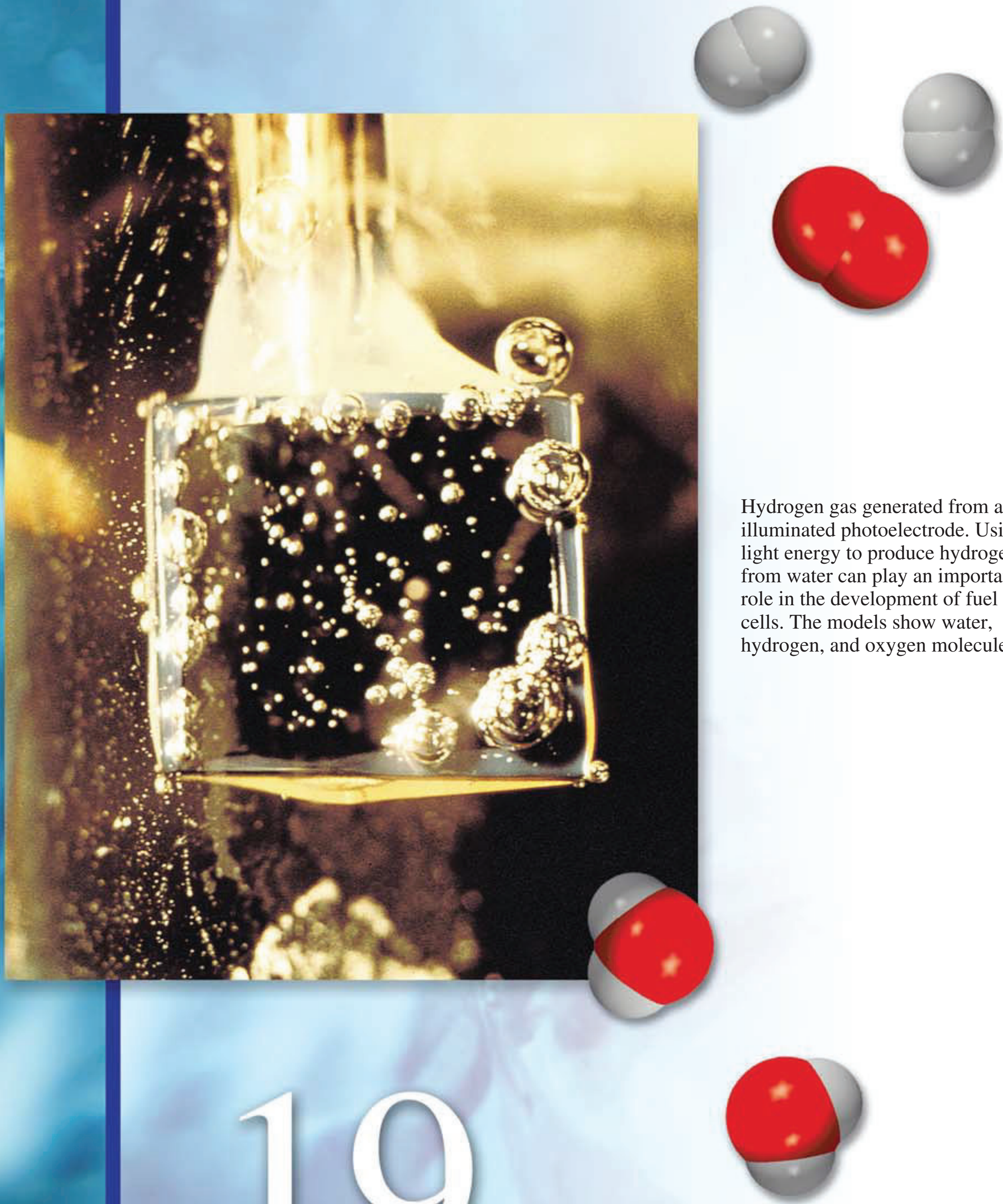
Electrochemistry



Hydrogen gas generated from an illuminated photoelectrode. Using light energy to produce hydrogen from water can play an important role in the development of fuel cells. The models show water, hydrogen, and oxygen molecules.

19

19.2 Galvanic Cells

In Section 4.4 we saw that when a piece of zinc metal is placed in a $CuSO_4$ solution, Zn is oxidized to Zn^{2+} ions while Cu^{2+} ions are reduced to metallic copper (see Figure 4.10):

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

The electrons are transferred directly from the reducing agent (Zn) to the oxidizing agent (Cu^{2+}) in solution. However, if we physically separate the oxidizing agent from the reducing agent, the transfer of electrons can take place via an external conducting medium (a metal wire). As the reaction progresses, it sets up a constant flow of electrons and hence generates electricity (that is, it produces electrical work such as driving an electric motor).

The experimental apparatus for generating electricity through the use of a spontaneous reaction is called a ***galvanic cell*** or *voltaic cell,* after the Italian scientists Luigi Galvani and Alessandro Volta, who constructed early versions of the device. Figure 19.1 shows the essential components of a galvanic cell. A zinc bar is immersed in a $ZnSO_4$ solution, and a copper bar is immersed in a $CuSO_4$ solution. The cell operates on the principle that the oxidation of Zn to Zn^{2+} and the reduction of Cu^{2+} to Cu can be made to take place simultaneously in separate locations with the transfer

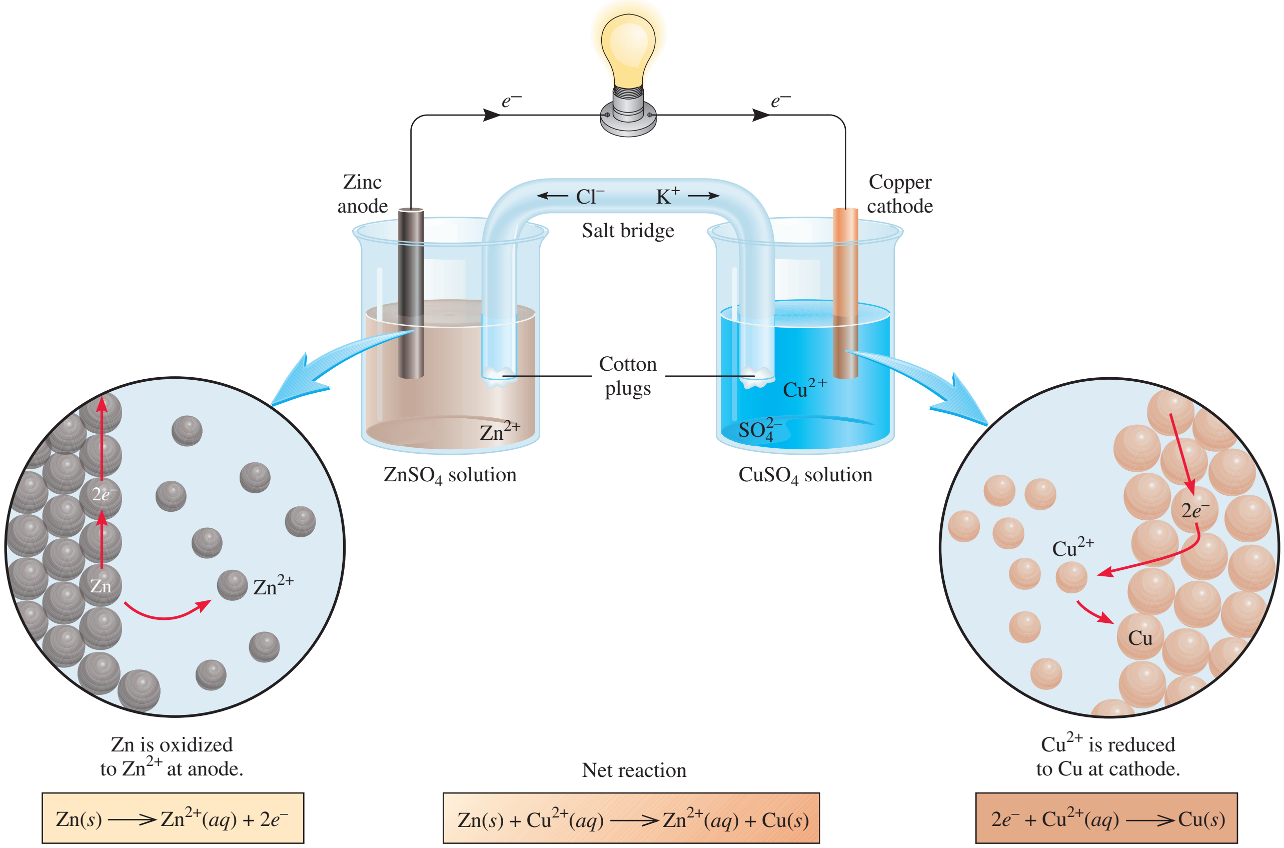


Figure 19.1 *A galvanic cell. The salt bridge (an inverted U tube) containing a KCl solution provides an electrically conducting medium between two solutions. The openings of the U tube are loosely plugged with cotton balls to prevent the KCl solution from flowing into the containers while allowing the anions and cations to move across. The lightbulb is lit as electrons flow externally from the Zn electrode (anode) to the Cu electrode (cathode).*

of electrons between them occurring through an external wire. The zinc and copper bars are called *electrodes.* This particular arrangement of electrodes (Zn and Cu) and solutions ($ZnSO_4$ and $CuSO_4$) is called the Daniell cell. By definition, the ***anode*** in a galvanic cell is *the electrode at which oxidation occurs* and the ***cathode*** is *the electrode at which reduction occurs.*

Alphabetically anode precedes cathode and oxidation precedes reduction. Therefore, anode is where oxidation occurs and cathode is where reduction takes place.

For the Daniell cell, the ***half-cell reactions,*** that is, *the oxidation and reduction reactions at the electrodes,* are

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

Half-cell reactions are similar to the half-reactions discussed earlier.

Note that unless the two solutions are separated from each other, the Cu^{2+} ions will react directly with the zinc bar:

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

and no useful electrical work will be obtained.

To complete the electrical circuit, the solutions must be connected by a conducting medium through which the cations and anions can move from one electrode compartment to the other. This requirement is satisfied by a *salt bridge,* which, in its simplest form, is an inverted U tube containing an inert electrolyte solution, such as KCl or NH_4NO_3, whose ions will not react with other ions in solution or with the electrodes (see Figure 19.1). During the course of the overall redox reaction, electrons flow externally from the anode (Zn electrode) through the wire to the cathode (Cu electrode). In the solution, the cations (Zn^{2+}, Cu^{2+}, and K^+) move toward the cathode, while the anions (SO_4^{2-} and Cl^-) move toward the anode. Without the salt bridge connecting the two solutions, the buildup of positive charge in the anode compartment (due to the formation of Zn^{2+} ions) and negative charge in the cathode compartment (created when some of the Cu^{2+} ions are reduced to Cu) would quickly prevent the cell from operating.

An electric current flows from the anode to the cathode because there is a difference in electrical potential energy between the electrodes. This flow of electric current is analogous to that of water down a waterfall, which occurs because there is a difference in gravitational potential energy, or the flow of gas from a high-pressure region to a low-pressure region. Experimentally, the *difference in electrical potential between the anode and the cathode* is measured by a voltmeter (Figure 19.2). The voltage

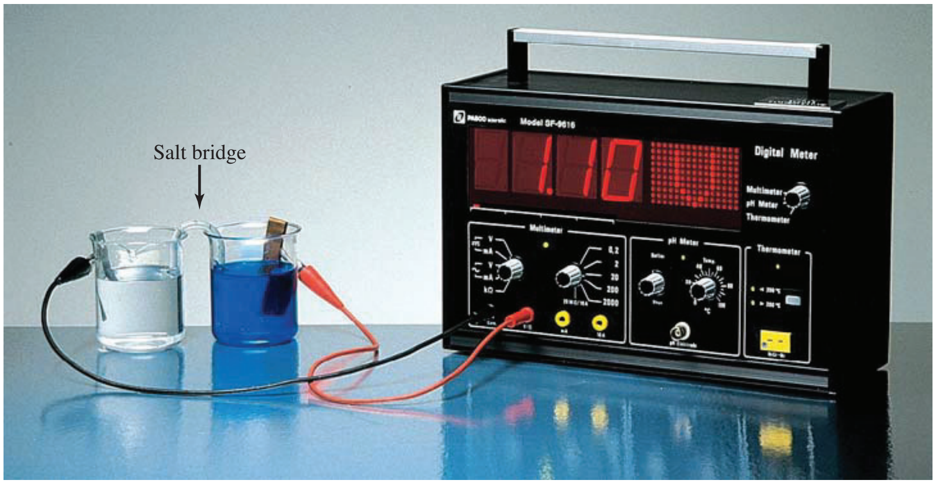


Figure 19.2 *Practical setup of the galvanic cell described in Figure 19.1. Note the U tube (salt bridge) connecting the two beakers. When the concentrations of $ZnSO_4$ and $CuSO_4$ are 1 molar (1 M) at 25°C, the cell voltage is 1.10 V. No current flows between the electrodes during a voltage measurement.*

across the electrodes of a galvanic cell is called the ***cell voltage,*** or *cell potential.* Another common term for cell voltage is the ***electromotive force*** or ***emf (E),*** which, despite its name, is a measure of voltage, not force. We will see that the voltage of a cell depends not only on the nature of the electrodes and the ions, but also on the concentrations of the ions and the temperature at which the cell is operated.

The conventional notation for representing galvanic cells is the *cell diagram.* For the Daniell cell shown in Figure 19.1, if we assume that the concentrations of Zn^{2+} and Cu^{2+} ions are 1 M, the cell diagram is

$$Zn(s)|Zn^{2+}(1\ M)\|Cu^{2+}(1\ M)|Cu(s)$$

The single vertical line represents a phase boundary. For example, the zinc electrode is a solid and the Zn^{2+} ions (from $ZnSO_4$) are in solution. Thus, we draw a line between Zn and Zn^{2+} to show the phase boundary. The double vertical lines denote the salt bridge. By convention, the anode is written first, to the left of the double lines and the other components appear in the order in which we would encounter them in moving from the anode to the cathode.

19.3 Standard Reduction Potentials

When the concentrations of the Cu^{2+} and Zn^{2+} ions are both 1.0 M, we find that the voltage or emf of the Daniell cell is 1.10 V at 25°C (see Figure 19.2). This voltage must be related directly to the redox reactions, but how? Just as the overall cell reaction can be thought of as the sum of two half-cell reactions, the measured emf of the cell can be treated as the sum of the electrical potentials at the Zn and Cu electrodes. Knowing one of these electrode potentials, we could obtain the other by subtraction (from 1.10 V). It is impossible to measure the potential of just a single electrode, but if we arbitrarily set the potential value of a particular electrode at zero, we can use it to determine the relative potentials of other electrodes. The hydrogen electrode, shown in Figure 19.3, serves as the reference for this purpose. Hydrogen gas is bubbled into a hydrochloric acid solution at 25°C. The platinum electrode has two functions. First, it provides a surface on which the dissociation of hydrogen molecules can take place:

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

Second, it serves as an electrical conductor to the external circuit.

The choice of an arbitrary reference for measuring electrode potential is analogous to choosing the surface of the ocean as the reference for altitude, calling it zero meters, and then referring to any terrestrial altitude as being a certain number of meters above or below sea level.

Under standard-state conditions (when the pressure of H_2 is 1 atm and the concentration of the HCl solution is 1 M; see Table 18.2), the potential for the reduction of H^+ at 25°C is taken to be *exactly* zero:

$$2H^+(1\ M) + 2e^- \longrightarrow H_2(1\ \text{atm}) \qquad E° = 0\ V$$

The superscript "°" denotes standard-state conditions, and $E°$ is the ***standard reduction potential,*** or *the voltage associated with a reduction reaction at an electrode when all solutes are 1 M and all gases are at 1 atm.* Thus, the standard reduction potential of the hydrogen electrode is defined as zero. The hydrogen electrode is called the *standard hydrogen electrode (SHE).*

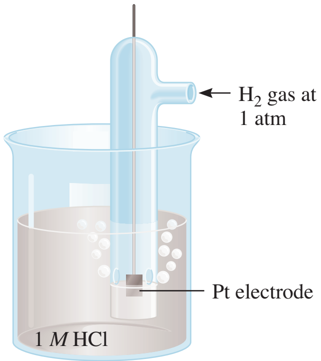


Figure 19.3 *A hydrogen electrode operating under standard-state conditions. Hydrogen gas at 1 atm is bubbled through a 1 M HCl solution. The platinum electrode is part of the hydrogen electrode.*

We can use the SHE to measure the potentials of other kinds of electrodes. For example, Figure 19.4(a) shows a galvanic cell with a zinc electrode and a SHE. In this case, the zinc electrode is the anode and the SHE is the cathode. We deduce this fact from the decrease in mass of the zinc electrode during the operation of the cell,

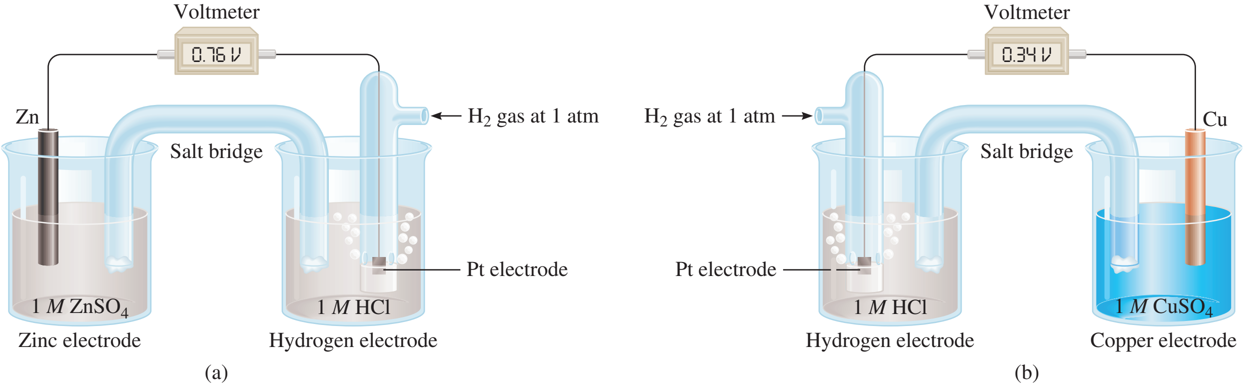


Figure 19.4 *(a) A cell consisting of a zinc electrode and a hydrogen electrode. (b) A cell consisting of a copper electrode and a hydrogen electrode. Both cells are operating under standard-state conditions. Note that in (a) the SHE acts as the cathode, but in (b) it acts as the anode. As mentioned in Figure 19.2, no current flows between the electrodes during a voltage measurement.*

which is consistent with the loss of zinc to the solution caused by the oxidation reaction:

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

The cell diagram is

$$\mathrm{Zn}(s)|\mathrm{Zn}^{2+}(1\,M)||\mathrm{H}^+(1\,M)|\mathrm{H}_2(1\text{ atm})|\mathrm{Pt}(s)$$

As mentioned earlier, the Pt electrode provides the surface on which the reduction takes place. When all the reactants are in their standard states (that is, H_2 at 1 atm, H^+ and Zn^{2+} ions at 1 M), the emf of the cell is 0.76 V at 25°C, We can write the half-cell reactions as follows:

$$\begin{array}{rr} \text{Anode (oxidation):} & \mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(1\,M) + 2e^- \\ \text{Cathode (reduction):} & \underline{2\mathrm{H}^+(1\,M) + 2e^- \longrightarrow \mathrm{H}_2(1\text{ atm})} \\ \text{Overall:} & \mathrm{Zn}(s) + 2\mathrm{H}^+(1\,M) \longrightarrow \mathrm{Zn}^{2+}(1\,M) + \mathrm{H}_2(1\text{ atm}) \end{array}$$

By convention, the ***standard emf*** of the cell, E°_{cell}, which is composed of a contribution from the anode and a contribution from the cathode, is given by

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \tag{19.1}$$

where *both* E°_{cathode} and E°_{anode} are the standard reduction potentials of the electrodes. For the Zn-SHE cell, we write

$$E^\circ_{\text{cell}} = E^\circ_{\mathrm{H^+/H_2}} - E^\circ_{\mathrm{Zn^{2+}/Zn}}$$
$$0.76\text{ V} = 0 - E^\circ_{\mathrm{Zn^{2+}/Zn}}$$

where the subscript H^+/H_2 means $2H^+ + 2e^- \rightarrow H_2$ and the subscript Zn^{2+}/Zn means $Zn^{2+} + 2e^- \rightarrow Zn$. Thus, the standard reduction potential of zinc, $E^\circ_{\mathrm{Zn^{2+}/Zn}}$, is −0.76 V.

The standard electrode potential of copper can be obtained in a similar fashion, by using a cell with a copper electrode and a SHE [Figure 19.4(b)]. In this case, the copper electrode is the cathode because its mass increases during the operation of the cell, as is consistent with the reduction reaction:

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

The cell diagram is

$$\mathrm{Pt}(s)|\mathrm{H_2}(1\text{ atm})|\mathrm{H^+}(1\,M)||\mathrm{Cu^{2+}}(1\,M)|\mathrm{Cu}(s)$$

and the half-cell reactions are

$$\begin{array}{rr} \text{Anode (oxidation):} & \mathrm{H_2}(1\text{ atm}) \longrightarrow 2\mathrm{H^+}(1\,M) + 2e^- \\ \text{Cathode (reduction):} & \mathrm{Cu^{2+}}(1\,M) + 2e^- \longrightarrow \mathrm{Cu}(s) \\ \hline \text{Overall:} & \mathrm{H_2}(1\text{ atm}) + \mathrm{Cu^{2+}}(1\,M) \longrightarrow 2\mathrm{H^+}(1\,M) + \mathrm{Cu}(s) \end{array}$$

Under standard-state conditions and at 25°C, the emf of the cell is 0.34 V, so we write

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ 0.34\text{ V} &= E^\circ_{\mathrm{Cu^{2+}/Cu}} - E^\circ_{\mathrm{H^+/H_2}} \\ &= E^\circ_{\mathrm{Cu^{2+}/Cu}} - 0 \end{aligned}$$

In this case, the standard reduction potential of copper, $E^\circ_{\mathrm{Cu^{2+}/Cu}}$, is 0.34 V, where the subscript means $\mathrm{Cu^{2+}} + 2e^- \rightarrow \mathrm{Cu}$.

For the Daniell cell shown in Figure 19.1, we can now write

$$\begin{array}{rr} \text{Anode (oxidation):} & \mathrm{Zn}(s) \longrightarrow \mathrm{Zn^{2+}}(1\,M) + 2e^- \\ \text{Cathode (reduction):} & \mathrm{Cu^{2+}}(1\,M) + 2e^- \longrightarrow \mathrm{Cu}(s) \\ \hline \text{Overall:} & \mathrm{Zn}(s) + \mathrm{Cu^{2+}}(1\,M) \longrightarrow \mathrm{Zn^{2+}}(1\,M) + \mathrm{Cu}(s) \end{array}$$

The emf of the cell is

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= E^\circ_{\mathrm{Cu^{2+}/Cu}} - E^\circ_{\mathrm{Zn^{2+}/Zn}} \\ &= 0.34\text{ V} - (-0.76\text{ V}) \\ &= 1.10\text{ V} \end{aligned}$$

As in the case of ΔG° (p. 818), we can use the sign of E° to predict the extent of a redox reaction. A positive E° means the redox reaction will favor the formation of products at equilibrium. Conversely, a negative E° means that more reactants than products will be formed at equilibrium. We will examine the relationships among E°_{cell}, ΔG°, and K later in this chapter.

Table 19.1 lists standard reduction potentials for a number of half-cell reactions. By definition, the SHE has an E° value of 0.00 V. Below the SHE the negative standard reduction potentials increase, and above it the positive standard reduction potentials increase. It is important to know the following points about the table in calculations:

The activity series in Figure 4.16 is based on data given in Table 19.1.

1. The E° values apply to the half-cell reactions as read in the forward (left to right) direction.
2. The more positive E° is, the greater the tendency for the substance to be reduced. For example, the half-cell reaction

$$\mathrm{F_2}(1\text{ atm}) + 2e^- \longrightarrow 2\mathrm{F^-}(1\,M) \qquad E^\circ = 2.87\text{ V}$$

has the highest positive E° value among all the half-cell reactions. Thus, F_2 is the *strongest* oxidizing agent because it has the greatest tendency to be reduced. At the other extreme is the reaction

$$\mathrm{Li^+}(1\,M) + e^- \longrightarrow \mathrm{Li}(s) \qquad E^\circ = -3.05\text{ V}$$

TABLE 19.1 **Standard Reduction Potentials at 25°C***

Half-Reaction	$E°$(V)
$\mathrm{F_2}(g) + 2e^- \longrightarrow \mathrm{2F^-}(aq)$	+2.87
$\mathrm{O_3}(g) + \mathrm{2H^+}(aq) + 2e^- \longrightarrow \mathrm{O_2}(g) + \mathrm{H_2O}$	+2.07
$\mathrm{Co^{3+}}(aq) + e^- \longrightarrow \mathrm{Co^{2+}}(aq)$	+1.82
$\mathrm{H_2O_2}(aq) + \mathrm{2H^+}(aq) + 2e^- \longrightarrow \mathrm{2H_2O}$	+1.77
$\mathrm{PbO_2}(s) + \mathrm{4H^+}(aq) + \mathrm{SO_4^{2-}}(aq) + 2e^- \longrightarrow \mathrm{PbSO_4}(s) + \mathrm{2H_2O}$	+1.70
$\mathrm{Ce^{4+}}(aq) + e^- \longrightarrow \mathrm{Ce^{3+}}(aq)$	+1.61
$\mathrm{MnO_4^-}(aq) + \mathrm{8H^+}(aq) + 5e^- \longrightarrow \mathrm{Mn^{2+}}(aq) + \mathrm{4H_2O}$	+1.51
$\mathrm{Au^{3+}}(aq) + 3e^- \longrightarrow \mathrm{Au}(s)$	+1.50
$\mathrm{Cl_2}(g) + 2e^- \longrightarrow \mathrm{2Cl^-}(aq)$	+1.36
$\mathrm{Cr_2O_7^{2-}}(aq) + \mathrm{14H^+}(aq) + 6e^- \longrightarrow \mathrm{2Cr^{3+}}(aq) + \mathrm{7H_2O}$	+1.33
$\mathrm{MnO_2}(s) + \mathrm{4H^+}(aq) + 2e^- \longrightarrow \mathrm{Mn^{2+}}(aq) + \mathrm{2H_2O}$	+1.23
$\mathrm{O_2}(g) + \mathrm{4H^+}(aq) + 4e^- \longrightarrow \mathrm{2H_2O}$	+1.23
$\mathrm{Br_2}(l) + 2e^- \longrightarrow \mathrm{2Br^-}(aq)$	+1.07
$\mathrm{NO_3^-}(aq) + \mathrm{4H^+}(aq) + 3e^- \longrightarrow \mathrm{NO}(g) + \mathrm{2H_2O}$	+0.96
$\mathrm{2Hg^{2+}}(aq) + 2e^- \longrightarrow \mathrm{Hg_2^{2+}}(aq)$	+0.92
$\mathrm{Hg_2^{2+}}(aq) + 2e^- \longrightarrow \mathrm{2Hg}(l)$	+0.85
$\mathrm{Ag^+}(aq) + e^- \longrightarrow \mathrm{Ag}(s)$	+0.80
$\mathrm{Fe^{3+}}(aq) + e^- \longrightarrow \mathrm{Fe^{2+}}(aq)$	+0.77
$\mathrm{O_2}(g) + \mathrm{2H^+}(aq) + 2e^- \longrightarrow \mathrm{H_2O_2}(aq)$	+0.68
$\mathrm{MnO_4^-}(aq) + \mathrm{2H_2O} + 3e^- \longrightarrow \mathrm{MnO_2}(s) + \mathrm{4OH^-}(aq)$	+0.59
$\mathrm{I_2}(s) + 2e^- \longrightarrow \mathrm{2I^-}(aq)$	+0.53
$\mathrm{O_2}(g) + \mathrm{2H_2O} + 4e^- \longrightarrow \mathrm{4OH^-}(aq)$	+0.40
$\mathrm{Cu^{2+}}(aq) + 2e^- \longrightarrow \mathrm{Cu}(s)$	+0.34
$\mathrm{AgCl}(s) + e^- \longrightarrow \mathrm{Ag}(s) + \mathrm{Cl^-}(aq)$	+0.22
$\mathrm{SO_4^{2-}}(aq) + \mathrm{4H^+}(aq) + 2e^- \longrightarrow \mathrm{SO_2}(g) + \mathrm{2H_2O}$	+0.20
$\mathrm{Cu^{2+}}(aq) + e^- \longrightarrow \mathrm{Cu^+}(aq)$	+0.15
$\mathrm{Sn^{4+}}(aq) + 2e^- \longrightarrow \mathrm{Sn^{2+}}(aq)$	+0.13
$\mathrm{2H^+}(aq) + 2e^- \longrightarrow \mathrm{H_2}(g)$	0.00
$\mathrm{Pb^{2+}}(aq) + 2e^- \longrightarrow \mathrm{Pb}(s)$	−0.13
$\mathrm{Sn^{2+}}(aq) + 2e^- \longrightarrow \mathrm{Sn}(s)$	−0.14
$\mathrm{Ni^{2+}}(aq) + 2e^- \longrightarrow \mathrm{Ni}(s)$	−0.25
$\mathrm{Co^{2+}}(aq) + 2e^- \longrightarrow \mathrm{Co}(s)$	−0.28
$\mathrm{PbSO_4}(s) + 2e^- \longrightarrow \mathrm{Pb}(s) + \mathrm{SO_4^{2-}}(aq)$	−0.31
$\mathrm{Cd^{2+}}(aq) + 2e^- \longrightarrow \mathrm{Cd}(s)$	−0.40
$\mathrm{Fe^{2+}}(aq) + 2e^- \longrightarrow \mathrm{Fe}(s)$	−0.44
$\mathrm{Cr^{3+}}(aq) + 3e^- \longrightarrow \mathrm{Cr}(s)$	−0.74
$\mathrm{Zn^{2+}}(aq) + 2e^- \longrightarrow \mathrm{Zn}(s)$	−0.76
$\mathrm{2H_2O} + 2e^- \longrightarrow \mathrm{H_2}(g) + \mathrm{2OH^-}(aq)$	−0.83
$\mathrm{Mn^{2+}}(aq) + 2e^- \longrightarrow \mathrm{Mn}(s)$	−1.18
$\mathrm{Al^{3+}}(aq) + 3e^- \longrightarrow \mathrm{Al}(s)$	−1.66
$\mathrm{Be^{2+}}(aq) + 2e^- \longrightarrow \mathrm{Be}(s)$	−1.85
$\mathrm{Mg^{2+}}(aq) + 2e^- \longrightarrow \mathrm{Mg}(s)$	−2.37
$\mathrm{Na^+}(aq) + e^- \longrightarrow \mathrm{Na}(s)$	−2.71
$\mathrm{Ca^{2+}}(aq) + 2e^- \longrightarrow \mathrm{Ca}(s)$	−2.87
$\mathrm{Sr^{2+}}(aq) + 2e^- \longrightarrow \mathrm{Sr}(s)$	−2.89
$\mathrm{Ba^{2+}}(aq) + 2e^- \longrightarrow \mathrm{Ba}(s)$	−2.90
$\mathrm{K^+}(aq) + e^- \longrightarrow \mathrm{K}(s)$	−2.93
$\mathrm{Li^+}(aq) + e^- \longrightarrow \mathrm{Li}(s)$	−3.05

↑ Increasing strength as oxidizing agent

Increasing strength as reducing agent ↓

*For all half-reactions the concentration is 1 *M* for dissolved species and the pressure is 1 atm for gases. These are the standard-state values.

which has the most negative $E°$ value. Thus, Li^+ is the *weakest* oxidizing agent because it is the most difficult species to reduce. Conversely, we say that F^- is the weakest reducing agent and Li metal is the strongest reducing agent. Under standard-state conditions, the oxidizing agents (the species on the left-hand side of the half-reactions in Table 19.1) increase in strength from bottom to top and the reducing agents (the species on the right-hand side of the half-reactions) increase in strength from top to bottom.

3. The half-cell reactions are reversible. Depending on the conditions, any electrode can act either as an anode or as a cathode. Earlier we saw that the SHE is the cathode (H^+ is reduced to H_2) when coupled with zinc in a cell and that it becomes the anode (H_2 is oxidized to H^+) when used in a cell with copper.
4. Under standard-state conditions, any species on the left of a given half-cell reaction will react spontaneously with a species that appears on the right of any half-cell reaction located *below* it in Table 19.1. This principle is sometimes called the *diagonal rule.* In the case of the Daniell cell

$$Cu^{2+}(1\,M) + 2e^- \longrightarrow Cu(s) \qquad E° = 0.34\ V$$

$$Zn^{2+}(1\,M) + 2e^- \longrightarrow Zn(s) \qquad E° = -0.76\ V$$

The diagonal red line shows that Cu^{2+} is the oxidizing agent and Zn is the reducing agent.

We see that the substance on the left of the first half-cell reaction is Cu^{2+} and the substance on the right in the second half-cell reaction is Zn. Therefore, as we saw earlier, Zn spontaneously reduces Cu^{2+} to form Zn^{2+} and Cu.

5. Changing the stoichiometric coefficients of a half-cell reaction *does not* affect the value of $E°$ because electrode potentials are intensive properties. This means that the value of $E°$ is unaffected by the size of the electrodes or the amount of solutions present. For example,

$$I_2(s) + 2e^- \longrightarrow 2I^-(1\,M) \qquad E° = 0.53\ V$$

but $E°$ does not change if we multiply the half-reaction by 2:

$$2I_2(s) + 4e^- \longrightarrow 4I^-(1\,M) \qquad E° = 0.53\ V$$

6. Like ΔH, ΔG, and ΔS, the sign of $E°$ changes but its magnitude remains the same when we reverse a reaction.

As Examples 19.2 and 19.3 show, Table 19.1 enables us to predict the outcome of redox reactions under standard-state conditions, whether they take place in a galvanic cell, where the reducing agent and oxidizing agent are physically separated from each other, or in a beaker, where the reactants are all mixed together.

EXAMPLE 19.2

Predict what will happen if molecular bromine (Br_2) is added to a solution containing NaCl and NaI at 25°C. Assume all species are in their standard states.

Strategy To predict what redox reaction(s) will take place, we need to compare the standard reduction potentials of Cl_2, Br_2, and I_2 and apply the diagonal rule.

(Continued)

Solution From Table 19.1, we write the standard reduction potentials as follows:

$$\begin{aligned} \mathrm{Cl_2(1\ atm)} + 2e^- &\longrightarrow \mathrm{2Cl^-}(1\,M) \qquad & E° &= 1.36\ \mathrm{V}\\ \mathrm{Br_2}(l) + 2e^- &\longrightarrow \mathrm{2Br^-}(1\,M) & E° &= 1.07\ \mathrm{V}\\ \mathrm{I_2}(s) + 2e^- &\longrightarrow \mathrm{2I^-}(1\,M) & E° &= 0.53\ \mathrm{V} \end{aligned}$$

Applying the diagonal rule we see that Br_2 will oxidize I^- but will not oxidize Cl^-. Therefore, the only redox reaction that will occur appreciably under standard-state conditions is

$$\begin{aligned} &\text{Oxidation:} & \mathrm{2I^-}(1\,M) &\longrightarrow \mathrm{I_2}(s) + 2e^-\\ &\text{Reduction:} & \mathrm{Br_2}(l) + 2e^- &\longrightarrow \mathrm{2Br^-}(1\,M)\\ \hline &\text{Overall:} & \mathrm{2I^-}(1\,M) + \mathrm{Br_2}(l) &\longrightarrow \mathrm{I_2}(s) + \mathrm{2Br^-}(1\,M) \end{aligned}$$

Check We can confirm our conclusion by calculating $E°_{\mathrm{cell}}$. Try it. Note that the Na^+ ions are inert and do not enter into the redox reaction.

Practice Exercise Can Sn reduce $Zn^{2+}(aq)$ under standard-state conditions?

EXAMPLE 19.3

A galvanic cell consists of a Mg electrode in a 1.0 M $Mg(NO_3)_2$ solution and a Ag electrode in a 1.0 M $AgNO_3$ solution. Calculate the standard emf of this cell at 25°C.

Strategy At first it may not be clear how to assign the electrodes in the galvanic cell. From Table 19.1 we write the standard reduction potentials of Ag and Mg and apply the diagonal rule to determine which is the anode and which is the cathode.

Solution The standard reduction potentials are

$$\begin{aligned} \mathrm{Ag^+}(1.0\,M) + e^- &\longrightarrow \mathrm{Ag}(s) \qquad & E° &= 0.80\ \mathrm{V}\\ \mathrm{Mg^{2+}}(1.0\,M) + 2e^- &\longrightarrow \mathrm{Mg}(s) & E° &= -2.37\ \mathrm{V} \end{aligned}$$

Applying the diagonal rule, we see that Ag^+ will oxidize Mg:

$$\begin{aligned} &\text{Anode (oxidation):} & \mathrm{Mg}(s) &\longrightarrow \mathrm{Mg^{2+}}(1.0\,M) + 2e^-\\ &\text{Cathode (reduction):} & \mathrm{2Ag^+}(1.0\,M) + 2e^- &\longrightarrow \mathrm{2Ag}(s)\\ \hline &\text{Overall:} & \mathrm{Mg}(s) + \mathrm{2Ag^+}(1.0\,M) &\longrightarrow \mathrm{Mg^{2+}}(1.0\,M) + \mathrm{2Ag}(s) \end{aligned}$$

Note that in order to balance the overall equation we multiplied the reduction of Ag^+ by 2. We can do so because, as an intensive property, $E°$ is not affected by this procedure. We find the emf of the cell by using Equation (19.1) and Table 19.1:

$$\begin{aligned} E°_{\mathrm{cell}} &= E°_{\mathrm{cathode}} - E°_{\mathrm{anode}}\\ &= E°_{\mathrm{Ag^+/Ag}} - E°_{\mathrm{Mg^{2+}/Mg}}\\ &= 0.80\ \mathrm{V} - (-2.37\ \mathrm{V})\\ &= 3.17\ \mathrm{V} \end{aligned}$$

Check The positive value of $E°$ shows that the forward reaction is favored.

Practice Exercise What is the standard emf of a galvanic cell made of a Cd electrode in a 1.0 M $Cd(NO_3)_2$ solution and a Cr electrode in a 1.0 M $Cr(NO_3)_3$ solution at 25°C?

19.4 Thermodynamics of Redox Reactions

Our next step is to see how E°_{cell} is related to thermodynamic quantities such as ΔG° and K. In a galvanic cell, chemical energy is converted to electrical energy to do electrical work such as running an electric motor. Electrical energy, in this case, is the product of the emf of the cell and the total electrical charge (in coulombs) that passes through the cell:

$$\begin{aligned}\text{electrical energy} &= \text{coulombs} \times \text{volts}\\ &= \text{joules}\end{aligned}$$

The equality means that

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

The total charge is determined by the number of electrons that pass through the cell, so we have

$$\text{total charge} = \text{number of } e^- \times \text{charge of one } e^-$$

In general, it is more convenient to express the total charge in molar quantities. The charge of one mole of electrons is called the ***Faraday constant (F),*** after the English chemist and physicist Michael Faraday,[†] where

$$\begin{aligned}1\ F &= 6.022 \times 10^{23}\ e^-/\text{mol } e^- \times 1.602 \times 10^{-19}\ \text{C}/e^-\\ &= 9.647 \times 10^4\ \text{C/mol } e^-\end{aligned}$$

In most calculations, we round the Faraday constant to 96,500 C/mol e^-.

Therefore, the total charge can now be expressed as nF, where n is the number of moles of electrons exchanged between the oxidizing agent and reducing agent in the overall redox equation for the electrochemical process.

The sign convention for electrical work is the same as that for *P-V* work, discussed in Section 6.3.

[†] Michael Faraday (1791–1867). English chemist and physicist. Faraday is regarded by many as the greatest experimental scientist of the nineteenth century. He started as an apprentice to a bookbinder at the age of 13, but became interested in science after reading a book on chemistry. Faraday invented the electric motor and was the first person to demonstrate the principle governing electrical generators. Besides making notable contributions to the fields of electricity and magnetism, Faraday also worked on optical activity, and discovered and named benzene.

Therefore, we can write

$$\Delta G = -nFE_{\text{cell}} \tag{19.2}$$

For a spontaneous reaction, ΔG is negative. Because both n and F are positive quantities, it follows that E_{cell} must also be positive. For reactions in which reactants and products are in their standard states (1 M or 1 atm), Equation (19.2) becomes

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} \tag{19.3}$$

TABLE 19.2 Relationships Among ΔG°, K, and E°_{cell}

ΔG°	K	E°_{cell}	Reaction Under Standard-State Conditions
Negative	>1	Positive	Favors formation of products.
0	$=1$	0	Reactants and products are equally favored.
Positive	<1	Negative	Favors formation of reactants.

EXAMPLE 19.5

Calculate the standard free-energy change for the following reaction at 25°C:

$$2\text{Au}(s) + 3\text{Ca}^{2+}(1.0\,M) \longrightarrow 2\text{Au}^{3+}(1.0\,M) + 3\text{Ca}(s)$$

Strategy The relationship between the standard free energy change and the standard emf of the cell is given by Equation (19.3): $\Delta G^\circ = -nFE^\circ_{\text{cell}}$. Thus, if we can determine E°_{cell}, we can calculate ΔG°. We can determine the E°_{cell} of a hypothetical galvanic cell made up of two couples (Au^{3+}/Au and Ca^{2+}/Ca) from the standard reduction potentials in Table 19.1.

(Continued)

Solution The half-cell reactions are

$$\begin{aligned} &\text{Anode (oxidation):} & 2\text{Au}(s) &\longrightarrow 2\text{Au}^{3+}(1.0\,M) + 6e^- \\ &\text{Cathode (reduction):} & 3\text{Ca}^{2+}(1.0\,M) + 6e^- &\longrightarrow 3\text{Ca}(s) \end{aligned}$$

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= E^\circ_{\text{Ca}^{2+}/\text{Ca}} - E^\circ_{\text{Au}^{3+}/\text{Au}} \\ &= -2.87\text{ V} - 1.50\text{ V} \\ &= -4.37\text{ V} \end{aligned}$$

Now we use Equation (19.3):

$$\Delta G^\circ = -nFE^\circ$$

The overall reaction shows that $n = 6$, so

$$\begin{aligned} \Delta G^\circ &= -(6)(96{,}500\text{ J/V}\cdot\text{mol})(-4.37\text{ V}) \\ &= 2.53 \times 10^6\text{ J/mol} \\ &= \boxed{2.53 \times 10^3\text{ kJ/mol}} \end{aligned}$$

Check The large positive value of ΔG° tells us that the reaction favors the reactants at equilibrium. The result is consistent with the fact that E° for the galvanic cell is negative.

Practice Exercise Calculate ΔG° for the following reaction at 25°C:

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

19.5 The Effect of Concentration on Cell Emf

So far we have focused on redox reactions in which reactants and products are in their standard states, but standard-state conditions are often difficult, and sometimes impossible, to maintain. However, there is a mathematical relationship between the emf of a galvanic cell and the concentration of reactants and products in a redox reaction under nonstandard-state conditions. This equation is derived next.

The Nernst Equation

Consider a redox reaction of the type

$$a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$$

From Equation (18.13),

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

Because $\Delta G = -nFE$ and $\Delta G^\circ = -nFE^\circ$, the equation can be expressed as

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

Dividing the equation through by $-nF$, we get

$$E = E^\circ - \frac{RT}{nF} \ln Q \qquad (19.7)$$

where Q is the reaction quotient (see Section 14.4). Equation (19.7) is known as the ***Nernst*[†] *equation.*** At 298 K, Equation (19.7) can be rewritten as

Note that the Nernst equation is used to calculate the cell voltage under non-standard state conditions.

$$\boxed{E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q} \qquad (19.8)$$

or, expressing Equation (19.8) using the base-10 logarithm of Q:

$$\boxed{E = E^\circ - \frac{0.0592 \text{ V}}{n} \log Q} \qquad (19.9)$$

During the operation of a galvanic cell, electrons flow from the anode to the cathode, resulting in product formation and a decrease in reactant concentration. Thus, Q increases, which means that E decreases. Eventually, the cell reaches equilibrium. At equilibrium, there is no net transfer of electrons, so $E = 0$ and $Q = K$, where K is the equilibrium constant.

The Nernst equation enables us to calculate E as a function of reactant and product concentrations in a redox reaction. For example, for the Daniell cell in Figure 19.1

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

The Nernst equation for this cell at 25°C can be written as

$$E = 1.10 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Remember that concentrations of pure solids (and pure liquids) do not appear in the expression for Q.

If the ratio $[\text{Zn}^{2+}]/[\text{Cu}^{2+}]$ is less than 1, $\ln([\text{Zn}^{2+}]/[\text{Cu}^{2+}])$ is a negative number, so that the second term on the right-hand side of the preceding equation is positive. Under this condition E is greater than the standard emf E°. If the ratio is greater than 1, E is smaller than E°.

You will not be required to calculate changes in voltage. However, you should be able to predict if voltages will increase or decrease with changes from standard conditions.
You may also be able to explain why voltages may increase or decreased using the Nernst equation.

[†] Walter Hermann Nernst (1864–1941). German chemist and physicist. Nernst's work was mainly on electrolyte solution and thermodynamics. He also invented an electric piano. Nernst was awarded the Nobel Prize in Chemistry in 1920 for his contribution to thermodynamics.

Concentration Cells

Because electrode potential depends on ion concentrations, it is possible to construct a galvanic cell from two half-cells composed of the *same* material but differing in ion concentrations. Such a cell is called a *concentration cell.*

Consider a situation in which zinc electrodes are put into two aqueous solutions of zinc sulfate at 0.10 *M* and 1.0 *M* concentrations. The two solutions are connected by a salt bridge, and the electrodes are joined by a piece of wire in an arrangement like that shown in Figure 19.1. According to Le Châtelier's principle, the tendency for the reduction

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

increases with increasing concentration of Zn^{2+} ions. Therefore, reduction should occur in the more concentrated compartment and oxidation should take place on the more dilute side. The cell diagram is

$$\mathrm{Zn}(s)\,|\,\mathrm{Zn}^{2+}(0.10\,M)\,\|\,\mathrm{Zn}^{2+}(1.0\,M)\,|\,\mathrm{Zn}(s)$$

and the half-reactions are

$$\begin{array}{rrcl}
\text{Oxidation:} & \mathrm{Zn}(s) & \longrightarrow & \mathrm{Zn}^{2+}(0.10\,M) + 2e^- \\
\text{Reduction:} & \mathrm{Zn}^{2+}(1.0\,M) + 2e^- & \longrightarrow & \mathrm{Zn}(s) \\
\hline
\text{Overall:} & Zn^{2+}(1.0\,M) & \longrightarrow & \mathrm{Zn}^{2+}(0.10\,M)
\end{array}$$

The emf of the cell is

$$E = E^\circ - \frac{0.0257\ \mathrm{V}}{2} \ln \frac{[\mathrm{Zn}^{2+}]_{\mathrm{dil}}}{[\mathrm{Zn}^{2+}]_{\mathrm{conc}}}$$

where the subscripts "dil" and "conc" refer to the 0.10 *M* and 1.0 *M* concentrations, respectively. The E° for this cell is zero (the same electrode and the same type of ions are involved), so

$$\begin{aligned} E &= 0 - \frac{0.0257\ \mathrm{V}}{2} \ln \frac{0.10}{1.0} \\ &= 0.0296\ \mathrm{V} \end{aligned}$$

$1\ \mathrm{m}M = 1 \times 10^{-3}\ M.$

19.8 Electrolysis

In contrast to spontaneous redox reactions, which result in the conversion of chemical energy into electrical energy, ***electrolysis*** is the process in which *electrical energy is used to cause a nonspontaneous chemical reaction to occur.* An ***electrolytic cell*** is *an apparatus for carrying out electrolysis.* The same principles underlie electrolysis and the processes that take place in galvanic cells. Here we will discuss three examples of electrolysis based on those principles. Then we will look at the quantitative aspects of electrolysis.

Electrolysis of Molten Sodium Chloride

In its molten state, sodium chloride, an ionic compound, can be electrolyzed to form sodium metal and chlorine. Figure 19.17(a) is a diagram of a *Downs cell,* which is used for large-scale electrolysis of NaCl. In molten NaCl, the cations and anions are the Na^+ and Cl^- ions, respectively. Figure 19.17(b) is a simplified diagram showing the reactions that occur at the electrodes. The electrolytic cell contains a pair of electrodes connected to the battery. The battery serves as an "electron pump," driving electrons to the cathode, where reduction occurs, and withdrawing electrons from the anode, where oxidation occurs. The reactions at the electrodes are

$$\begin{array}{rrcl} \text{Anode (oxidation):} & 2\text{Cl}^-(l) & \longrightarrow & \text{Cl}_2(g) + 2e^- \\ \text{Cathode (reduction):} & 2\text{Na}^+(l) + 2e^- & \longrightarrow & 2\text{Na}(l) \\ \hline \text{Overall:} & 2\text{Na}^+(l) + 2\text{Cl}^-(l) & \longrightarrow & 2\text{Na}(l) + \text{Cl}_2(g) \end{array}$$

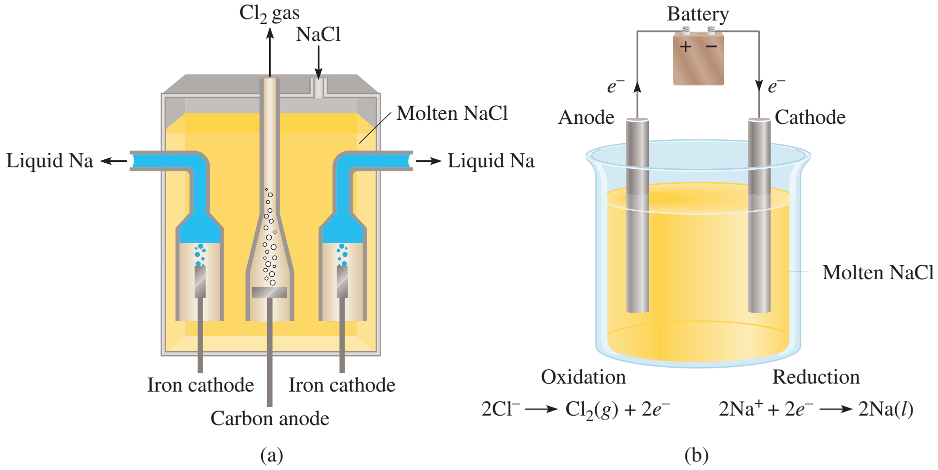
This process is a major source of pure sodium metal and chlorine gas.

Theoretical estimates show that the $E°$ value for the overall process is about -4 V, which means that this is a nonspontaneous process. Therefore, a *minimum* of 4 V must be supplied by the battery to carry out the reaction. In practice, a higher voltage is necessary because of inefficiencies in the electrolytic process and because of overvoltage, to be discussed shortly.

Electrolysis of Water

Water in a beaker under atmospheric conditions (1 atm and 25°C) will not spontaneously decompose to form hydrogen and oxygen gas because the standard free-energy change for the reaction is a large positive quantity:

$$2\text{H}_2\text{O}(l) \longrightarrow 2\text{H}_2(g) + \text{O}_2(g) \qquad \Delta G° = 474.4 \text{ kJ/mol}$$



(a) (b)

Figure 19.17 *(a) A practical arrangement called a Downs cell for the electrolysis of molten NaCl (m.p. = 801°C). The sodium metal formed at the cathodes is in the liquid state. Since liquid sodium metal is lighter than molten NaCl, the sodium floats to the surface, as shown, and is collected. Chlorine gas forms at the anode and is collected at the top. (b) A simplified diagram showing the electrode reactions during the electrolysis of molten NaCl. The battery is needed to drive the nonspontaneous reactions.*

However, this reaction can be induced in a cell like the one shown in Figure 19.18. This electrolytic cell consists of a pair of electrodes made of a nonreactive metal, such as platinum, immersed in water. When the electrodes are connected to the battery, nothing happens because there are not enough ions in pure water to carry much of an electric current. (Remember that at 25°C, pure water has only 1×10^{-7} M H^+ ions and 1×10^{-7} M OH^- ions.) On the other hand, the reaction occurs readily in a 0.1 M H_2SO_4 solution because there are a sufficient number of ions to conduct electricity. Immediately, gas bubbles begin to appear at both electrodes.

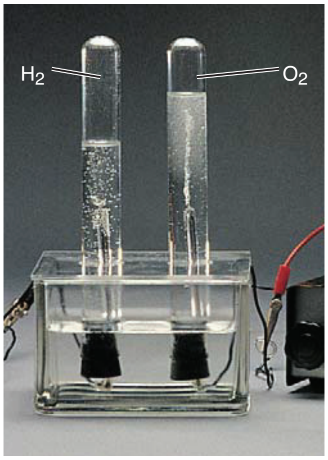


Figure 19.18 *Apparatus for small-scale electrolysis of water. The volume of hydrogen gas generated at the cathode is twice that of oxygen gas generated at the anode.*

Figure 19.19 shows the electrode reactions. The process at the anode is

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$$

while at the cathode we have

$$H^+(aq) + e^- \longrightarrow \tfrac{1}{2}H_2(g)$$

The overall reaction is given by

$$\begin{array}{rl} \text{Anode (oxidation):} & 2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^- \\ \text{Cathode (reduction):} & \underline{4[H^+(aq) + e^- \longrightarrow \tfrac{1}{2}H_2(g)]} \\ \text{Overall:} & 2H_2O(l) \longrightarrow 2H_2(g) + O_2(g) \end{array}$$

Note that no net H_2SO_4 is consumed.

Quantitative Aspects of Electrolysis

The quantitative treatment of electrolysis was developed primarily by Faraday. He observed that the mass of product formed (or reactant consumed) at an electrode is proportional to both the amount of electricity transferred at the electrode and the molar mass of the substance in question. For example, in the electrolysis of molten NaCl, the cathode reaction tells us that one Na atom is produced when one Na^+ ion accepts an electron from the electrode. To reduce 1 mole of Na^+ ions, we must supply Avogadro's number (6.02×10^{23}) of electrons to the cathode. On the other hand, the stoichiometry of the anode reaction shows that oxidation of two Cl^- ions yields one chlorine molecule. Therefore, the formation of 1 mole of Cl_2 results in the transfer of 2 moles of electrons from the Cl^- ions to the anode. Similarly, it takes 2 moles of electrons to reduce 1 mole of Mg^{2+} ions and 3 moles of electrons to reduce 1 mole of Al^{3+} ions:

$$Mg^{2+} + 2e^- \longrightarrow Mg$$
$$Al^{3+} + 3e^- \longrightarrow Al$$

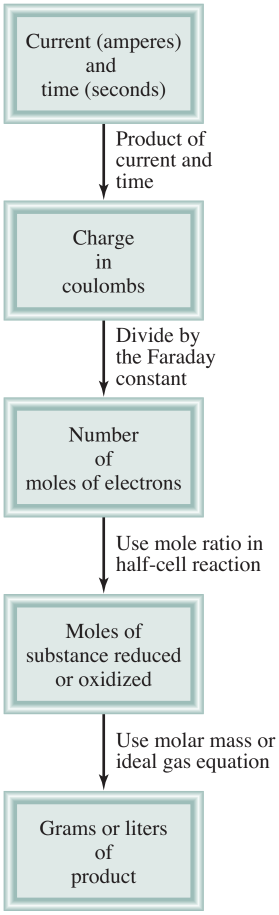


Figure 19.20 *Steps involved in calculating amounts of substances reduced or oxidized in electrolysis.*

In an electrolysis experiment, we generally measure the current (in amperes, A) that passes through an electrolytic cell in a given period of time. The relationship between charge (in coulombs, C) and current is

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

that is, a coulomb is the quantity of electrical charge passing any point in the circuit in 1 second when the current is 1 ampere.

Figure 19.20 shows the steps involved in calculating the quantities of substances produced in electrolysis. Let us illustrate the approach by considering molten $CaCl_2$ in an electrolytic cell. Suppose a current of 0.452 A is passed through the cell for 1.50 h. How much product will be formed at the anode and at the cathode? In solving electrolysis problems of this type, the first step is to determine which species will be oxidized at the anode and which species will be reduced at the cathode. Here the choice is straightforward because we only have Ca^{2+} and Cl^- ions in molten $CaCl_2$. Thus, we write the half- and overall cell reactions as

$$\begin{array}{rrcl}
\text{Anode (oxidation):} & 2\text{Cl}^-(l) & \longrightarrow & \text{Cl}_2(g) + 2e^- \\
\text{Cathode (reduction):} & \text{Ca}^{2+}(l) + 2e^- & \longrightarrow & \text{Ca}(l) \\
\hline
\text{Overall:} & \text{Ca}^{2+}(l) + 2\text{Cl}^-(l) & \longrightarrow & \text{Ca}(l) + \text{Cl}_2(g)
\end{array}$$

The quantities of calcium metal and chlorine gas formed depend on the number of electrons that pass through the electrolytic cell, which in turn depends on current × time, or charge:

$$?\ \text{C} = 0.452\ \cancel{\text{A}} \times 1.50\ \cancel{\text{h}} \times \frac{3600\ \cancel{\text{s}}}{1\ \cancel{\text{h}}} \times \frac{1\ \text{C}}{1\ \cancel{\text{A}} \cdot \cancel{\text{s}}} = 2.44 \times 10^3\ \text{C}$$

Because 1 mole e^- = 96,500 C and 2 mol e^- are required to reduce 1 mole of Ca^{2+} ions, the mass of Ca metal formed at the cathode is calculated as follows:

$$?\ \text{g Ca} = 2.44 \times 10^3\ \cancel{\text{C}} \times \frac{1\ \cancel{\text{mol}\ e^-}}{96{,}500\ \cancel{\text{C}}} \times \frac{1\ \cancel{\text{mol Ca}}}{2\ \cancel{\text{mol}\ e^-}} \times \frac{40.08\ \text{g Ca}}{1\ \cancel{\text{mol Ca}}} = 0.507\ \text{g Ca}$$

The anode reaction indicates that 1 mole of chlorine is produced per 2 mol e^- of electricity. Hence the mass of chlorine gas formed is

$$?\ \text{g Cl}_2 = 2.44 \times 10^3\ \cancel{\text{C}} \times \frac{1\ \cancel{\text{mol}\ e^-}}{96{,}500\ \cancel{\text{C}}} \times \frac{1\ \cancel{\text{mol Cl}_2}}{2\ \cancel{\text{mol}\ e^-}} \times \frac{70.90\ \text{g Cl}_2}{1\ \cancel{\text{mol Cl}_2}} = 0.896\ \text{g Cl}_2$$

Example 19.9 applies this approach to the electrolysis in an aqueous solution.

EXAMPLE 19.9

A current of 1.26 A is passed through an electrolytic cell containing a dilute sulfuric acid solution for 7.44 h. Write the half-cell reactions and calculate the volume of gases generated at STP.

Strategy Earlier (see p. 867) we saw that the half-cell reactions for the process are

$$\begin{array}{rrcl}
\text{Anode (oxidation):} & 2\text{H}_2\text{O}(l) & \longrightarrow & \text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \\
\text{Cathode (reduction):} & 4[\text{H}^+(aq) + e^- & \longrightarrow & \tfrac{1}{2}\text{H}_2(g)] \\
\hline
\text{Overall:} & 2\text{H}_2\text{O}(l) & \longrightarrow & 2\text{H}_2(g) + \text{O}_2(g)
\end{array}$$

(Continued)

According to Figure 19.20, we carry out the following conversion steps to calculate the quantity of O_2 in moles:

$$\text{current} \times \text{time} \rightarrow \text{coulombs} \rightarrow \text{moles of } e^- \rightarrow \text{moles of } O_2$$

Then, using the ideal gas equation we can calculate the volume of O_2 in liters at STP. A similar procedure can be used for H_2.

Solution First we calculate the number of coulombs of electricity that pass through the cell:

$$? \text{ C} = 1.26 \cancel{\text{A}} \times 7.44 \cancel{\text{h}} \times \frac{3600 \cancel{\text{s}}}{1 \cancel{\text{h}}} \times \frac{1 \text{ C}}{1 \cancel{\text{A}} \cdot \cancel{\text{s}}} = 3.37 \times 10^4 \text{ C}$$

Next, we convert number of coulombs to number of moles of electrons

$$3.37 \times 10^4 \cancel{\text{C}} \times \frac{\cancel{1 \text{ mol}}\ e^-}{96{,}500 \cancel{\text{C}}} = 0.349 \text{ mol } e^-$$

(Continued)

From the oxidation half-reaction we see that 1 mol $O_2 \bumpeq 4$ mol e^-. Therefore, the number of moles of O_2 generated is

$$0.349 \cancel{\text{mol } e^-} \times \frac{1 \text{ mol } O_2}{4 \cancel{\text{mol } e^-}} = 0.0873 \text{ mol } O_2$$

The volume of 0.0873 mol O_2 at STP is given by

$$\begin{aligned} V &= \frac{nRT}{P} \\ &= \frac{(0.0873 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(273 \text{ K})}{1 \text{ atm}} = 1.96 \text{ L} \end{aligned}$$

The procedure for hydrogen is similar. To simplify, we combine the first two steps to calculate the number of moles of H_2 generated:

$$3.37 \times 10^4 \cancel{\text{C}} \times \frac{1 \cancel{\text{mol } e^-}}{96{,}500 \cancel{\text{C}}} \times \frac{1 \text{ mol } H_2}{2 \cancel{\text{mol } e^-}} = 0.175 \text{ mol } H_2$$

The volume of 0.175 mol H_2 at STP is given by

$$\begin{aligned} V &= \frac{nRT}{P} \\ &= \frac{(0.175 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(273 \text{ K})}{1 \text{ atm}} \\ &= 3.92 \text{ L} \end{aligned}$$

Check Note that the volume of H_2 is twice that of O_2 (see Figure 19.18), which is what we would expect based on Avogadro's law (at the same temperature and pressure, volume is directly proportional to the number of moles of gases).

Practice Exercise A constant current is passed through an electrolytic cell containing molten $MgCl_2$ for 18 h. If 4.8×10^5 g of Cl_2 are obtained, what is the current in amperes?

Key Equations

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$	(19.1)	Calculating the standard emf of a galvanic cell.
$\Delta G = -nFE_{\text{cell}}$	(19.2)	Relating free-energy change to the emf of the cell.
$\Delta G^\circ = -nFE^\circ_{\text{cell}}$	(19.3)	Relating the standard free-energy change to the standard emf of the cell.
$E = E^\circ - \dfrac{0.0592\ \text{V}}{n}\log Q$	(19.9)	Relating the emf of the cell to the concentrations under nonstandard state conditions.

Answers to Practice Exercises

19.1 $5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \longrightarrow 5\text{Fe}^{3+} + \text{Mn}^{2+} + 4\text{H}_2\text{O}$.
19.2 No. **19.3** 0.34 V. **19.4** 1×10^{-42}.
19.5 $\Delta G^\circ = -4.1 \times 10^2$ kJ/mol. **19.6** Yes, $E = +0.01$ V.
19.7 0.38 V. **19.8** Anode, O_2; cathode, H_2.
19.9 2.0×10^4 A.