical electrolysis of the molten oxide. A mixture of Al_2O_3 and Na_3AlF_6, however, has a melting point of 1000°C, and the resulting molten mixture can be used to obtain aluminum metal electrolytically. Because of this discovery by Hall and Heroult, the price of aluminum plunged (see Table 17.3), and its use became economically feasible.

Bauxite is not pure aluminum oxide (called *alumina*); it also contains the oxides of iron, silicon, and titanium, and various silicate materials. To obtain the pure hydrated alumina ($Al_2O_3 \cdot nH_2O$), the crude bauxite is treated with aqueous sodium hydroxide. Being amphoteric, alumina dissolves in the basic solution:

$$Al_2O_3(s) + 2OH^-(aq) \longrightarrow 2AlO_2^-(aq) + H_2O(l)$$

The other metal oxides, which are basic, remain as solids. The solution containing the aluminate ion (AlO_2^-) is separated from the sludge of the other oxides and is acidified with carbon dioxide gas, causing the hydrated alumina to reprecipitate:

$$2CO_2(g) + 2AlO_2^-(aq) + (n + 1)H_2O(l) \longrightarrow 2HCO_3^-(aq) + Al_2O_3 \cdot nH_2O(s)$$

The purified alumina is then mixed with cryolite and melted, and the aluminum ion is reduced to aluminum metal in an electrolytic cell of the type shown in Fig. 17.22. Because the electrolyte solution contains a large number of aluminum-containing ions, the chemistry is not completely clear. However, the alumina probably reacts with the cryolite anion as follows:

$$Al_2O_3 + 4AlF_6^{3-} \longrightarrow 3Al_2OF_6^{2-} + 6F^-$$

The electrode reactions are thought to be

$$\text{Cathode reaction:} \qquad AlF_6^{3-} + 3e^- \longrightarrow Al + 6F^-$$
$$\text{Anode reaction:} \qquad 2Al_2OF_6^{2-} + 12F^- + C \longrightarrow 4AlF_6^{3-} + CO_2 + 4e^-$$

The overall cell reaction can be written as

$$2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$$

The aluminum produced in this electrolytic process is 99.5% pure. To be useful as a structural material, aluminum is alloyed with metals such as zinc (used for trailer and aircraft construction) and manganese (used for cooking utensils, storage tanks, and highway signs). The production of aluminum consumes about 5% of all the electricity used in the United States.

TABLE 17.3 The Price of Aluminum over the Past Century

Date	Price of Aluminum ($/lb)*
1855	100,000
1885	100
1890	2
1895	0.50
1970	0.30
1980	0.80
1990	0.74

*Note the precipitous drop in price after the discovery of the Hall–Heroult process.

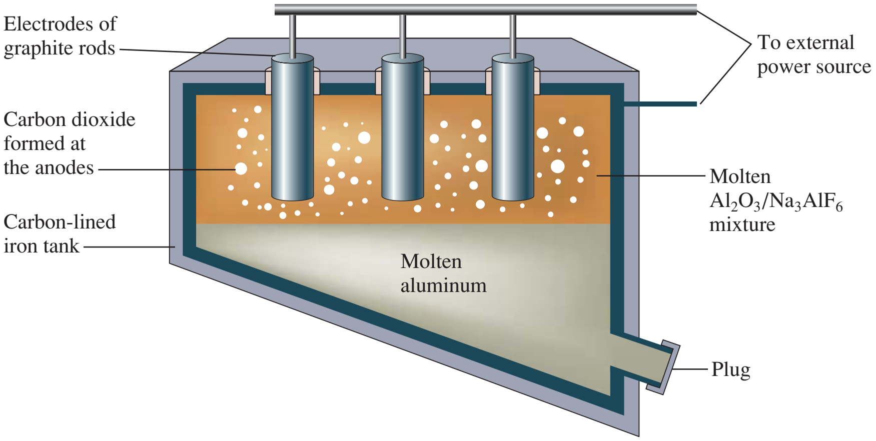


FIGURE 17.22
A schematic diagram of an electrolytic cell for producing aluminum by the Hall–Heroult process. Because molten aluminum is more dense than the mixture of molten cryolite and alumina, it settles to the bottom of the cell and is drawn off periodically. The graphite electrodes are gradually eaten away and must be replaced from time to time. The cell operates at a current flow of up to 250,000 A.

Electrorefining of Metals

Purification of metals is another important application of electrolysis. For example, impure copper from the chemical reduction of copper ore is cast into large slabs that serve as the anodes for electrolytic cells. Aqueous copper sulfate is the electrolyte, and thin sheets of ultrapure copper function as the cathodes (see Fig. 17.23).

The main reaction at the anode is

$$Cu \longrightarrow Cu^{2+} + 2e^-$$

Other metals such as iron and zinc are also oxidized from the impure anode:

$$Zn \longrightarrow Zn^{2+} + 2e^-$$
$$Fe \longrightarrow Fe^{2+} + 2e^-$$

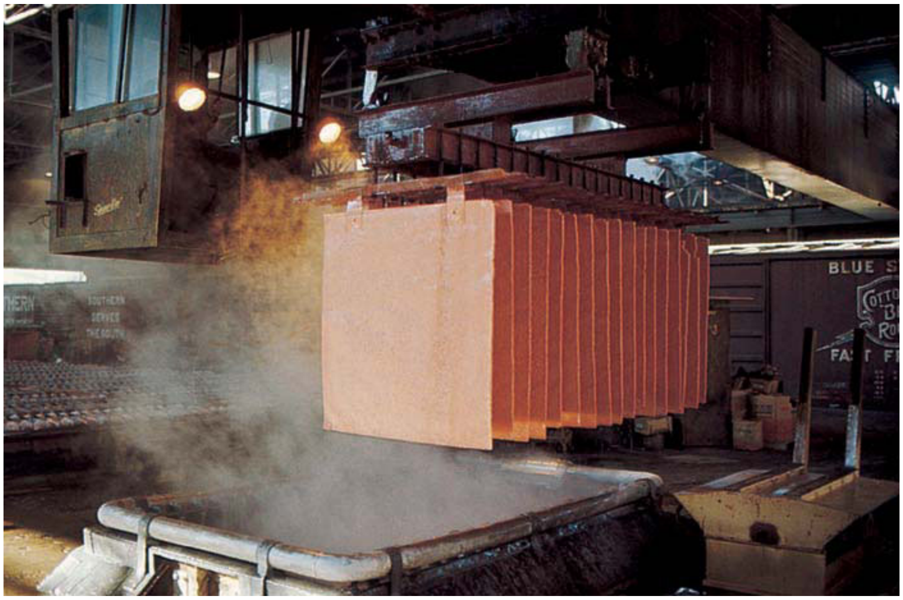


FIGURE 17.23
Ultrapure copper sheets that serve as the cathodes are lowered between slabs of impure copper that serve as the anodes into a tank containing an aqueous solution of copper sulfate ($CuSO_4$). It takes about four weeks for the anodes to dissolve and for the pure copper to be deposited on the cathodes.

(a)

(b)

FIGURE 17.24
(a) A silver-plated teapot. Silver plating is often used to beautify and protect cutlery and items of table service.
(b) Schematic of the electroplating of a spoon. The item to be plated is the cathode, and the anode is a silver bar. Silver is plated out at the cathode: $Ag^+ + e^- \rightarrow Ag$. Note that a salt bridge is not needed here because Ag^+ ions are involved at both electrodes.

Noble metal impurities in the anode are not oxidized at the voltage used; they fall to the bottom of the cell to form a sludge, which is processed to remove the valuable silver, gold, and platinum.

The Cu^{2+} ions from the solution are deposited onto the cathode

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

producing copper that is 99.95% pure.

Metal Plating

Metals that readily corrode can often be protected by the application of a thin coating of a metal that resists corrosion. Examples are "tin" cans, which are actually steel cans with a thin coating of tin, and chrome-plated steel bumpers for automobiles.

An object can be plated by making it the cathode in a tank containing ions of the plating metal. The silver plating of a spoon is shown schematically in Fig. 17.24(b). In an actual plating process, the solution also contains ligands that form complexes with the silver ion. By lowering the concentration of Ag^+ in this way, a smooth, even coating of silver is obtained.

Electrolysis of Sodium Chloride

Addition of a nonvolatile solute lowers the melting point of the solvent, molten NaCl in this case.

Sodium metal is mainly produced by the electrolysis of molten sodium chloride. Because solid NaCl has a rather high melting point (800°C), it is usually mixed with solid $CaCl_2$ to lower the melting point to about (600°C). The mixture is then electrolyzed in a **Downs cell,** as illustrated in Fig. 17.25, where the reactions are

$$\text{Anode reaction:} \qquad 2Cl^- \longrightarrow Cl_2 + 2e^-$$
$$\text{Cathode reaction:} \qquad Na^+ + e^- \longrightarrow Na$$

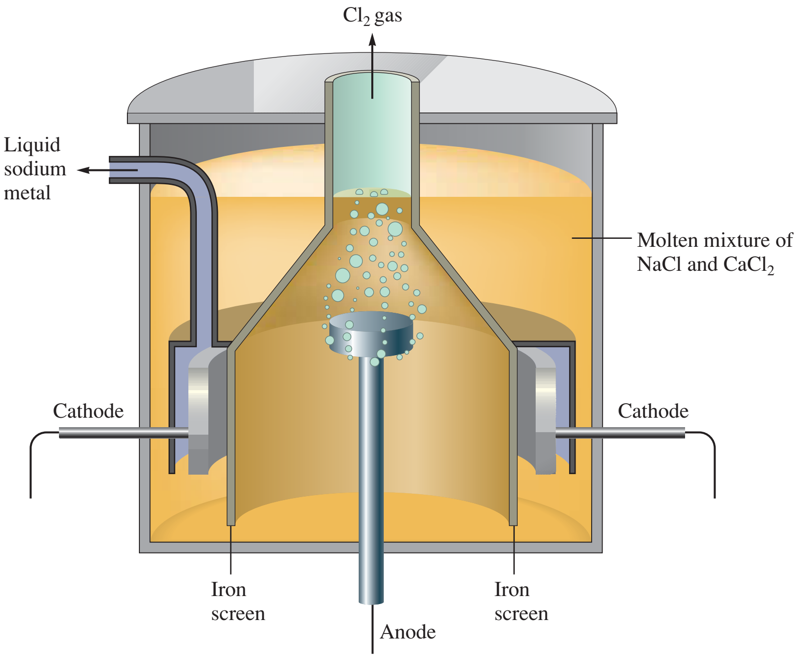


FIGURE 17.25
The Downs cell for the electrolysis of molten sodium chloride. The cell is designed so that the sodium and chlorine produced cannot come into contact with each other to re-form NaCl.

At the temperatures in the Downs cell, the sodium is liquid and is drained off, then cooled, and cast into blocks. Because it is so reactive, sodium must be stored in an inert solvent, such as mineral oil, to prevent its oxidation.

Electrolysis of aqueous sodium chloride (brine) is an important industrial process for the production of chlorine and sodium hydroxide. In fact, this process is the second largest consumer of electricity in the United States, after the production of aluminum. Sodium is not produced in this process under normal circumstances because H_2O is more easily reduced than Na^+, as the standard reduction potentials show:

$$\begin{aligned} Na^+ + e^- &\longrightarrow Na & \mathscr{E}° &= -2.71\text{ V} \\ 2H_2O + 2e^- &\longrightarrow H_2 + 2OH^- & \mathscr{E}° &= -0.83\text{ V} \end{aligned}$$

Hydrogen, not sodium, is produced at the cathode.

For the reasons we discussed in Section 17.7, chlorine gas is produced at the anode. Thus the electrolysis of brine produces hydrogen and chlorine:

$$\begin{aligned} &\text{Anode reaction:} & 2Cl^- &\longrightarrow Cl_2 + 2e^- \\ &\text{Cathode reaction:} & 2H_2O + 2e^- &\longrightarrow H_2 + 2OH^- \end{aligned}$$

It leaves a solution containing dissolved NaOH and NaCl.

The contamination of the sodium hydroxide by NaCl can be virtually eliminated using a special **mercury cell** for electrolyzing brine (see Fig. 17.26). In this cell, mercury is the conductor at the cathode, and because hydrogen gas has an extremely high overvoltage with a mercury electrode, Na^+ is reduced instead of H_2O. The resulting sodium metal dissolves in the mercury, forming a liquid alloy, which is then pumped to a chamber where the dissolved sodium reacts with water to produce hydrogen:

$$2Na(s) + 2H_2O(l) \longrightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g)$$

Relatively pure solid NaOH can be recovered from the aqueous solution, and the regenerated mercury is then pumped back to the electrolysis cell. This process, called the **chlor–alkali process,** was the main method for producing chlorine and sodium hydroxide in the United States for many years. However, because of the environmental problems associated with the mercury cell, it has been largely displaced in the

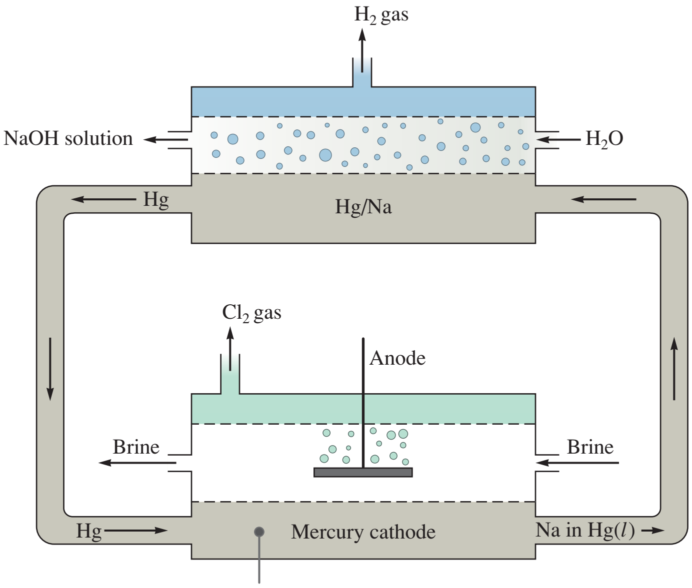


FIGURE 17.26
The mercury cell for production of chlorine and sodium hydroxide. The large overvoltage required to produce hydrogen at a mercury electrode means that Na^+ ions are reduced rather than water. The sodium formed dissolves in the liquid mercury and is pumped to a chamber where it reacts with water.

chlor–alkali industry by other technologies. In the United States, nearly 75% of the chlor–alkali production is now carried out in diaphragm cells. In a diaphragm cell the cathode and anode are separated by a diaphragm that allows passage of H_2O molecules, Na^+ ions, and, to a limited extent, Cl^- ions. The diaphragm does not allow OH^- ions to pass through it. Thus the H_2 and OH^- formed at the cathode are kept separate from the Cl_2 formed at the anode. The major disadvantage of this process is that the aqueous effluent pumped from the cathode compartment contains a mixture of sodium hydroxide and unreacted sodium chloride, which must be separated if pure sodium hydroxide is a desired product.

In the past 30 years, a new process has been developed in the chlor–alkali industry that employs a membrane to separate the anode and cathode compartments in brine electrolysis cells. The membrane is superior to a diaphragm because the membrane is impermeable to anions. Only cations can flow through the membrane. Because neither Cl^- nor OH^- ions can pass through the membrane separating the anode and cathode compartments, NaCl contamination of the NaOH formed at the cathode does not occur. Although membrane technology is now just becoming prominent in the United States, it is the dominant method for chlor–alkali production in Japan.

Key Terms

electrochemistry

Section 17.1

oxidation–reduction (redox) reaction
reducing agent
oxidizing agent
oxidation
reduction
half-reactions
salt bridge
porous disk
galvanic cell
anode
cathode

For Review

Electrochemistry

- The study of the interchange of chemical and electrical energy
- Employs oxidation–reduction reactions
- Galvanic cell: chemical energy is transformed into electrical energy by separating the oxidizing and reducing agents and forcing the electrons to travel through a wire
- Electrolytic cell: electrical energy is used to produce a chemical change

Galvanic cell

- Anode: the electrode where oxidation occurs
- Cathode: the electrode where reduction occurs

cell potential (electromotive force)
volt
voltmeter
potentiometer

Section 17.2

standard hydrogen electrode
standard reduction potentials

Section 17.3

faraday

Section 17.4

concentration cell
Nernst equation
glass electrode
ion-selective electrode

Section 17.5

battery
lead storage battery
dry cell battery
fuel cell

Section 17.6

corrosion
galvanizing
cathodic protection

Section 17.7

electrolytic cell
electrolysis
ampere

Section 17.8

Downs cell
mercury cell
chlor–alkali process

- The driving force behind the electron transfer is called the cell potential ($\mathscr{E}_{\text{cell}}$)
  - The potential is measured in units of volts (V), defined as a joule of work per coulomb of charge:

$$\mathscr{E}(\text{V}) = \frac{-\text{work (J)}}{\text{charge (C)}} = -\frac{w}{q}$$

  - A system of half-reactions, called standard reduction potentials, can be used to calculate the potentials of various cells
    - The half-reaction $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$ is arbitrarily assigned a potential of 0 V

Free energy and work

- The maximum work that a cell can perform is

$$-w_{\max} = q\mathscr{E}_{\max}$$

where $\mathscr{E}_{\max}$ represents the cell potential when no current is flowing

- The actual work obtained from a cell is always less than the maximum because energy is lost through frictional heating of the wire when current flows
- For a process carried out at constant temperature and pressure, the change in free energy equals the maximum useful work obtainable from that process:

$$\Delta G = w_{\max} = -q\mathscr{E}_{\max} = -nF\mathscr{E}$$

where F (faraday) equals 96,485 C and n is the number of moles of electrons transferred in the process

Concentration cell

- A galvanic cell in which both compartments have the same components but at different concentrations
- The electrons flow in the direction that tends to equalize the concentrations

Nernst equation

- Shows how the cell potential depends on the concentrations of the cell components:

$$\mathscr{E} = \mathscr{E}_0 - \frac{0.0591}{n}\log Q \qquad \text{at } 25^\circ\text{C}$$

- When a galvanic cell is at equilibrium, $\mathscr{E} = 0$ and $Q = K$

Batteries

- A battery consists of a galvanic cell or group of cells connected in series that serve as a source of direct current
- Lead storage battery
  - Anode: lead
  - Cathode: lead coated with PbO_2
  - Electrolyte: $\text{H}_2\text{SO}_4(aq)$
- Dry cell battery
  - Contains a moist paste instead of a liquid electrolyte
  - Anode: usually Zn
  - Cathode: carbon rod in contact with an oxidizing agent (which varies depending on the application)

Fuel cells

- Galvanic cells in which the reactants are continuously supplied
- The H_2/O_2 fuel cell is based on the reaction between H_2 and O_2 to form water

Corrosion

- Involves the oxidation of metals to form mainly oxides and sulfides

- Some metals, such as aluminum and chromium, form a thin protective oxide coating that prevents further corrosion
- The corrosion of iron to form rust is an electrochemical process
  - The Fe^{2+} ions formed at anodic areas of the surface migrate through the moisture layer to cathodic regions, where they react with oxygen from the air
  - Iron can be protected from corrosion by coating it with paint or with a thin layer of metal such as chromium, tin, or zinc; by alloying; and by cathodic protection

Electrolysis

- Used to place a thin coating of metal onto steel
- Used to produce pure metals such as aluminum and copper

REVIEW QUESTIONS

1. What is electrochemistry? What are redox reactions? Explain the difference between a galvanic and an electrolytic cell.
2. Galvanic cells harness spontaneous oxidation–reduction reactions to produce work by producing a current. They do so by controlling the flow of electrons from the species oxidized to the species reduced. How is a galvanic cell designed? What is in the cathode compartment? The anode compartment? What purpose do electrodes serve? Which way do electrons always flow in the wire connecting the two electrodes in a galvanic cell? Why is it necessary to use a salt bridge or a porous disk in a galvanic cell? Which way do cations flow in the salt bridge? Which way do the anions flow? What is a cell potential and what is a volt?
3. Table 17.1 lists common half-reactions along with the standard reduction potential associated with each half-reaction. These standard reduction potentials are all relative to some standard. What is the standard (zero point)? If $\mathscr{E}°$ is positive for a half-reaction, what does it mean? If $\mathscr{E}°$ is negative for a half-reaction, what does it mean? Which species in Table 17.1 is most easily reduced? Least easily reduced? The reverse of the half-reactions in Table 17.1 are the oxidation half-reactions. How are standard oxidation potentials determined? In Table 17.1, which species is the best reducing agent? The worst reducing agent?

   To determine the standard cell potential for a redox reaction, the standard reduction potential is added to the standard oxidation potential. What must be true about this sum if the cell is to be spontaneous (produce a galvanic cell)? Standard reduction and oxidation potentials are intensive. What does this mean? Summarize how line notation is used to describe galvanic cells.
4. Consider the equation $\Delta G° = -nF\mathscr{E}°$. What are the four terms in this equation? Why does a minus sign appear in the equation? What does the superscript ° indicate?
5. The Nernst equation allows determination of the cell potential for a galvanic cell at nonstandard conditions. Write out the Nernst equation. What are nonstandard conditions? What do $\mathscr{E}$, $\mathscr{E}°$, n, and Q stand for in the Nernst equation? What does the Nernst equation reduce to when a redox reaction is at equilibrium? What are the signs of $\Delta G°$ and $\mathscr{E}°$ when $K < 1$? When $K > 1$? When $K = 1$? Explain the following statement: $\mathscr{E}$ determines spontaneity, while $\mathscr{E}°$ determines the equilibrium position. Under what conditions can you use $\mathscr{E}°$ to predict spontaneity?
6. What are concentration cells? What is $\mathscr{E}°$ in a concentration cell? What is the driving force for a concentration cell to produce a voltage? Is the higher or the lower ion concentration solution present at the anode? When the anode ion concentration is decreased and/or the cathode ion concentration is increased, both

give rise to larger cell potentials. Why? Concentration cells are commonly used to calculate the value of equilibrium constants for various reactions. For example, the silver concentration cell illustrated in Fig. 17.9 can be used to determine the K_{sp} value for AgCl(s). To do so, NaCl is added to the anode compartment until no more precipitate forms. The [Cl^-] in solution is then determined somehow. What happens to $\mathscr{E}_{\text{cell}}$ when NaCl is added to the anode compartment? To calculate the K_{sp} value, [Ag^+] must be calculated. Given the value of $\mathscr{E}_{\text{cell}}$, how is [$\text{Ag}^+$] determined at the anode?

7. Batteries are galvanic cells. What happens to $\mathscr{E}_{\text{cell}}$ as a battery discharges? Does a battery represent a system at equilibrium? Explain. What is $\mathscr{E}_{\text{cell}}$ when a battery reaches equilibrium? How are batteries and fuel cells alike? How are they different? The U.S. space program utilizes hydrogen–oxygen fuel cells to produce power for its spacecraft. What is a hydrogen–oxygen fuel cell?
8. Not all spontaneous redox reactions produce wonderful results. Corrosion is an example of a spontaneous redox process that has negative effects. What happens in the corrosion of a metal such as iron? What must be present for the corrosion of iron to take place? How can moisture and salt increase the severity of corrosion? Explain how the following protect metals from corrosion:
   a. paint
   b. durable oxide coatings
   c. galvanizing
   d. sacrificial metal
   e. alloying
   f. cathodic protection
9. What characterizes an electrolytic cell? What is an ampere? When the current applied to an electrolytic cell is multiplied by the time in seconds, what quantity is determined? How is this quantity converted to moles of electrons required? How are moles of electrons required converted to moles of metal plated out? What does plating mean? How do you predict the cathode and the anode half-reactions in an electrolytic cell? Why is the electrolysis of molten salts much easier to predict in terms of what occurs at the anode and cathode than the electrolysis of aqueous dissolved salts? What is overvoltage?
10. Electrolysis has many important industrial applications. What are some of these applications? The electrolysis of molten NaCl is the major process by which sodium metal is produced. However, the electrolysis of aqueous NaCl does not produce sodium metal under normal circumstances. Why? What is purification of a metal by electrolysis?

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

1. Sketch a galvanic cell, and explain how it works. Look at Figs. 17.1 and 17.2. Explain what is occurring in each container and why the cell in Fig. 17.2 "works" but the one in Fig. 17.1 does not.

2. In making a specific galvanic cell, explain how one decides on the electrodes and the solutions to use in the cell.

3. You want to "plate out" nickel metal from a nickel nitrate solution onto a piece of metal inserted into the solution. Should you use copper or zinc? Explain.

4. A copper penny can be dissolved in nitric acid but not in hydrochloric acid. Using reduction potentials from the book, show why this is so. What are the products of the reaction? Newer pennies contain a mixture of zinc and copper. What happens to the zinc in the penny when the coin is placed in nitric acid? Hydrochloric acid? Support your explanations with data from the book, and include balanced equations for all reactions.

5. Sketch a cell that forms iron metal from iron(II) while changing chromium metal to chromium(III). Calculate the voltage, show the electron flow, label the anode and cathode, and balance the overall cell equation.

6. Which of the following is the best reducing agent: F_2, H_2, Na, Na^+, F^-? Explain. Order as many of these species as possible from the best to the worst oxidizing agent. Why can't you order all of them? From Table 17.1 choose the species that is the best oxidizing agent. Choose the best reducing agent. Explain.

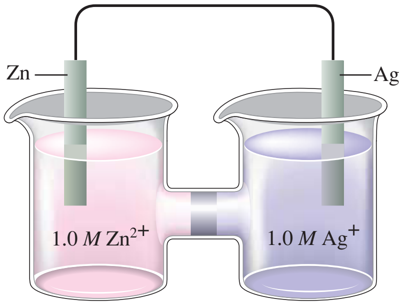
7. You are told that metal A is a better reducing agent than metal B. What, if anything, can be said about A^+ and B^+? Explain.

8. Explain the following relationships: ΔG and w, cell potential and w, cell potential and ΔG, cell potential and Q. Using these relationships, explain how you could make a cell in which both electrodes are the same metal and both solutions contain the same compound, but at different concentrations. Why does such a cell run spontaneously?

9. Explain why cell potentials are not multiplied by the coefficients in the balanced redox equation. (Use the relationship between ΔG and cell potential to do this.)

10. What is the difference between $\mathscr{E}$ and $\mathscr{E}^\circ$? When is $\mathscr{E}$ equal to zero? When is $\mathscr{E}^\circ$ equal to zero? (Consider "regular" galvanic cells as well as concentration cells.)

11. Consider the following galvanic cell:



What happens to $\mathscr{E}$ as the concentration of Zn^{2+} is increased? As the concentration of Ag^+ is increased? What happens to $\mathscr{E}^\circ$ in these cases?

12. Look up the reduction potential for Fe^{3+} to Fe^{2+}. Look up the reduction potential for Fe^{2+} to Fe. Finally, look up the reduction potential for Fe^{3+} to Fe. You should notice that adding the reduction potentials for the first two does not give the potential for the third. Why not? Show how you can use the first two potentials to calculate the third potential.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide.*

Review of Oxidation–Reduction Reactions

If you have trouble with these exercises, you should review Sections 4.9 and 4.10.

13. Define *oxidation* and *reduction* in terms of both change in oxidation number and electron loss or gain.

14. Assign oxidation numbers to all the atoms in each of the following.

a. HNO_3
b. $CuCl_2$
c. O_2
d. H_2O_2
e. $C_6H_{12}O_6$
f. Ag
g. $PbSO_4$
h. PbO_2
i. $Na_2C_2O_4$
j. CO_2
k. $(NH_4)_2Ce(SO_4)_3$
l. Cr_2O_3

15. Specify which of the following equations represent oxidation–reduction reactions, and indicate the oxidizing agent, the reducing agent, the species being oxidized, and the species being reduced.
a. $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$
b. $2AgNO_3(aq) + Cu(s) \rightarrow Cu(NO_3)_2(aq) + 2Ag(s)$
c. $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$
d. $2H^+(aq) + 2CrO_4^{2-}(aq) \rightarrow Cr_2O_7^{2-}(aq) + H_2O(l)$

16. Balance each of the following equations by the half-reaction method for the pH conditions specified.
a. $Cr(s) + NO_3^-(aq) \rightarrow Cr^{3+}(aq) + NO(g)$ (acidic)
b. $Al(s) + MnO_4^-(aq) \rightarrow Al^{3+}(aq) + Mn^{2+}(aq)$ (acidic)
c. $CH_3OH(aq) + Ce^{4+}(aq) \rightarrow CO_2(aq) + Ce^{3+}(aq)$ (acidic)
d. $PO_3^{3-}(aq) + MnO_4^-(aq) \rightarrow PO_4^{3-}(aq) + MnO_2(s)$ (basic)
e. $Mg(s) + OCl^-(aq) \rightarrow Mg(OH)_2(s) + Cl^-(aq)$ (basic)
f. $H_2CO(aq) + Ag(NH_3)_2^+(aq) \rightarrow HCO_3^-(aq) + Ag(s) + NH_3(aq)$ (basic)

Questions

17. When magnesium metal is added to a beaker of $HCl(aq)$, a gas is produced. Knowing that magnesium is oxidized and that hydrogen is reduced, write the balanced equation for the reaction. How many electrons are transferred in the balanced equation? What quantity of useful work can be obtained when Mg is added directly to the beaker of HCl? How can you harness this reaction to do useful work?

18. How can one construct a galvanic cell from two substances, each having a negative standard reduction potential?

19. The free energy change for a reaction, ΔG, is an extensive property. What is an extensive property? Surprisingly, one can calculate ΔG from the cell potential, $\mathscr{E}$, for the reaction. This is surprising because $\mathscr{E}$ is an intensive property. How can the extensive property ΔG be calculated from the intensive property $\mathscr{E}$?

20. What is wrong with the following statement: The best concentration cell will consist of the substance having the most positive standard reduction potential. What drives a concentration cell to produce a large voltage?

21. When jump-starting a car with a dead battery, the ground jumper should be attached to a remote part of the engine block. Why?

22. In theory, most metals should easily corrode in air. Why? A group of metals called the noble metals are relatively difficult to corrode in air. Some noble metals include: gold, platinum, and silver. Reference Table 17.1 to come up with a possible reason why the noble metals are relatively difficult to corrode.

23. Consider the electrolysis of a molten salt of some metal. What information must you know to calculate the mass of metal plated out in the electrolytic cell?

24. Although aluminum is one of the most abundant elements on earth, production of pure Al proved very difficult until the late 1800s. At this time, the Hall–Heroult process made it relatively easy to produce pure Al. Why was pure Al so difficult to produce and what was the key discovery behind the Hall–Heroult process?

Exercises

In this section similar exercises are paired.

Galvanic Cells, Cell Potentials, Standard Reduction Potentials, and Free Energy

25. Sketch the galvanic cells based on the following overall reactions. Show the direction of electron flow and identify the cathode and anode. Give the overall balanced reaction. Assume that all concentrations are 1.0 *M* and that all partial pressures are 1.0 atm.

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

b. $Cu^{2+}(aq) + Mg(s) \rightleftharpoons Mg^{2+}(aq) + Cu(s)$

26. Sketch the galvanic cells based on the following overall reactions. Show the direction of electron flow, the direction of ion migration through the salt bridge, and identify the cathode and anode. Give the overall balanced reaction. Assume that all concentrations are 1.0 *M* and that all partial pressures are 1.0 atm.

a. $IO_3^-(aq) + Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + I_2(aq)$

b. $Zn(s) + Ag^+(aq) \rightleftharpoons Zn^{2+}(aq) + Ag(s)$

27. Calculate $\mathscr{E}^\circ$ values for the galvanic cells in Exercise 25.

28. Calculate $\mathscr{E}^\circ$ values for the galvanic cells in Exercise 26.

29. Sketch the galvanic cells based on the following half-reactions. Show the direction of electron flow, show the direction of ion migration through the salt bridge, and identify the cathode and anode. Give the overall balanced reaction, and determine $\mathscr{E}^\circ$ for the galvanic cells. Assume that all concentrations are 1.0 *M* and that all partial pressures are 1.0 atm.

a. $Cl_2 + 2e^- \rightarrow 2Cl^- \qquad \mathscr{E}^\circ = 1.36\text{ V}$
$Br_2 + 2e^- \rightarrow 2Br^- \qquad \mathscr{E}^\circ = 1.09\text{ V}$

b. $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \qquad \mathscr{E}^\circ = 1.51\text{ V}$
$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O \qquad \mathscr{E}^\circ = 1.60\text{ V}$

30. Sketch the galvanic cells based on the following half-reactions. Show the direction of electron flow, show the direction of ion migration through the salt bridge, and identify the cathode and anode. Give the overall balanced reaction, and determine $\mathscr{E}^\circ$ for the galvanic cells. Assume that all concentrations are 1.0 *M* and that all partial pressures are 1.0 atm.

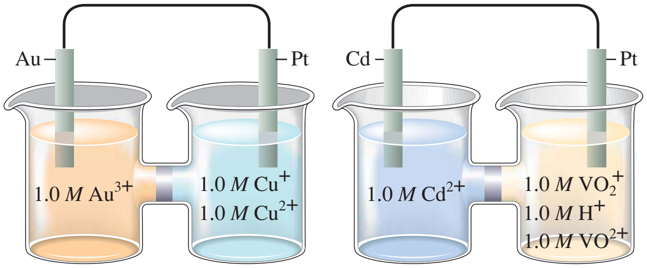
a. $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad \mathscr{E}^\circ = 1.78\text{ V}$
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad \mathscr{E}^\circ = 0.68\text{ V}$

b. $Mn^{2+} + 2e^- \rightarrow Mn \qquad \mathscr{E}^\circ = -1.18\text{ V}$
$Fe^{3+} + 3e^- \rightarrow Fe \qquad \mathscr{E}^\circ = -0.036\text{ V}$

31. Give the standard line notation for each cell in Exercises 25 and 29.

32. Give the standard line notation for each cell in Exercises 26 and 30.

33. Consider the following galvanic cells:



(a) (b)

For each galvanic cell, give the balanced cell reaction and determine $\mathscr{E}^\circ$. Standard reduction potentials are found in Table 17.1.

34. Give the balanced cell reaction and determine $\mathscr{E}^\circ$ for the galvanic cells based on the following half-reactions. Standard reduction potentials are found in Table 17.1.

a. $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

b. $2H^+ + 2e^- \rightarrow H_2$
$Al^{3+} + 3e^- \rightarrow Al$

35. Calculate $\mathscr{E}^\circ$ values for the following cells. Which reactions are spontaneous as written (under standard conditions)? Balance the reactions. Standard reduction potentials are found in Table 17.1.

a. $MnO_4^-(aq) + I^-(aq) \rightleftharpoons I_2(aq) + Mn^{2+}(aq)$

b. $MnO_4^-(aq) + F^-(aq) \rightleftharpoons F_2(g) + Mn^{2+}(aq)$

36. Calculate $\mathscr{E}^\circ$ values for the following cells. Which reactions are spontaneous as written (under standard conditions)? Balance the reactions that are not already balanced. Standard reduction potentials are found in Table 17.1.

a. $H_2(g) \rightleftharpoons H^+(aq) + H^-(aq)$

b. $Au^{3+}(aq) + Ag(s) \rightleftharpoons Ag^+(aq) + Au(s)$

37. Chlorine dioxide (ClO_2), which is produced by the reaction

$$2NaClO_2(aq) + Cl_2(g) \longrightarrow 2ClO_2(g) + 2NaCl(aq)$$

has been tested as a disinfectant for municipal water treatment. Using data from Table 17.1, calculate $\mathscr{E}^\circ$ and ΔG° at 25°C for the production of ClO_2.

38. The amount of manganese in steel is determined by changing it to permanganate ion. The steel is first dissolved in nitric acid, producing Mn^{2+} ions. These ions are then oxidized to the deeply colored MnO_4^- ions by periodate ion (IO_4^-) in acid solution.

a. Complete and balance an equation describing each of the above reactions.

b. Calculate $\mathscr{E}^\circ$ and ΔG° at 25°C for each reaction.

39. Calculate the maximum amount of work that can be obtained from the galvanic cells at standard conditions in Exercise 33.

40. Calculate the maximum amount of work that can be obtained from the galvanic cells at standard conditions in Exercise 34.

41. Calculate $\mathscr{E}^\circ$ for the reaction

$$CH_3OH(l) + \tfrac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

using values of ΔG_f° in Appendix 4.

42. The equation $\Delta G^\circ = -nF\mathscr{E}^\circ$ also can be applied to half-reactions. Use standard reduction potentials to estimate ΔG_f° for $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$. (ΔG_f° for $e^- = 0$.)

43. Using data from Table 17.1, place the following in order of increasing strength as oxidizing agents (all under standard conditions).

$$Cd^{2+},\quad IO_3^-,\quad K^+,\quad H_2O,\quad AuCl_4^-,\quad I_2$$

44. Using data from Table 17.1, place the following in order of increasing strength as reducing agents (all under standard conditions).

$$Cu^+,\quad F^-,\quad H^-,\quad H_2O,\quad I_2,\quad K$$

45. Answer the following questions using data from Table 17.1 (all under standard conditions).

a. Is $H^+(aq)$ capable of oxidizing $Cu(s)$ to $Cu^{2+}(aq)$?
b. Is $Fe^{3+}(aq)$ capable of oxidizing $I^-(aq)$?
c. Is $H_2(g)$ capable of reducing $Ag^+(aq)$?
d. Is $Fe^{2+}(aq)$ capable of reducing $Cr^{3+}(aq)$ to $Cr^{2+}(aq)$?

46. Consider only the species (at standard conditions)

$$Na^+,\quad Cl^-,\quad Ag^+,\quad Ag,\quad Zn^{2+},\quad Zn,\quad Pb$$

in answering the following questions. Give reasons for your answers. (Use data from Table 17.1.)

a. Which is the strongest oxidizing agent?
b. Which is the strongest reducing agent?
c. Which species can be oxidized by $SO_4^{2-}(aq)$ in acid?
d. Which species can be reduced by $Al(s)$?

47. Use the table of standard reduction potentials (Table 17.1) to pick a reagent that is capable of each of the following oxidations (under standard conditions in acidic solution).

a. Oxidize Br^- to Br_2 but not oxidize Cl^- to Cl_2
b. Oxidize Mn to Mn^{2+} but not oxidize Ni to Ni^{2+}

48. Use the table of standard reduction potentials (Table 17.1) to pick a reagent that is capable of each of the following reductions (under standard conditions in acidic solution).

a. Reduce Cu^{2+} to Cu but not reduce Cu^{2+} to Cu^+.
b. Reduce Br_2 to Br^- but not reduce I_2 to I^-.

49. Hydrazine is somewhat toxic. Use the half-reactions shown below to explain why household bleach (a highly alkaline solution of sodium hypochlorite) should not be mixed with household ammonia or glass cleansers that contain ammonia.

$$ClO^- + H_2O + 2e^- \longrightarrow 2OH^- + Cl^- \qquad \mathscr{E}^\circ = 0.90\text{ V}$$
$$N_2H_4 + 2H_2O + 2e^- \longrightarrow 2NH_3 + 2OH^- \qquad \mathscr{E}^\circ = -0.10\text{ V}$$

50. The compound with the formula TlI_3 is a black solid. Given the following standard reduction potentials,

$$Tl^{3+} + 2e^- \longrightarrow Tl^+ \qquad \mathscr{E}^\circ = 1.25\text{ V}$$
$$I_3^- + 2e^- \longrightarrow 3I^- \qquad \mathscr{E}^\circ = 0.55\text{ V}$$

would you formulate this compound as thallium(III) iodide or thallium(I) triiodide?

The Nernst Equation

51. A galvanic cell is based on the following half-reactions at 25°C:

$$Ag^+ + e^- \longrightarrow Ag$$
$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$$

Predict whether $\mathscr{E}_{\text{cell}}$ is larger or smaller than $\mathscr{E}^\circ_{\text{cell}}$ for the following cases.

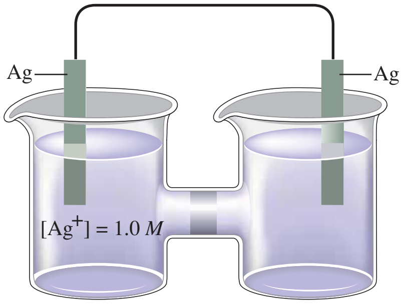
a. $[Ag^+] = 1.0\ M$, $[H_2O_2] = 2.0\ M$, $[H^+] = 2.0\ M$
b. $[Ag^+] = 2.0\ M$, $[H_2O_2] = 1.0\ M$, $[H^+] = 1.0 \times 10^{-7}\ M$

52. Consider the concentration cell in Fig. 17.10. If the Fe^{2+} concentration in the right compartment is changed from 0.1 *M* to $1 \times 10^{-7}\ M\ Fe^{2+}$, predict the direction of electron flow, and designate the anode and cathode compartments.

53. Consider the concentration cell shown below. Calculate the cell potential at 25°C when the concentration of Ag^+ in the compartment on the right is the following.

a. 1.0 *M*
b. 2.0 *M*
c. 0.10 *M*
d. $4.0 \times 10^{-5}\ M$
e. Calculate the potential when both solutions are 0.10 *M* in Ag^+.

For each case, also identify the cathode, the anode, and the direction in which electrons flow.



54. Consider a concentration cell similar to the one shown in Exercise 53, except that both electrodes are made of Ni and in the left-hand compartment $[Ni^{2+}] = 1.0\ M$. Calculate the cell potential at 25°C when the concentration of Ni^{2+} in the compartment on the right has each of the following values.

a. 1.0 *M*
b. 2.0 *M*
c. 0.10 *M*
d. $4.0 \times 10^{-5}\ M$
e. Calculate the potential when both solutions are 2.5 *M* in Ni^{2+}.

For each case, also identify the cathode, anode, and the direction in which electrons flow.

55. The overall reaction in the lead storage battery is

$$Pb(s) + PbO_2(s) + 2H^+(aq) + 2HSO_4^-(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

Calculate $\mathscr{E}$ at 25°C for this battery when $[H_2SO_4] = 4.5\ M$, that is, $[H^+] = [HSO_4^-] = 4.5\ M$. At 25°C, $\mathscr{E}^\circ = 2.04$ V for the lead storage battery.

56. Calculate the pH of the cathode compartment for the following reaction given $\mathscr{E}_{\text{cell}} = 3.01$ V when $[Cr^{3+}] = 0.15\ M$, $[Al^{3+}] = 0.30\ M$, and $[Cr_2O_7^{2-}] = 0.55\ M$.

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

57. Consider the cell described below:

$$Zn|Zn^{2+}(1.00\ M)||Cu^{2+}(1.00\ M)|Cu$$

Calculate the cell potential after the reaction has operated long enough for the $[Zn^{2+}]$ to have changed by 0.20 mol/L. (Assume $T = 25°C$.)

58. Consider the cell described below:

$$Al|Al^{3+}(1.00\ M)||Pb^{2+}(1.00\ M)|Pb$$

Calculate the cell potential after the reaction has operated long enough for the $[Al^{3+}]$ to have changed by 0.60 mol/L. (Assume $T = 25°C$.)

59. An electrochemical cell consists of a standard hydrogen electrode and a copper metal electrode.

a. What is the potential of the cell at 25°C if the copper electrode is placed in a solution in which $[Cu^{2+}] = 2.5 \times 10^{-4}\ M$?

b. The copper electrode is placed in a solution of unknown $[Cu^{2+}]$. The measured potential at 25°C is 0.195 V. What is $[Cu^{2+}]$? (Assume Cu^{2+} is reduced.)

60. An electrochemical cell consists of a nickel metal electrode immersed in a solution with $[Ni^{2+}] = 1.0\ M$ separated by a porous disk from an aluminum metal electrode.

a. What is the potential of this cell at 25°C if the aluminum electrode is placed in a solution in which $[Al^{3+}] = 7.2 \times 10^{-3}\ M$?

b. When the aluminum electrode is placed in a certain solution in which $[Al^{3+}]$ is unknown, the measured cell potential at 25°C is 1.62 V. Calculate $[Al^{3+}]$ in the unknown solution. (Assume Al is oxidized.)

61. An electrochemical cell consists of a standard hydrogen electrode and a copper metal electrode. If the copper electrode is placed in a solution of 0.10 *M* NaOH that is saturated with $Cu(OH)_2$, what is the cell potential at 25°C? (For $Cu(OH)_2$, $K_{sp} = 1.6 \times 10^{-19}$.)

62. An electrochemical cell consists of a nickel metal electrode immersed in a solution with $[Ni^{2+}] = 1.0\ M$ separated by a porous disk from an aluminum metal electrode immersed in a solution with $[Al^{3+}] = 1.0\ M$. Sodium hydroxide is added to the aluminum compartment, causing $Al(OH)_3(s)$ to precipitate. After precipitation of $Al(OH)_3$ has ceased, the concentration of OH^- is $1.0 \times 10^{-4}\ M$ and the measured cell potential is 1.82 V. Calculate the K_{sp} value for $Al(OH)_3$.

$$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq) \qquad K_{sp} = ?$$

63. Consider a concentration cell that has both electrodes made of some metal M. Solution A in one compartment of the cell contains 1.0 *M* M^{2+}. Solution B in the other cell compartment has a volume of 1.00 L. At the beginning of the experiment 0.0100 mol of $M(NO_3)_2$ and 0.0100 mol of Na_2SO_4 are dissolved in solution B (ignore volume changes), where the reaction

$$M^{2+}(aq) + SO_4{}^{2-}(aq) \rightleftharpoons MSO_4(s)$$

occurs. For this reaction equilibrium is rapidly established, whereupon the cell potential is found to be +0.44 V at 25°C. Assume that the process

$$M^{2+} + 2e^- \longrightarrow M$$

has a standard reduction potential of −0.31 V and that no other redox process occurs in the cell. Calculate the value of K_{sp} for $MSO_4(s)$ at 25°C.

64. You have a concentration cell in which the cathode has a silver electrode with 0.10 *M* Ag^+. The anode also has a silver electrode with $Ag^+(aq)$, 0.050 *M* $S_2O_3{}^{2-}$, and $1.0 \times 10^{-3}\ M\ Ag(S_2O_3)_2{}^{3-}$. You read the voltage to be 0.76 V.

a. Calculate the concentration of Ag^+ at the cathode.

b. Determine the value of the equilibrium constant for the formation of $Ag(S_2O_3)_2{}^{3-}$.

$$Ag^+(aq) + 2S_2O_3{}^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2{}^{3-}(aq) \qquad K = ?$$

65. Calculate $\Delta G°$ and K at 25°C for the reactions in Exercises 25 and 29.

66. Calculate $\Delta G°$ and K at 25°C for the reactions in Exercises 26 and 30.

67. An excess of finely divided iron is stirred up with a solution that contains Cu^{2+} ion, and the system is allowed to come to equilibrium. The solid materials are then filtered off, and electrodes of solid copper and solid iron are inserted into the remaining solution. What is the value of the ratio $[Fe^{2+}]/[Cu^{2+}]$ at 25°C?

68. Consider the following reaction:

$$Ni^{2+}(aq) + Sn(s) \rightarrow Ni(s) + Sn^{2+}(aq)$$

Determine the minimum ratio of $[Sn^{2+}]/[Ni^{2+}]$ necessary to make this reaction spontaneous as written.

69. Under standard conditions, what reaction occurs, if any, when each of the following operations is performed?

a. Crystals of I_2 are added to a solution of NaCl.

b. Cl_2 gas is bubbled into a solution of NaI.

c. A silver wire is placed in a solution of $CuCl_2$.

d. An acidic solution of $FeSO_4$ is exposed to air.

For the reactions that occur, write a balanced equation and calculate $\mathscr{E}°$, $\Delta G°$, and K at 25°C.

70. A disproportionation reaction involves a substance that acts as both an oxidizing and a reducing agent, producing higher and lower oxidation states of the same element in the products. Which of the following disproportionation reactions are spontaneous under standard conditions? Calculate $\Delta G°$ and K at 25°C for those reactions that are spontaneous under standard conditions.

a. $2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$

b. $3Fe^{2+}(aq) \rightarrow 2Fe^{3+}(aq) + Fe(s)$

c. $HClO_2(aq) \rightarrow ClO_3{}^-(aq) + HClO(aq)$ (unbalanced)

Use the half-reactions:

$$ClO_3{}^- + 3H^+ + 2e^- \longrightarrow HClO_2 + H_2O \qquad \mathscr{E}° = 1.21\ V$$
$$HClO_2 + 2H^+ + 2e^- \longrightarrow HClO + H_2O \qquad \mathscr{E}° = 1.65\ V$$

71. Consider the galvanic cell based on the following half-reactions:

$$Au^{3+} + 3e^- \longrightarrow Au \qquad \mathscr{E}° = 1.50\ V$$
$$Tl^+ + e^- \longrightarrow Tl \qquad \mathscr{E}° = -0.34\ V$$

a. Determine the overall cell reaction and calculate $\mathscr{E}°_{cell}$.

b. Calculate $\Delta G°$ and K for the cell reaction at 25°C.

c. Calculate $\mathscr{E}_{cell}$ at 25°C when $[Au^{3+}] = 1.0 \times 10^{-2}\ M$ and $[Tl^+] = 1.0 \times 10^{-4}\ M$.

72. Consider the following galvanic cell at 25°C:

$$Pt|Cr^{2+}(0.30\ M), Cr^{3+}(2.0\ M)||Co^{2+}(0.20\ M)|Co$$

The overall reaction and equilibrium constant value are

$$2Cr^{2+}(aq) + Co^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + Co(s) \quad K = 2.79 \times 10^7$$

Calculate the cell potential, $\mathscr{E}$, for this galvanic cell and ΔG for the cell reaction at these conditions.

73. Calculate K_{sp} for iron(II) sulfide given the following data:

$$FeS(s) + 2e^- \rightarrow Fe(s) + S^{2-}(aq) \qquad \mathscr{E}° = -1.01\text{ V}$$
$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s) \qquad \mathscr{E}° = -0.44\text{ V}$$

74. For the following half-reaction, $\mathscr{E}° = -2.07$ V:

$$AlF_6^{3-} + 3e^- \longrightarrow Al + 6F^-$$

Using data from Table 17.1, calculate the equilibrium constant at 25°C for the reaction

$$Al^{3+}(aq) + 6F^-(aq) \rightleftharpoons AlF_6^{3-}(aq) \quad K = ?$$

75. Calculate the value of the equilibrium constant for the reaction of zinc metal in a solution of silver nitrate at 25°C.

76. The solubility product for CuI(*s*) is 1.1×10^{-12}. Calculate the value of $\mathscr{E}°$ for the half-reaction

$$CuI + e^- \longrightarrow Cu + I^-$$

Electrolysis

77. How long will it take to plate out each of the following with a current of 100.0 A?

a. 1.0 kg Al from aqueous Al^{3+}
b. 1.0 g Ni from aqueous Ni^{2+}
c. 5.0 mol Ag from aqueous Ag^+

78. The electrolysis of BiO^+ produces pure bismuth. How long would it take to produce 10.0 g of Bi by the electrolysis of a BiO^+ solution using a current of 25.0 A?

79. What mass of each of the following substances can be produced in 1.0 h with a current of 15 A?

a. Co from aqueous Co^{2+}
b. Hf from aqueous Hf^{4+}
c. I_2 from aqueous KI
d. Cr from molten CrO_3

80. Aluminum is produced commercially by the electrolysis of Al_2O_3 in the presence of a molten salt. If a plant has a continuous capacity of 1.00 million amp, what mass of aluminum can be produced in 2.00 h?

81. An unknown metal M is electrolyzed. It took 74.1 s for a current of 2.00 amp to plate out 0.107 g of the metal from a solution containing $M(NO_3)_3$. Identify the metal.

82. Electrolysis of an alkaline earth metal chloride using a current of 5.00 A for 748 s deposits 0.471 g of metal at the cathode. What is the identity of the alkaline earth metal chloride?

83. What volume of F_2 gas, at 25°C and 1.00 atm, is produced when molten KF is electrolyzed by a current of 10.0 A for 2.00 h? What mass of potassium metal is produced? At which electrode does each reaction occur?

84. What volumes of $H_2(g)$ and $O_2(g)$ at STP are produced from the electrolysis of water by a current of 2.50 A in 15.0 min?

85. One of the few industrial-scale processes that produce organic compounds electrochemically is used by the Monsanto Company to produce 1,4-dicyanobutane. The reduction reaction is

$$2CH_2{=}CHCN + 2H^+ + 2e^- \longrightarrow NC{-}(CH_2)_4{-}CN$$

The $NC{-}(CH_2)_4{-}CN$ is then chemically reduced using hydrogen gas to $H_2N{-}(CH_2)_6{-}NH_2$, which is used in the production of nylon. What current must be used to produce 150. kg of $NC{-}(CH_2)_4{-}CN$ per hour?

86. A single Hall–Heroult cell (as shown in Fig. 17.22) produces about 1 ton of aluminum in 24 hours. What current must be used to accomplish this?

87. It took 2.30 min using a current of 2.00 A to plate out all the silver from 0.250 L of a solution containing Ag^+. What was the original concentration of Ag^+ in the solution?

88. A solution containing Pt^{4+} is electrolyzed with a current of 4.00 A. How long will it take to plate out 99% of the platinum in 0.50 L of a 0.010 *M* solution of Pt^{4+}?

89. A solution at 25°C contains 1.0 *M* Cd^{2+}, 1.0 *M* Ag^+, 1.0 *M* Au^{3+}, and 1.0 *M* Ni^{2+} in the cathode compartment of an electrolytic cell. Predict the order in which the metals will plate out as the voltage is gradually increased.

90. Consider the following half-reactions:

$$IrCl_6^{3-} + 3e^- \longrightarrow Ir + 6Cl^- \qquad \mathscr{E}° = 0.77\text{ V}$$
$$PtCl_4^{2-} + 2e^- \longrightarrow Pt + 4Cl^- \qquad \mathscr{E}° = 0.73\text{ V}$$
$$PdCl_4^{2-} + 2e^- \longrightarrow Pd + 4Cl^- \qquad \mathscr{E}° = 0.62\text{ V}$$

A hydrochloric acid solution contains platinum, palladium, and iridium as chloro-complex ions. The solution is a constant 1.0 *M* in chloride ion and 0.020 *M* in each complex ion. Is it feasible to separate the three metals from this solution by electrolysis? (Assume that 99% of a metal must be plated out before another metal begins to plate out.)

91. What reactions take place at the cathode and the anode when each of the following is electrolyzed?

a. molten $NiBr_2$
b. molten AlF_3
c. molten MnI_2

92. What reactions take place at the cathode and the anode when each of the following is electrolyzed? (Assume standard conditions.)

a. 1.0 *M* $NiBr_2$ solution
b. 1.0 *M* AlF_3 solution
c. 1.0 *M* MnI_2 solution

Additional Exercises

93. The saturated calomel electrode, abbreviated SCE, is often used as a reference electrode in making electrochemical measurements. The SCE is composed of mercury in contact with a saturated solution of calomel (Hg_2Cl_2). The electrolyte solution is saturated KCl. $\mathscr{E}_{SCE}$ is +0.242 V relative to the standard hydrogen electrode. Calculate the potential for each of the following galvanic cells containing a saturated calomel electrode and the given half-cell components at standard conditions. In each case, indicate whether the SCE is the cathode or the anode. Standard reduction potentials are found in Table 17.1.

a. $Cu^{2+} + 2e^- \longrightarrow Cu$
b. $Fe^{3+} + e^- \longrightarrow Fe^{2+}$
c. $AgCl + e^- \longrightarrow Ag + Cl^-$
d. $Al^{3+} + 3e^- \longrightarrow Al$
e. $Ni^{2+} + 2e^- \longrightarrow Ni$

94. Consider the following half-reactions:

$$\begin{aligned} Pt^{2+} + 2e^- &\longrightarrow Pt & \mathscr{E}^\circ &= 1.188\text{ V} \\ PtCl_4^{2-} + 2e^- &\longrightarrow Pt + 4Cl^- & \mathscr{E}^\circ &= 0.755\text{ V} \\ NO_3^- + 4H^+ + 3e^- &\longrightarrow NO + 2H_2O & \mathscr{E}^\circ &= 0.96\text{ V} \end{aligned}$$

Explain why platinum metal will dissolve in aqua regia (a mixture of hydrochloric and nitric acids) but not in either concentrated nitric or concentrated hydrochloric acid individually.

95. Consider the standard galvanic cell based on the following half-reactions

$$\begin{aligned} Cu^{2+} + 2e^- &\longrightarrow Cu \\ Ag^+ + e^- &\longrightarrow Ag \end{aligned}$$

The electrodes in this cell are Ag(*s*) and Cu(*s*). Does the cell potential increase, decrease, or remain the same when the following changes occur to the standard cell?

a. $CuSO_4(s)$ is added to the copper half-cell compartment (assume no volume change).
b. $NH_3(aq)$ is added to the copper half-cell compartment. *Hint:* Cu^{2+} reacts with NH_3 to form $Cu(NH_3)_4{}^{2+}(aq)$.
c. NaCl(*s*) is added to the silver half-cell compartment. *Hint:* Ag^+ reacts with Cl^- to form AgCl(*s*).
d. Water is added to both half-cell compartments until the volume of solution is doubled.
e. The silver electrode is replaced with a platinum electrode.

$$Pt^{2+} + 2e^- \longrightarrow Pt \qquad \mathscr{E}^\circ = 1.19\text{ V}$$

96. A standard galvanic cell is constructed so that the overall cell reaction is

$$2Al^{3+}(aq) + 3M(s) \longrightarrow 3M^{2+}(aq) + 2Al(s)$$

where M is an unknown metal. If $\Delta G^\circ = -411$ kJ for the overall cell reaction, identify the metal used to construct the standard cell.

97. The black silver sulfide discoloration of silverware can be removed by heating the silver article in a sodium carbonate solution in an aluminum pan. The reaction is

$$3Ag_2S(s) + 2Al(s) \rightleftharpoons 6Ag(s) + 3S^{2-}(aq) + 2Al^{3+}(aq)$$

a. Using data in Appendix 4, calculate ΔG°, K, and $\mathscr{E}^\circ$ for the above reaction at 25°C. (For $Al^{3+}(aq)$, $\Delta G_f^\circ = -480.$ kJ/mol.)
b. Calculate the value of the standard reduction potential for the following half-reaction:

$$2e^- + Ag_2S(s) \longrightarrow 2Ag(s) + S^{2-}(aq)$$

98. In 1973 the wreckage of the Civil War ironclad USS *Monitor* was discovered near Cape Hatteras, North Carolina. (The *Monitor* and the CSS *Virginia* [formerly the USS *Merrimack*] fought the first battle between iron-armored ships.) In 1987 investigations were begun to see if the ship could be salvaged. It was reported in *Time* (June 22, 1987) that scientists were considering adding sacrificial anodes of zinc to the rapidly corroding metal hull of the *Monitor.* Describe how attaching zinc to the hull would protect the *Monitor* from further corrosion.

99. When aluminum foil is placed in hydrochloric acid, nothing happens for the first 30 seconds or so. This is followed by vigorous bubbling and the eventual disappearance of the foil. Explain these observations.

100. Which of the following statements concerning corrosion is/are true? For the false statements, correct them.

a. Corrosion is an example of an electrolytic process.
b. Corrosion of steel involves the reduction of iron coupled with the oxidation of oxygen.
c. Steel rusts more easily in the dry (arid) Southwest states than in the humid Midwest states.
d. Salting roads in the winter has the added benefit of hindering the corrosion of steel.
e. The key to cathodic protection is to connect via a wire a metal more easily oxidized than iron to the steel surface to be protected.

101. A patent attorney has asked for your advice concerning the merits of a patent application that describes a single aqueous galvanic cell capable of producing a 12-V potential. Comment.

102. The overall reaction and equilibrium constant value for a hydrogen–oxygen fuel cell at 298 K is

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad K = 1.28 \times 10^{83}$$

a. Calculate $\mathscr{E}^\circ$ and ΔG° at 298 K for the fuel cell reaction.
b. Predict the signs of ΔH° and ΔS° for the fuel cell reaction.
c. As temperature increases, does the maximum amount of work obtained from the fuel cell reaction increase, decrease, or remain the same? Explain.

103. What is the maximum work that can be obtained from a hydrogen–oxygen fuel cell at standard conditions that produces 1.00 kg of water at 25°C? Why do we say that this is the maximum work that can be obtained? What are the advantages and disadvantages in using fuel cells rather than the corresponding combustion reactions to produce electricity?

104. The overall reaction and standard cell potential at 25°C for the rechargeable nickel–cadmium alkaline battery is

$$\begin{aligned} &Cd(s) + NiO_2(s) + 2H_2O(l) \longrightarrow \\ &\qquad Ni(OH)_2(s) + Cd(OH)_2(s) \qquad \mathscr{E}^\circ = 1.10\text{ V} \end{aligned}$$

For every mole of Cd consumed in the cell, what is the maximum useful work that can be obtained at standard conditions?

105. An experimental fuel cell has been designed that uses carbon monoxide as fuel. The overall reaction is

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$

The two half-cell reactions are

$$\begin{aligned} CO + O^{2-} &\longrightarrow CO_2 + 2e^- \\ O_2 + 4e^- &\longrightarrow 2O^{2-} \end{aligned}$$

The two half-reactions are carried out in separate compartments connected with a solid mixture of CeO_2 and Gd_2O_3. Oxide ions can move through this solid at high temperatures (about 800°C). ΔG for the overall reaction at 800°C under certain concentration conditions is -380 kJ. Calculate the cell potential for this fuel cell at the same temperature and concentration conditions.

106. A fuel cell designed to react grain alcohol with oxygen has the following net reaction:

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

The maximum work 1 mol of alcohol can yield by this process is 1320 kJ. What is the theoretical maximum voltage this cell can achieve?

107. Gold is produced electrochemically from an aqueous solution of $Au(CN)_2^-$ containing an excess of CN^-. Gold metal and oxygen gas are produced at the electrodes. What amount (moles) of O_2 will be produced during the production of 1.00 mol of gold?

108. In the electrolysis of a sodium chloride solution, what volume of $H_2(g)$ is produced in the same time it takes to produce 257 L of $Cl_2(g)$, with both volumes measured at 50.°C and 2.50 atm?

109. An aqueous solution of an unknown salt of ruthenium is electrolyzed by a current of 2.50 A passing for 50.0 min. If 2.618 g Ru is produced at the cathode, what is the charge on the ruthenium ions in solution?

110. It takes 15 kWh (kilowatt-hours) of electrical energy to produce 1.0 kg of aluminum metal from aluminum oxide by the Hall–Heroult process. Compare this to the amount of energy necessary to melt 1.0 kg of aluminum metal. Why is it economically feasible to recycle aluminum cans? (The enthalpy of fusion for aluminum metal is 10.7 kJ/mol [1 watt = 1 J/s].)

Challenge Problems

111. Combine the equations

$$\Delta G^\circ = -nF\mathscr{E}^\circ \quad \text{and} \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

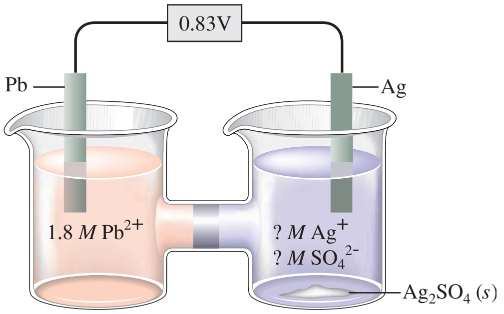
to derive an expression for $\mathscr{E}^\circ$ as a function of temperature. Describe how one can graphically determine ΔH° and ΔS° from measurements of $\mathscr{E}^\circ$ at different temperatures, assuming that ΔH° and ΔS° do not depend on temperature. What property would you look for in designing a reference half-cell that would produce a potential relatively stable with respect to temperature?

112. The overall reaction in the lead storage battery is

$$Pb(s) + PbO_2(s) + 2H^+(aq) + 2HSO_4^-(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

- **a.** For the cell reaction $\Delta H^\circ = -315.9$ kJ and $\Delta S^\circ = 263.5$ J/K. Calculate $\mathscr{E}^\circ$ at −20.°C. Assume ΔH° and ΔS° do not depend on temperature.
- **b.** Calculate $\mathscr{E}$ at −20.°C when $[HSO_4^-] = [H^+] = 4.5\ M$.
- **c.** Consider your answer to Exercise 55. Why does it seem that batteries fail more often on cold days than on warm days?

113. Consider the following galvanic cell:



Calculate the K_{sp} value for $Ag_2SO_4(s)$. Note that to obtain silver ions in the right compartment (the cathode compartment), excess solid Ag_2SO_4 was added and some of the salt dissolved.

114. A zinc–copper battery is constructed as follows at 25°C:

$$Zn|Zn^{2+}(0.10\ M)||Cu^{2+}(2.50\ M)|Cu$$

The mass of each electrode is 200. g.

- **a.** Calculate the cell potential when this battery is first connected.
- **b.** Calculate the cell potential after 10.0 A of current has flowed for 10.0 h. (Assume each half-cell contains 1.00 L of solution.)
- **c.** Calculate the mass of each electrode after 10.0 h.
- **d.** How long can this battery deliver a current of 10.0 A before it goes dead?

115. A galvanic cell is based on the following half-reactions:

$$Fe^{2+} + 2e^- \longrightarrow Fe(s) \qquad \mathscr{E}^\circ = -0.440\ V$$
$$2H^+ + 2e^- \longrightarrow H_2(g) \qquad \mathscr{E}^\circ = 0.000\ V$$

where the iron compartment contains an iron electrode and $[Fe^{2+}] = 1.00 \times 10^{-3}\ M$ and the hydrogen compartment contains a platinum electrode, $P_{H_2} = 1.00$ atm, and a weak acid, HA, at an initial concentration of 1.00 *M*. If the observed cell potential is 0.333 V at 25°C, calculate the K_a value for the weak acid HA.

116. Consider a cell based on the following half-reactions:

$$Au^{3+} + 3e^- \longrightarrow Au \qquad \mathscr{E}^\circ = 1.50\ V$$
$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad \mathscr{E}^\circ = 0.77\ V$$

- **a.** Draw this cell under standard conditions, labeling the anode, the cathode, the direction of electron flow, and the concentrations, as appropriate.
- **b.** When enough NaCl(*s*) is added to the compartment containing gold to make the $[Cl^-] = 0.10\ M$, the cell potential is observed to be 0.31 V. Assume that Au^{3+} is reduced and assume that the reaction in the compartment containing gold is

$$Au^{3+}(aq) + 4Cl^-(aq) \rightleftharpoons AuCl_4^-(aq)$$

Calculate the value of *K* for this reaction at 25°C.

117. The measurement of pH using a glass electrode obeys the Nernst equation. The typical response of a pH meter at 25.00°C is given by the equation

$$\mathscr{E}_{meas} = \mathscr{E}_{ref} + 0.05916\ pH$$

where $\mathscr{E}_{ref}$ contains the potential of the reference electrode and all other potentials that arise in the cell that are not related to the hydrogen ion concentration. Assume that $\mathscr{E}_{ref} = 0.250$ V and that $\mathscr{E}_{meas} = 0.480$ V.

- **a.** What is the uncertainty in the values of pH and $[H^+]$ if the uncertainty in the measured potential is ±1 mV (±0.001 V)?
- **b.** To what precision must the potential be measured for the uncertainty in pH to be ±0.02 pH unit?

118. Zirconium is one of the few metals that retains its structural integrity upon exposure to radiation. For this reason, the fuel rods in most nuclear reactors are made of zirconium. Answer the following questions about the redox properties of zirconium based on the half-reaction

$$ZrO_2 \cdot H_2O + H_2O + 4e^- \longrightarrow Zr + 4OH^- \qquad \mathscr{E}^\circ = -2.36\ V$$

a. Is zirconium metal capable of reducing water to form hydrogen gas at standard conditions?

b. Write a balanced equation for the reduction of water by zirconium metal.

c. Calculate $\mathscr{E}°$, $\Delta G°$, and K for the reduction of water by zirconium metal.

d. The reduction of water by zirconium occurred during the accident at Three Mile Island, Pennsylvania, in 1979. The hydrogen produced was successfully vented and no chemical explosion occurred. If 1.00×10^3 kg of Zr reacts, what mass of H_2 is produced? What volume of H_2 at 1.0 atm and 1000.°C is produced?

e. At Chernobyl, USSR, in 1986, hydrogen was produced by the reaction of superheated steam with the graphite reactor core:

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$$

A chemical explosion involving the hydrogen gas did occur at Chernobyl. In light of this fact, do you think it was a correct decision to vent the hydrogen and other radioactive gases into the atmosphere at Three Mile Island? Explain.

119. A galvanic cell is based on the following half-reactions:

$$\begin{aligned} Ag^+ + e^- &\longrightarrow Ag(s) \qquad \mathscr{E}° = 0.80\ V \\ Cu^{2+} + 2e^- &\longrightarrow Cu(s) \qquad \mathscr{E}° = 0.34\ V \end{aligned}$$

In this cell, the silver compartment contains a silver electrode and excess $AgCl(s)$ ($K_{sp} = 1.6 \times 10^{-10}$), and the copper compartment contains a copper electrode and $[Cu^{2+}] = 2.0\ M$.

a. Calculate the potential for this cell at 25°C.

b. Assuming 1.0 L of 2.0 M Cu^{2+} in the copper compartment, calculate the moles of NH_3 that would have to be added to give a cell potential of 0.52 V at 25°C (assume no volume change on addition of NH_3).

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4{}^{2+}(aq) \qquad K = 1.0 \times 10^{13}$$

120. Given the following two standard reduction potentials,

$$\begin{aligned} M^{3+} + 3e^- &\rightarrow M \qquad \mathscr{E}° = -0.10\ V \\ M^{2+} + 2e^- &\rightarrow M \qquad \mathscr{E}° = -0.50\ V \end{aligned}$$

solve for the standard reduction potential of the half-reaction

$$M^{3+} + e^- \rightarrow M^{2+}$$

(*Hint:* You must use the extensive property $\Delta G°$ to determine the standard reduction potential.)

121. You make a galvanic cell with a piece of nickel, 1.0 M $Ni^{2+}(aq)$, a piece of silver, and 1.0 M $Ag^+(aq)$. Calculate the concentrations of $Ag^+(aq)$ and $Ni^{2+}(aq)$ once the cell is "dead."

122. A chemist wishes to determine the concentration of $CrO_4{}^{2-}$ electrochemically. A cell is constructed consisting of a saturated calomel electrode (SCE; see Exercise 93) and a silver wire coated with Ag_2CrO_4. The $\mathscr{E}°$ value for the following half-reaction is +0.446 V relative to the standard hydrogen electrode:

$$Ag_2CrO_4 + 2e^- \longrightarrow 2Ag + CrO_4{}^{2-}$$

a. Calculate $\mathscr{E}_{cell}$ and ΔG at 25°C for the cell reaction when $[CrO_4{}^{2-}] = 1.00$ mol/L.

b. Write the Nernst equation for the cell. Assume that the SCE concentrations are constant.

c. If the coated silver wire is placed in a solution (at 25°C) in which $[CrO_4{}^{2-}] = 1.00 \times 10^{-5}\ M$, what is the expected cell potential?

d. The measured cell potential at 25°C is 0.504 V when the coated wire is dipped into a solution of unknown $[CrO_4{}^{2-}]$. What is $[CrO_4{}^{2-}]$ for this solution?

e. Using data from this problem and from Table 17.1, calculate the solubility product (K_{sp}) for Ag_2CrO_4.

123. You have a concentration cell with Cu electrodes and $[Cu^{2+}] = 1.00\ M$ (right side) and $1.0 \times 10^{-4}\ M$ (left side).

a. Calculate the potential for this cell at 25°C.

b. The Cu^{2+} ion reacts with NH_3 to form $Cu(NH_3)_4{}^{2+}$ where the stepwise formation constants are $K_1 = 1.0 \times 10^3$, $K_2 = 1.0 \times 10^4$, $K_3 = 1.0 \times 10^3$, and $K_4 = 1.0 \times 10^3$. Calculate the new cell potential after enough NH_3 is added to the left cell compartment such that at equilibrium $[NH_3] = 2.0\ M$.

124. When copper reacts with nitric acid, a mixture of $NO(g)$ and $NO_2(g)$ is evolved. The volume ratio of the two product gases depends on the concentration of the nitric acid according to the equilibrium

$$2H^+(aq) + 2NO_3{}^-(aq) + NO(g) \rightleftharpoons 3NO_2(g) + H_2O(l)$$

Consider the following standard reduction potentials at 25°C:

$$3e^- + 4H^+(aq) + NO_3{}^-(aq) \longrightarrow NO(g) + 2H_2O(l) \qquad \mathscr{E}° = 0.957\ V$$

$$e^- + 2H^+(aq) + NO_3{}^-(aq) \longrightarrow NO_2(g) + 2H_2O(l) \qquad \mathscr{E}° = 0.775\ V$$

a. Calculate the equilibrium constant for the above reaction.

b. What concentration of nitric acid will produce a NO and NO_2 mixture with only 0.20% NO_2 (by moles) at 25°C and 1.00 atm? Assume that no other gases are present and that the change in acid concentration can be neglected.

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

125. The following standard reduction potentials have been determined for the aqueous chemistry of indium:

$$\begin{aligned} In^{3+}(aq) + 2e^- &\longrightarrow In^+(aq) \qquad \mathscr{E}° = -0.444\ V \\ In^+(aq) + e^- &\longrightarrow In(s) \qquad \mathscr{E}° = -0.126\ V \end{aligned}$$

a. What is the equilibrium constant for the disproportionation reaction, where a species is both oxidized and reduced, shown below?

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

b. What is $\Delta G_f°$ for $In^+(aq)$ if $\Delta G_f° = -97.9$ kJ/mol for $In^{3+}(aq)$?

126. An electrochemical cell is set up using the following balanced reaction:

$$M^{a+}(aq) + N(s) \longrightarrow N^{2+}(aq) + M(s)$$

Given the standard reduction potentials are:

$$\begin{aligned} M^{a+} + ae^- &\longrightarrow M \qquad \mathscr{E}° = +0.400\ V \\ N^{2+} + 2e^- &\longrightarrow N \qquad \mathscr{E}° = +0.240\ V \end{aligned}$$

The cell contains 0.10 M N^{2+} and produces a voltage of 0.180 V. If the concentration of M^{a+} is such that the value of the reaction quotient Q is 9.32×10^{-3}, calculate $[M^{a+}]$. Calculate w_{max} for this electrochemical cell.

127. Three electrochemical cells were connected in series so that the same quantity of electrical current passes through all three cells. In the first cell, 1.15 g of chromium metal was deposited from a chromium(III) nitrate solution. In the second cell, 3.15 g of osmium was deposited from a solution made of Os^{n+} and nitrate ions. What is the name of the salt? In the third cell, the electrical charge passed through a solution containing X^{2+} ions caused deposition of 2.11 g of metallic X. What is the electron configuration of X?

Marathon Problems

These problems are designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

128. A galvanic cell is based on the following half-reactions:

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \qquad \mathscr{E}° = 0.34\text{ V}$$
$$V^{2+}(aq) + 2e^- \longrightarrow V(s) \qquad \mathscr{E}° = -1.20\text{ V}$$

In this cell, the copper compartment contains a copper electrode and $[Cu^{2+}] = 1.00$ M, and the vanadium compartment contains a vanadium electrode and V^{2+} at an unknown concentration. The compartment containing the vanadium (1.00 L of solution) was titrated with 0.0800 M H_2EDTA^{2-}, resulting in the reaction

$$H_2EDTA^{2-}(aq) + V^{2+}(aq) \rightleftharpoons VEDTA^{2-}(aq) + 2H^+(aq) \qquad K = ?$$

The potential of the cell was monitored to determine the stoichiometric point for the process, which occurred at a volume of 500.0 mL of H_2EDTA^{2-} solution added. At the stoichiometric point, $\mathscr{E}_{cell}$ was observed to be 1.98 V. The solution was buffered at a pH of 10.00.

a. Calculate $\mathscr{E}_{cell}$ before the titration was carried out.

b. Calculate the value of the equilibrium constant, K, for the titration reaction.

c. Calculate $\mathscr{E}_{cell}$ at the halfway point in the titration.

129. The table below lists the cell potentials for the 10 possible galvanic cells assembled from the metals A, B, C, D, and E, and their respective 1.00 M 2+ ions in solution. Using the data in the table, establish a standard reduction potential table similar to Table 17.1 in the text. Assign a reduction potential of 0.00 V to the half-reaction that falls in the middle of the series. You should get two different tables. Explain why, and discuss what you could do to determine which table is correct.

	A(s) in A^{2+}(aq)	**B(s) in B^{2+}(aq)**	**C(s) in C^{2+}(aq)**	**D(s) in D^{2+}(aq)**
E(s) in E^{2+}(aq)	0.28 V	0.81 V	0.13 V	1.00 V
D(s) in D^{2+}(aq)	0.72 V	0.19 V	1.13 V	—
C(s) in C^{2+}(aq)	0.41 V	0.94 V	—	—
B(s) in B^{2+}(aq)	0.53 V	—	—	—

Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at **college.hmco.com/PIC/zumdahl7e.**