21

Electrochemistry

Corrosion is an undesirable electrochemical reaction with very serious economic consequences. Rust is formed when iron is oxidized in the presence of water.

OUTLINE

OBJECTIVES

After you have studied this chapter, you should be able to

- *Use the terminology of electrochemistry (terms such as "cell," "electrode," "cathode," "anode")*
- *Describe the differences between electrolytic cells and voltaic (galvanic) cells*
- *Recognize oxidation and reduction half-reactions, and know at which electrode each occurs*
- *Write half-reactions and overall cell reactions for electrolysis processes*
- *Use Faraday's Law of Electrolysis to calculate amounts of products formed, amounts of current passed, time elapsed, and oxidation state*
- *Describe the refining and plating of metals by electrolytic methods*
- *Describe the construction of simple voltaic cells from half-cells and a salt bridge, and understand the function of each component*
- *Write half-reactions and overall cell reactions for voltaic cells*

- *Compare various voltaic cells to determine the relative strengths of oxidizing and reducing agents*
- *Interpret standard reduction potentials*
- *Use standard reduction potentials, E^0, to calculate the potential of a standard voltaic cell, E^0_{cell}*
- *Use standard reduction potentials to identify the cathode and the anode in a standard cell*
- *Use standard reduction potentials to predict the spontaneity of a redox reaction*
- *Use standard reduction potentials to identify oxidizing and reducing agents in a cell or in a redox reaction*
- *Describe some corrosion processes and some methods for preventing corrosion*
- *Use the Nernst equation to relate electrode potentials and cell potentials to different concentrations and partial pressures*
- *Relate the standard cell potential (E^0_{cell}) to the standard Gibbs free energy change (ΔG^0) and the equilibrium constant (K)*
- *Distinguish between primary and secondary voltaic cells*
- *Describe the compositions and reactions of some useful primary and secondary cells (batteries)*
- *Describe the electrochemical processes involved in discharging and recharging a lead storage (automobile) battery*

Electrochemistry deals with the chemical changes produced by electric current and with the production of electricity by chemical reactions. Many metals are purified or are plated onto jewelry by electrochemical methods. Digital watches, automobile starters, calculators, and pacemakers are just a few devices that depend on electrochemically produced power. Corrosion of metals is an electrochemical process.

We learn much about chemical reactions from the study of electrochemistry. The amount of electrical energy consumed or produced can be measured quite accurately. All electrochemical reactions involve the transfer of electrons and are therefore *oxidation–reduction* reactions. The sites of oxidation and reduction are separated physically so that oxidation occurs at one location, and reduction occurs at the other. Electrochemical processes require some method of introducing a stream of electrons into a reacting chemical system and some means of withdrawing electrons. In most applications the reacting system is contained in a **cell,** and an electric current enters or exits by **electrodes.**

You should review oxidation–reduction (redox) reactions in text Section 4-5. See the *Saunders Interactive General Chemistry CD-ROM,* Screen 21.2, Redox Reactions.

We classify electrochemical cells into two types.

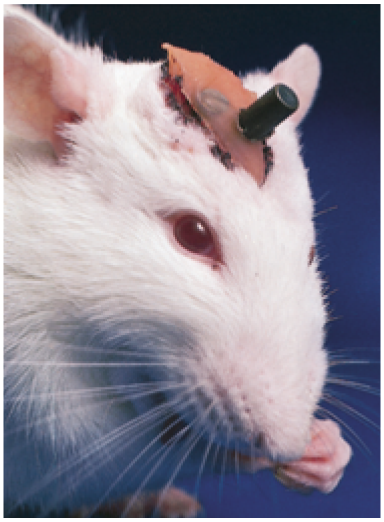
1. **Electrolytic cells** are those in which electrical energy from an external source causes *nonspontaneous* chemical reactions to occur.
2. **Voltaic cells** are those in which *spontaneous* chemical reactions produce electricity and supply it to an external circuit.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 21.4, Electrochemical Cells.

We will discuss several electrochemical cells. From experimental observations we deduce the electrode reactions and the overall reactions. We then construct simplified diagrams of the cells.

21-1 ELECTRICAL CONDUCTION

Electric current represents transfer of charge. Charge can be conducted through metals and through pure liquid electrolytes (that is, molten salts) or solutions containing electrolytes. The former type of conduction is called **metallic conduction.** It involves the flow of electrons with no similar movement of the atoms of the metal and no obvious changes in the metal (Section 13-17). **Ionic,** or **electrolytic, conduction** is the conduction of electric current by the motion of ions through a solution or a pure liquid. Positively charged ions migrate toward the negative electrode while negatively charged ions move toward the positive electrode. Both kinds of conduction, ionic and metallic, occur in electrochemical cells (Figure 21-1).



Many reactions that take place in living cells are redox reactions. These reactions can be studied with miniature electrodes.

21-2 ELECTRODES

Electrodes are surfaces on which oxidation or reduction half-reactions occur. They may or may not participate in the reactions. Those that do not react are called **inert electrodes.** Regardless of the kind of cell, electrolytic or voltaic, the electrodes are identified as follows.

> The **cathode** is defined as the electrode at which *reduction* occurs as electrons are gained by some species. The **anode** is the electrode at which *oxidation* occurs as electrons are lost by some species.

Each of these can be either the positive or the negative electrode.

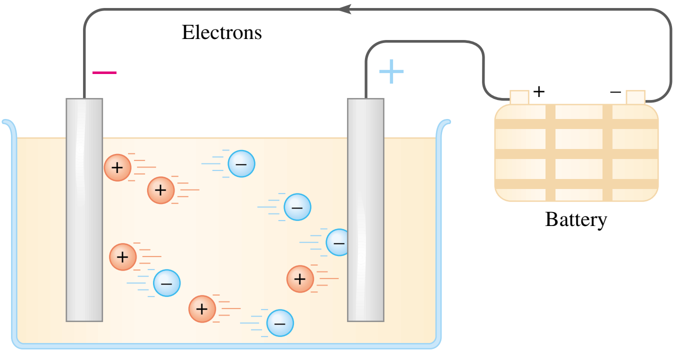


Figure 21-1 The motion of ions through a solution is an electric current. This accounts for ionic (electrolytic) conduction. Positively charged ions migrate toward the negative electrode, and negatively charged ions migrate toward the positive electrode. Here the rate of migration is greatly exaggerated for clarity. The ionic velocities are actually only slightly greater than random molecular speeds.

ELECTROLYTIC CELLS

In some electrochemical cells *nonspontaneous* chemical reactions are forced to occur by the input of electrical energy. This process is called **electrolysis.** An electrolytic cell consists of a container for the reaction material with electrodes immersed in the reaction material and connected to a source of direct current. Inert electrodes are often used so that they do not react.

Lysis means "splitting apart." In many electrolytic cells compounds are split into their constituent elements.

21-3 THE ELECTROLYSIS OF MOLTEN SODIUM CHLORIDE (THE DOWNS CELL)

Solid sodium chloride does not conduct electricity. Its ions vibrate about fixed positions, but they are not free to move throughout the crystal. Molten (melted) NaCl, however, is an excellent conductor because its ions are freely mobile. Consider a cell in which a source of direct current is connected by wires to two inert graphite electrodes (Figure 21-2a). They are immersed in a container of molten sodium chloride. When the current flows, we observe the following.

Molten NaCl, melting point 801°C, is a clear, colorless liquid that looks like water.

1. A pale green gas, which is chlorine, Cl_2, is liberated at one electrode.
2. Molten, silvery white metallic sodium, Na, forms at the other electrode and floats on top of the molten sodium chloride.

The metal remains liquid because its melting point is only 97.8°C. It floats because it is less dense than the molten NaCl.

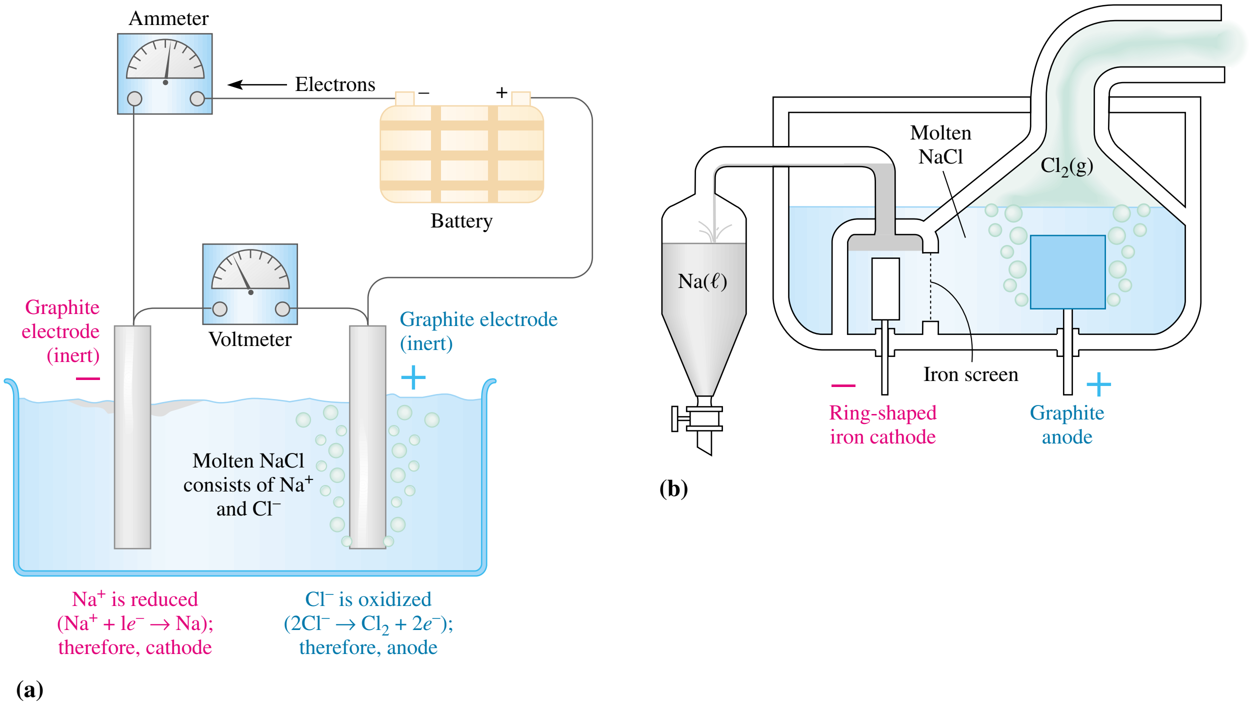


Figure 21-2 (a) Apparatus for electrolysis of molten sodium chloride. (b) The Downs cell, the apparatus in which molten sodium chloride is commercially electrolyzed to produce sodium metal and chlorine gas. The liquid Na floats on the denser molten NaCl.

From these observations we can deduce the processes of the cell. Chlorine must be produced by oxidation of Cl^- ions, and the electrode at which this happens must be the anode. Metallic sodium is produced by reduction of Na^+ ions at the cathode, where electrons are being forced into the cell.

In this chapter, as in Chapters 4 and 11, we often use red type to emphasize reduction and blue type to emphasize oxidation.

$$\begin{array}{rcll} 2\text{Cl}^- & \longrightarrow & \text{Cl}_2(g) + 2e^- & \text{(oxidation, anode half-reaction)} \\ 2[\text{Na}^+ + e^- & \longrightarrow & \text{Na}(\ell)] & \text{(reduction, cathode half-reaction)} \\ \hline \underbrace{2\text{Na}^+ + 2\text{Cl}^-}_{2\text{NaCl}(\ell)} & \longrightarrow & 2\text{Na}(\ell) + \text{Cl}_2(g) & \text{(overall cell reaction)} \end{array}$$

The direction of *spontaneous* flow for negatively charged particles is from negative to positive.

The formation of metallic Na and gaseous Cl_2 from NaCl is *nonspontaneous* except at temperatures very much higher than 801°C. The direct current (dc) source must supply electrical energy to force this reaction to occur. Electrons are used in the cathode half-reaction (reduction) and produced in the anode half-reaction (oxidation). They therefore travel through the wire from *anode* to *cathode*. The dc source forces electrons to flow nonspontaneously from the positive electrode to the negative electrode. The anode is the positive electrode and the cathode the negative electrode *in all electrolytic cells*. Figure 21-2a is a simplified diagram of the cell.

Sodium and chlorine must not be allowed to come in contact with each other because they react spontaneously, rapidly, and explosively to form sodium chloride. Figure 21-2b shows the Downs cell that is used for the industrial electrolysis of sodium chloride. The Downs cell is expensive to run, mainly because of the cost of construction, the cost of the electricity, and the cost of heating the NaCl to melt it. Nevertheless, electrolysis of a molten sodium salt is the most practical means by which metallic Na can be obtained, owing to its extremely high reactivity. Once liberated by the electrolysis, the liquid Na metal is drained off, cooled, and cast into blocks. These must be stored in an inert environment (e.g., in mineral oil) to prevent reaction with O_2 or other components of the atmosphere.

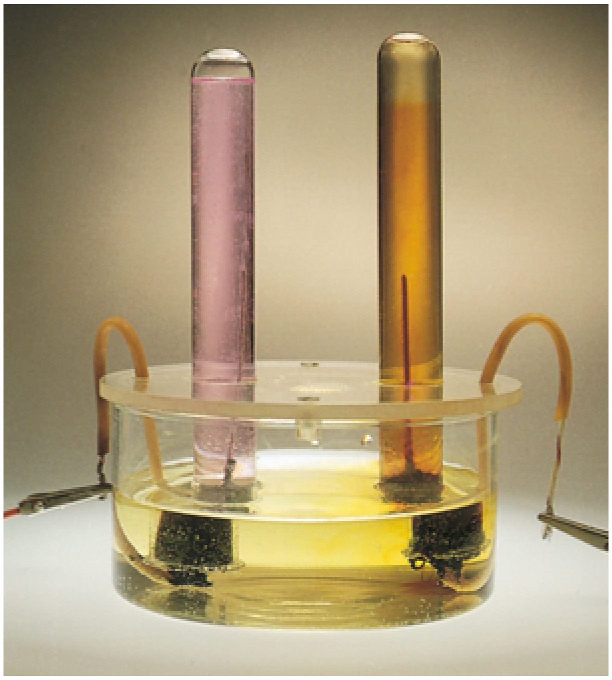
Electrolysis of NaCl in the Downs cell is the main commercial method of producing metallic sodium. The Cl_2 gas produced in the Downs cell is cooled, compressed, and marketed. This partially offsets the expense of producing metallic sodium, but most chlorine is produced by the cheaper electrolysis of aqueous NaCl.

21-4 THE ELECTROLYSIS OF AQUEOUS SODIUM CHLORIDE

Consider the electrolysis of a moderately concentrated solution of NaCl in water, using inert electrodes. The following experimental observations are made when a sufficiently high voltage is applied across the electrodes of a suitable cell.

1. H_2 gas is liberated at one electrode. The solution becomes basic in that vicinity.
2. Cl_2 gas is liberated at the other electrode.

Chloride ions are obviously being oxidized to Cl_2 in this cell, as they were in the electrolysis of molten NaCl. But Na^+ ions are not reduced to metallic Na. Instead, gaseous H_2 and aqueous OH^- ions are produced by reduction of H_2O molecules at the cathode. Water is more easily reduced than Na^+ ions. This is primarily because the reduction of Na^+ would produce the very active metal Na, whereas the reduction of H_2O produces the more stable products $H_2(g)$ and $OH^-(aq)$. The active metals Li, K, Ca, and Na (Table 4-12) displace H_2 from aqueous solutions, so we do not expect these metals to be produced in aqueous solution. Later in this chapter (Section 21-14) we learn the quantitative basis



The electrolysis of the aqueous solution of KI, another Group IA–Group VIIA salt. At the cathode (*left*), water is reduced to $H_2(g)$ and OH^- ions, turning the phenolphthalein indicator pink. The characteristic brownish color of aqueous I_2 appears at the anode (*right*).

for predicting which of several possible oxidations or reductions is favored. The half-reactions and overall cell reaction for this electrolysis are

$$\begin{array}{rcll}
2Cl^- & \longrightarrow & Cl_2 + 2e^- & \text{(oxidation, anode)} \\
2H_2O + 2e^- & \longrightarrow & 2OH^- + H_2 & \text{(reduction, cathode)} \\ \hline
2H_2O + 2Cl^- & \longrightarrow & 2OH^- + H_2 + Cl_2 & \text{(overall cell reaction as net ionic equation)} \\
\underbrace{+\ 2Na^+} & \longrightarrow & \underbrace{+\ 2Na^+} & \text{(spectator ions)} \\
2H_2O +\ 2NaCl & \longrightarrow & 2NaOH\ + H_2 + Cl_2 & \text{(overall cell reaction as formula unit equation)}
\end{array}$$

We will omit the notation that indicates states of substances—(s), (ℓ), (g), and (aq)—except where states are not obvious. This abbreviates writing equations.

The cell is illustrated in Figure 21-3. As before, the electrons flow from the anode (+) through the wire to the cathode (−).

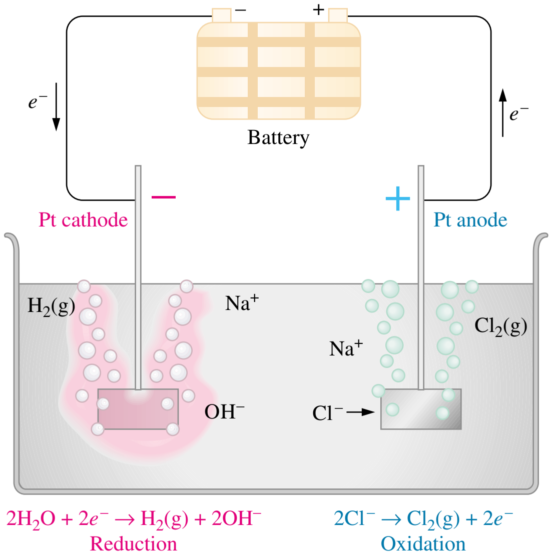


Figure 21-3 Electrolysis of aqueous NaCl solution. Although several reactions occur at both the anode and the cathode, the net result is the production of $H_2(g)$ and NaOH at the cathode and $Cl_2(g)$ at the anode. A few drops of phenolphthalein indicator were added to the solution. The solution turns pink at the cathode, where OH^- ions are formed.

Not surprisingly, the fluctuations in commercial prices of these widely used industrial products—H_2, Cl_2, and NaOH—have often paralleled one another.

The overall cell reaction produces gaseous H_2 and Cl_2 and an aqueous solution of NaOH, called caustic soda. Solid NaOH is then obtained by evaporation of the residual solution. This is the most important commercial preparation of each of these substances. It is much less expensive than the electrolysis of molten NaCl, because it is not necessary to heat the solution.

21-5 THE ELECTROLYSIS OF AQUEOUS SODIUM SULFATE

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 21.10, Electrolysis.

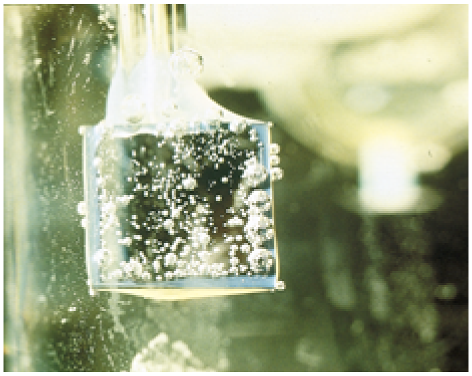
In the electrolysis of aqueous sodium sulfate using inert electrodes, we observe the following.

1. Gaseous H_2 is produced at one electrode. The solution becomes basic around that electrode.
2. Gaseous O_2 is produced at the other electrode. The solution becomes acidic around that electrode.

As in the previous example, water is reduced in preference to Na^+ at the cathode. Observation 2 suggests that water is also preferentially oxidized relative to the sulfate ion, SO_4^{2-}, at the anode (Figure 21-4).

$$\begin{array}{rcll} 2(2H_2O + 2e^- & \longrightarrow & H_2 + 2OH^-) & \text{(reduction, cathode)} \\ 2H_2O & \longrightarrow & O_2 + 4H^+ + 4e^- & \text{(oxidation, anode)} \\ \hline 6H_2O & \longrightarrow & 2H_2 + O_2 + \underbrace{4H^+ + 4OH^-}_{4H_2O} & \text{(overall cell reaction)} \\ 2H_2O & \longrightarrow & 2H_2 + O_2 & \text{(net reaction)} \end{array}$$

The net result is the electrolysis of water. This occurs because H_2O is more readily reduced than Na^+ and more readily oxidized than SO_4^{2-}. The ions of Na_2SO_4 conduct the current through the solution, but they take no part in the reaction.



Gaseous H_2 is produced from H_2O at an illuminated photoelectrode. Light from the sun may soon be used to produce hydrogen, the ultimate clean-burning fuel.

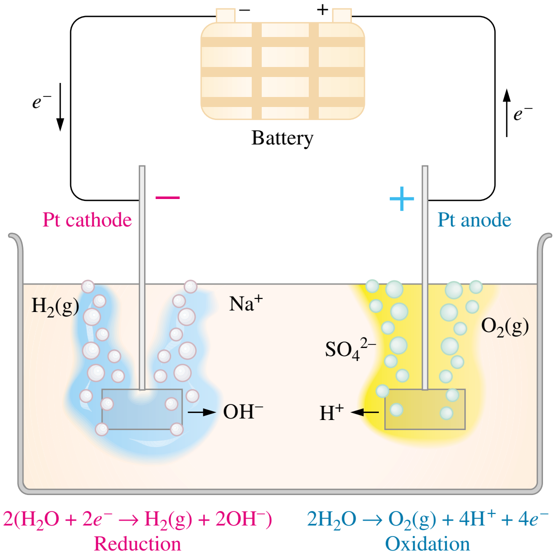


Figure 21-4 The electrolysis of aqueous Na_2SO_4 produces $H_2(g)$ at the cathode and O_2 at the anode. Bromthymol blue indicator has been added to the solution. This indicator turns blue in the basic solution near the cathode (where OH^- is produced) and yellow in the acidic solution near the anode (where H^+ is formed).

TABLE 21-1 *Amounts of Elements Produced at One Electrode in Electrolysis by 1 Faraday of Electricity*

Half-Reaction	Number of e^- in Half-Reaction	Product (electrode)	Amount Produced
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	1	Ag (cathode)	1 mol = 107.868 g
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	2	H_2 (cathode)	$\frac{1}{2}$ mol = 1.008 g
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	2	Cu (cathode)	$\frac{1}{2}$ mol = 31.773 g
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	3	Au (cathode)	$\frac{1}{3}$ mol = 65.656 g
$2Cl^- \longrightarrow Cl_2(g) + 2e^-$	2	Cl_2 (anode)	$\frac{1}{2}$ mol = 35.453 g = 11.2 L_{STP}
$2H_2O(\ell) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$	4	O_2 (anode)	$\frac{1}{4}$ mol = 8.000 g = 5.60 L_{STP}

21-6 FARADAY'S LAW OF ELECTROLYSIS

In 1832–1833, Michael Faraday's studies of electrolysis led to this conclusion.

> The amount of substance that undergoes oxidation or reduction at each electrode during electrolysis is directly proportional to the amount of electricity that passes through the cell.

This is **Faraday's Law of Electrolysis.** A quantitative unit of electricity is now called the faraday.

> One **faraday** is the amount of electricity that corresponds to the gain or loss, and therefore the passage, of 6.022×10^{23} electrons, or *one mole* of electrons.

A smaller electrical unit commonly used in chemistry, physics, and electronics is the **coulomb (C).** One coulomb is defined as the amount of charge that passes a given point when 1 ampere (A) of electric current flows for 1 second. One ampere of current equals 1 coulomb per second. One faraday is equal to 96,485 coulombs of charge.

$$1 \text{ ampere} = 1 \frac{\text{coulomb}}{\text{second}} \qquad \text{or} \qquad 1 \text{ A} = 1 \text{ C/s}$$

For comparison, a 100-watt household light bulb uses a current of about 0.8 ampere.

$$1 \text{ faraday} = 6.022 \times 10^{23}\ e^- = 96{,}485 \text{ C}$$

Table 21-1 shows the amounts of several elements produced during electrolysis by the passage of 1 faraday of electricity.

Michael Faraday (1791–1867) is considered the greatest experimental scientist of the nineteenth century. As a bookbinder's apprentice, he educated himself by extensive reading. Intrigued by his self-study of chemistry and by a lecture given by Sir Humphry Davy, the leading chemist of the day, Faraday applied for a position with Davy at the Royal Institution. He subsequently became director of that laboratory. His public lectures on science were very popular.

The amount of electricity in Examples 21-1 and 21-2 would be sufficient to light a 100-watt household light bulb for about 150 minutes, or 2.5 hours.

EXAMPLE 21-1 *Electrolysis*

Calculate the mass of copper metal produced during the passage of 2.50 amperes of current through a solution of copper(II) sulfate for 50.0 minutes.

Plan

The half-reaction that describes the reduction of copper(II) ions tells us the number of moles of electrons required to produce one mole of copper metal. Each mole of electrons corresponds to 1 faraday, or 9.65×10^4 coulombs, of charge. The product of current and time gives the number of coulombs.

When the number of significant figures in the calculation warrants, the value 96,485 coulombs is usually rounded to 96,500 coulombs (9.65×10^4 C).

current × time ⟶ no. of coulombs ⟶ mol of e^- passed ⟶ mass of Cu

Solution

The equation for the reduction of copper(II) ions to copper metal is

$$\begin{array}{cccc} Cu^{2+} + & 2e^- & \longrightarrow & Cu \\ 1\ \text{mol} & 2(6.02 \times 10^{23})e^- & & 1\ \text{mol} \\ 63.5\ \text{g} & 2(9.65 \times 10^4\ \text{C}) & & 63.5\ \text{g} \end{array}$$

(reduction, cathode)

We see that 63.5 grams of copper "plate out" for every 2 moles of electrons, or for every $2(9.65 \times 10^4$ coulombs) of charge. We first calculate the number of coulombs passing through the cell.

2.50 A = 2.50 C/s

$$\underline{?}\ \text{C} = 50.0\ \text{min} \times \frac{60\ \text{s}}{1\ \text{min}} \times \frac{2.50\ \text{C}}{\text{s}} = 7.50 \times 10^3\ \text{C}$$

We calculate the mass of copper produced by the passage of 7.50×10^3 coulombs.

$$\underline{?}\ \text{g Cu} = 7.50 \times 10^3\ \text{C} \times \frac{1\ \text{mol}\ e^-}{9.65 \times 10^4\ \text{C}} \times \frac{63.5\ \text{g Cu}}{2\ \text{mol}\ e^-} = \boxed{2.47\ \text{g Cu}}$$

(about the mass of a copper penny)

Notice how little copper is deposited by this considerable current in 50 minutes.

You should now work Exercises 26 and 32.

EXAMPLE 21-2 *Electrolysis*

What volume of oxygen gas (measured at STP) is produced by the oxidation of water in the electrolysis of copper(II) sulfate in Example 21-1?

Plan

We use the same approach as in Example 21-1. Here we relate the amount of charge passed to the number of moles, and hence the volume of O_2 gas produced at STP.

current × time ⟶ no. of coulombs ⟶ mol of e^- passed ⟶ L_{STP} of O_2

Solution

The equation for the oxidation of water and the equivalence between the number of coulombs and the volume of oxygen produced at STP are

$$\begin{array}{ccccc} 2H_2O & \longrightarrow & O_2 & + 4H^+ + & 4e^- \\ & & 1\ \text{mol} & & 4(6.02 \times 10^{23})e^- \\ & & 22.4\ L_{STP} & & 4(9.65 \times 10^4\ \text{C}) \end{array}$$

(oxidation, anode)

The number of coulombs passing through the cell is 7.50×10^3 C. For every $4(9.65 \times 10^4$ coulombs) passing through the cell, 22.4 L of O_2 at STP is produced.

$$\underline{?}\ L_{STP}\ O_2 = 7.50 \times 10^3\ C \times \frac{1\ \text{mol}\ e^-}{9.65 \times 10^4\ C} \times \frac{22.4\ L_{STP}\ O_2}{4\ \text{mol}\ e^-} = 0.435\ L_{STP}\ O_2$$

You should now work Exercise 28.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 21.11, Coulometry.

Notice how little product is formed by what seems to be a lot of electricity. This suggests why electrolytic production of gases and metals is so costly.

21-7 COMMERCIAL APPLICATIONS OF ELECTROLYTIC CELLS

Several elements are produced commercially by electrolysis. In Sections 21-3 to 21-5, we described some electrolytic cells that produce sodium (the Downs cell), chlorine, hydrogen, and oxygen. Electrolysis of molten compounds is also the common method of obtaining other Group IA metals, IIA metals (except barium), and aluminum (Section 22-3). Impure metals can also be refined electrolytically, as we will describe for copper in Section 22-8.

Metal-plated articles are common in our society. Jewelry and tableware are often plated with silver. Gold is plated onto jewelry and electrical contacts. Copper is plated onto many objects for decorative purposes (Figure 21-5). Some automobiles have steel bumpers plated

A family memento that has been electroplated with copper. To aid in electroplating onto nonconductors, such as shoes, the material is first soaked in a concentrated electrolyte solution to make it conductive.

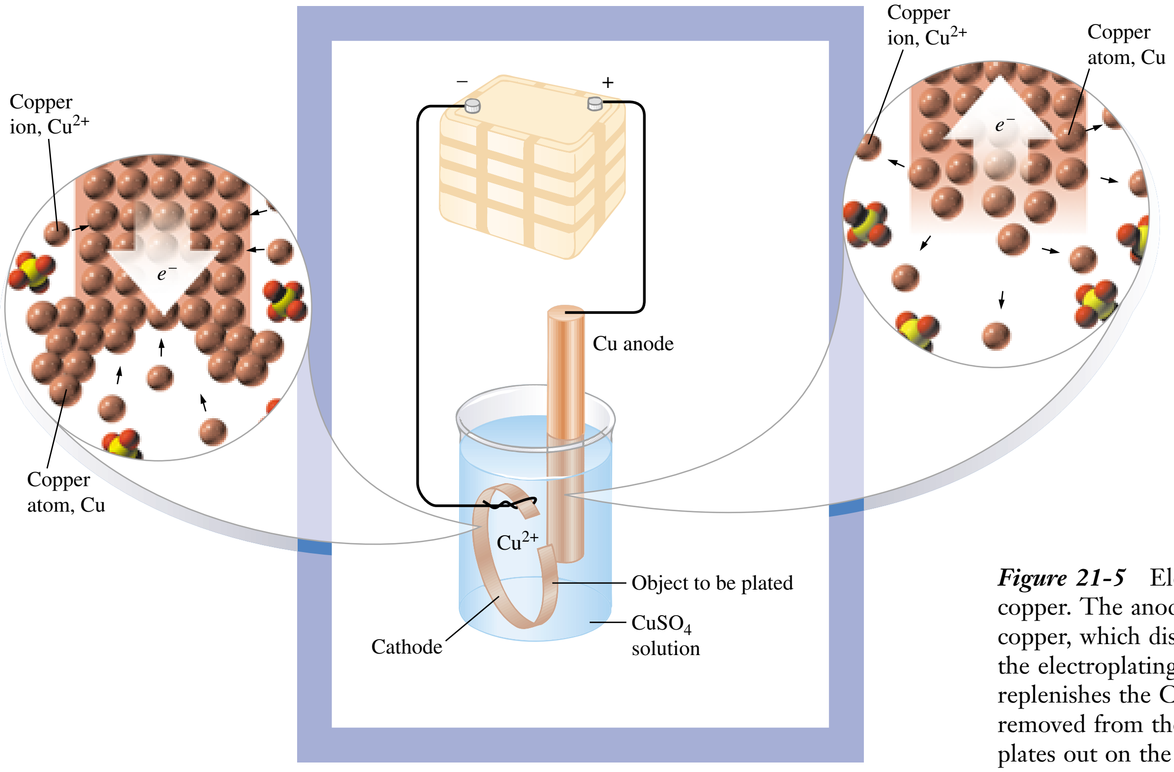


Figure 21-5 Electroplating with copper. The anode is made of pure copper, which dissolves during the electroplating process. This replenishes the Cu^{2+} ions that are removed from the solution as Cu plates out on the cathode.

with thin films of chromium. A chrome bumper requires approximately 3 seconds of electroplating to produce a smooth, shiny surface only 0.0002 mm thick. When the metal atoms are deposited too rapidly, they are not able to form extended lattices. Rapid plating of metal results in rough, grainy, black surfaces. Slower plating produces smooth surfaces. "Tin cans" are steel cans plated electrolytically with tin; these are sometimes replaced by cans plated in $\frac{1}{3}$ second with an extremely thin chromium film.

VOLTAIC OR GALVANIC CELLS

These are named for Allesandro Volta (1745–1827) and Luigi Galvani (1737–1798), two Italian physicists of the eighteenth century.

Voltaic, or **galvanic, cells** are electrochemical cells in which *spontaneous* oxidation–reduction reactions produce electrical energy. The two halves of the redox reaction are separated, requiring electron transfer to occur through an external circuit. In this way, useful electrical energy is obtained. Everyone is familiar with some voltaic cells. The batteries commonly used in flashlights, portable radios, photographic equipment, and many toys and appliances are voltaic cells. Automobile batteries consist of voltaic cells connected in series so that their voltages add. We will first consider some simple laboratory cells used to measure the potential difference, or voltage, of a reaction under study. We will then look at some common voltaic cells.

21-8 THE CONSTRUCTION OF SIMPLE VOLTAIC CELLS

Neither of these meters generates electrical energy.

A **half-cell** contains the oxidized and reduced forms of an element, or other more complex species, in contact with one another. A common kind of half-cell consists of a piece of metal (the electrode) immersed in a solution of its ions. Consider two such half-cells in separate beakers (Figure 21-6). The electrodes are connected by a wire. A voltmeter can be inserted into the circuit to measure the potential difference between the two electrodes, or an ammeter can be inserted to measure the current flow. The electric current is the result of the spontaneous redox reaction that occurs. We measure the potential of the cell.

Agar is a gelatinous material obtained from algae.

The circuit between the two solutions is completed by a **salt bridge.** This can be any medium through which ions can slowly pass. A salt bridge can be made by bending a piece of glass tubing into the shape of a "U," filling it with a hot saturated salt/5% agar solution, and allowing it to cool. The cooled mixture "sets" to the consistency of firm gelatin. As a result, the solution does not run out when the tube is inverted (see Figure 21-6), but the ions in the gel are still able to move. A salt bridge serves three functions.

1. It allows electrical contact between the two solutions.
2. It prevents mixing of the electrode solutions.
3. It maintains the electrical neutrality in each half-cell as ions flow into and out of the salt bridge.

When we show a concentration in a *standard cell* as 1 *M*, it is assumed to be *exactly* 1 *M*.

A cell in which all reactants and products are in their thermodynamic standard states (1 *M* for dissolved species and 1 atm partial pressure for gases) is called a **standard cell.**

21-9 THE ZINC–COPPER CELL

Consider a standard cell made up of two half-cells, one a strip of metallic Cu immersed in 1 *M* copper(II) sulfate solution and the other a strip of Zn immersed in 1 *M* zinc sulfate solution (see Figure 21-6). This cell is called the Daniell cell. The following experimental observations have been made about this cell.

1. The initial voltage is 1.100 volts.
2. The mass of the zinc electrode decreases. The concentration of Zn^{2+} increases in the solution around the zinc electrode as the cell operates.
3. The mass of the copper electrode increases. The concentration of Cu^{2+} decreases in the solution around this electrode as the cell operates.

The Zn electrode loses mass because some Zn metal is *oxidized* to Zn^{2+} ions, which go into solution. Thus the Zn electrode is the *anode*. At the *cathode*, Cu^{2+} ions are *reduced* to Cu metal. This plates out on the electrode, so its mass increases.

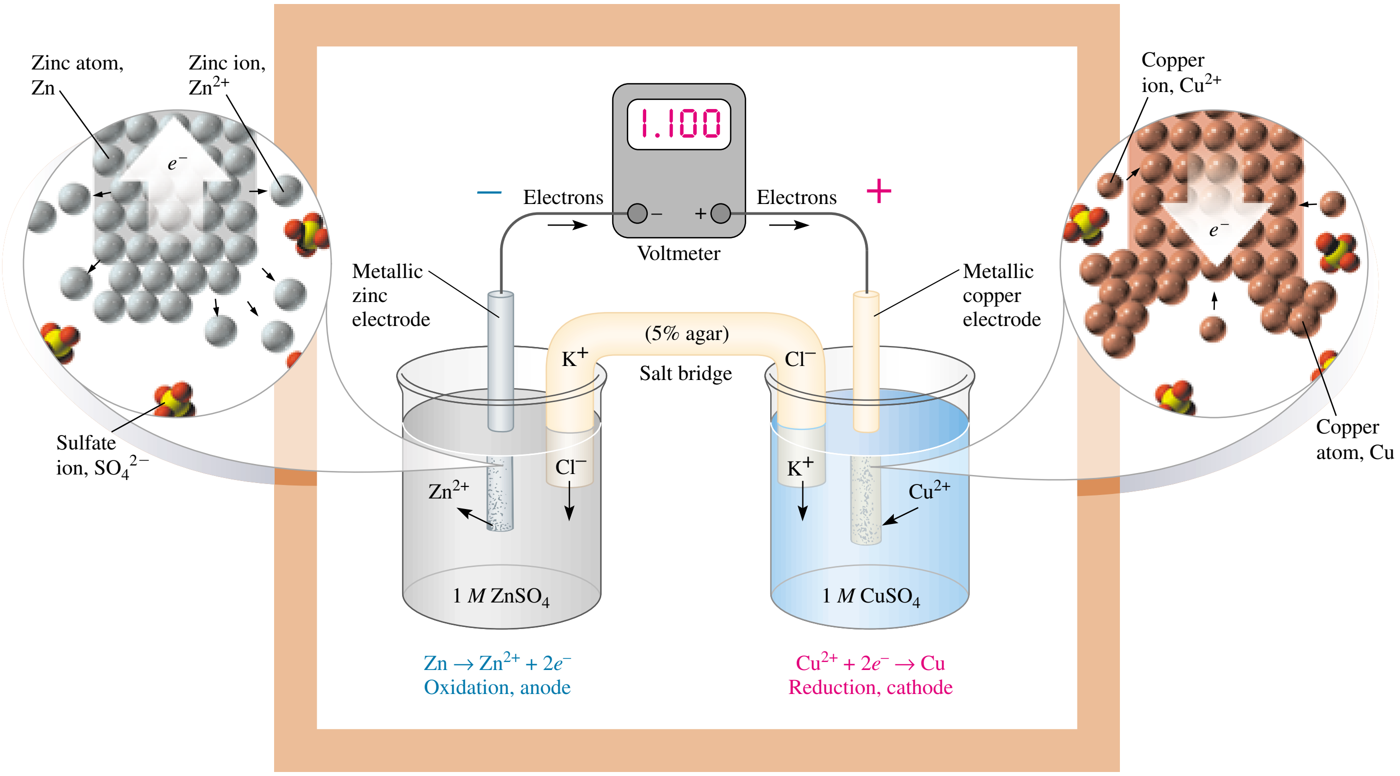


Figure 21-6 The zinc–copper voltaic cell utilizes the reaction

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

The standard potential of this cell is 1.10 volts. The standard cell can be represented as $Zn|Zn^{2+}(1\ M)||Cu^{2+}(1\ M)|Cu$.

$$\begin{array}{rcll} \mathrm{Zn} & \longrightarrow & \mathrm{Zn^{2+}} + 2e^- & \text{(oxidation, anode)} \\ \mathrm{Cu^{2+}} + 2e^- & \longrightarrow & \mathrm{Cu} & \text{(reduction, cathode)} \\ \hline \mathrm{Cu^{2+}} + \mathrm{Zn} & \longrightarrow & \mathrm{Cu} + \mathrm{Zn^{2+}} & \text{(overall cell reaction)} \end{array}$$

Compare the −/+, anode–cathode, and oxidation–reduction labels and the directions of electron flow in Figures 21-2a and 21-6.

Electrons are released at the anode and consumed at the cathode. They therefore flow through the wire from anode to cathode, as in all electrochemical cells. In all *voltaic* cells the electrons flow spontaneously from the negative electrode to the positive electrode. So, in contrast with electrolytic cells, the anode is negative and the cathode is positive. To maintain electroneutrality and complete the circuit, two Cl^- ions from the salt bridge migrate into the anode solution for every Zn^{2+} ion formed. Two K^+ ions migrate into

CHEMISTRY IN USE *Our Daily Lives*

A Spectacular View of One Mole of Electrons

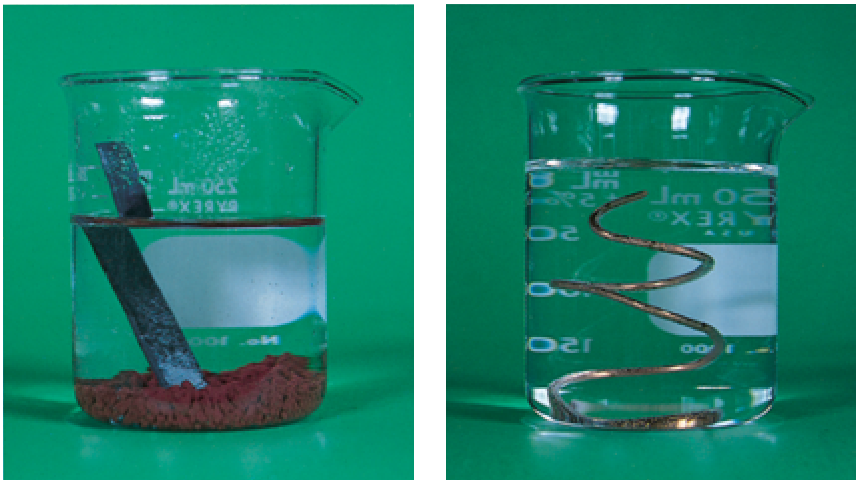
Early in our study of chemistry, we saw that atoms are made up of protons, neutrons, and electrons. We also discussed the incredibly large size of Avogadro's number, 6.022×10^{23}. Although individual atoms and molecules are invisible to the naked eye, one mole of atoms or molecules is easily detected. Because subatomic particles are even smaller than atoms and also invisible, you might never expect to see individual electrons. Let's consider the possibility, however, of seeing a faraday of charge. A faraday of charge contains Avogadro's number of electrons. Would this collection of 6.022×10^{23} electrons be visible? If so, what might it look like? It would look quite spectacular!

Throughout the 1980s, scientists carefully studied data collected during 5 million lightning flashes along the eastern United States. The data were collected by 36 instruments that were collectively known as the National Lightning Detection Network. The investigating scientists found that the electrical currents in lightning flashes over northern Florida measured about 45,000 amps, about double the 25,000-amp currents in lightning flashes over the New England states. This study showed that the amount of current flowing during lightning flashes was inversely proportional to the latitude (distance from the equator) of the storm.

One coulomb is the amount of charge that passes a point when a one-ampere current flows for one second (1 coulomb = 1 ampere·second). Thus, a current of 96,500 amps flowing for one second contains Avogadro's number of electrons, or one faraday of charge.

Measurements taken in northern Florida show that a typical two-second lightning strike over that section of the country would transfer approximately Avogadro's number of electrons between the clouds and the earth. So, for those living in northern Florida, a spectacular mental view of one mole of electrons can be obtained by visualizing a two-second lightning strike. Keep in mind that the average lightning strike lasts only a small fraction of a second, and that we can only have a mental view of a two-second lightning strike by extrapolation of what is seen in nature. Because New England lightning strikes produce only about half the current of lightning strikes over northern Florida, people in New England must try to imagine a four-second lightning strike.

Ronald DeLorenzo
Middle Georgia College



(*Left*) A strip of zinc was placed in a blue solution of copper(II) sulfate, $CuSO_4$. The copper has been displaced from solution and has fallen to the bottom of the beaker. The resulting zinc sulfate solution is colorless. This is the same overall reaction as the one that occurs when the two half-reactions are separated in the zinc–copper cell (see Figure 21-6). (*Right*) No reaction occurs when copper wire is placed in a colorless zinc sulfate solution. The reaction

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

is the *reverse* of the spontaneous reaction in Figure 21-6; it has a *negative* E^0_{cell} and is *nonspontaneous.*

the cathode solution to replace every Cu^{2+} ion reduced. Some Zn^{2+} ions from the anode vessel and some $SO_4{}^{2-}$ ions from the cathode vessel also migrate into the salt bridge. Neither Cl^- nor K^+ ions are oxidized or reduced in preference to the zinc metal or Cu^{2+} ions.

As the reaction proceeds, the cell voltage decreases. When the cell voltage reaches zero, the reaction has reached equilibrium, and no further net reaction occurs. At this point, however, the metal ion concentrations in the cell are *not* zero. This description applies to any voltaic cell.

Voltaic cells can be represented as follows for the zinc–copper cell.

$$\mathrm{Zn}|\underset{\nwarrow}{\mathrm{Zn}^{2+}}(1\ M)\overset{\substack{\text{salt bridge}\\ \downarrow}}{\|}\mathrm{Cu}^{2+}\ (1\ M)\underset{\nearrow}{|}\mathrm{Cu}$$

species (and concentrations)
in contact with electrode surfaces

In this representation, a single line (|) represents an interface at which a potential develops, that is, an electrode. It is conventional to write the anode half-cell on the left in this notation.

The same reaction occurs when a piece of Zn is dropped into a solution of $CuSO_4$. The Zn dissolves and the blue color of Cu^{2+} ions disappears. Copper forms on the Zn and then settles to the bottom of the container. But no electricity flows in an external circuit, because the two half-reactions are *not* physically separated.

✓ Problem-Solving Tip: *How to Tell the Anode from the Cathode*

The correspondence between the names *anode* and *cathode* and the charge on the electrode is *different* for electrolytic cells than for voltaic (galvanic) cells. Students sometimes get confused by trying to remember which is which. Check the definitions of these two terms in Section 21-2. The surest way to name these electrodes is to determine what process takes place at each one.

$$\text{anode} \Longleftrightarrow \text{oxidation} \qquad \text{and} \qquad \text{cathode} \Longleftrightarrow \text{reduction}$$

As a memory aid, both anode and oxidation begin with a vowel, whereas both cathode and reduction begin with a consonant.

21-10 THE COPPER–SILVER CELL

Now consider a similar standard voltaic cell consisting of a strip of Cu immersed in 1 *M* $CuSO_4$ solution and a strip of Ag immersed in 1 *M* $AgNO_3$ solution. A wire and a salt bridge complete the circuit. The following observations have been made.

1. The initial voltage of the cell is 0.462 volt.
2. The mass of the copper electrode decreases. The Cu^{2+} ion concentration increases in the solution around the copper electrode.
3. The mass of the silver electrode increases. The Ag^+ ion concentration decreases in the solution around the silver electrode.

In this cell the Cu electrode is the anode because Cu metal is oxidized to Cu^{2+} ions. The Ag electrode is the cathode because Ag^+ ions are reduced to metallic Ag (Figure 21-7).

$$\begin{array}{rcll} \text{Cu} & \longrightarrow & \text{Cu}^{2+} + 2e^- & \text{(oxidation, anode)} \\ 2(\text{Ag}^+ + e^- & \longrightarrow & \text{Ag}) & \text{(reduction, cathode)} \\ \hline \text{Cu} + 2\text{Ag}^+ & \longrightarrow & \text{Cu}^{2+} + 2\text{Ag} & \text{(overall cell reaction)} \end{array}$$

As before, ions from the salt bridge migrate to maintain electroneutrality. Some NO_3^- ions (from the cathode vessel) and some Cu^{2+} ions (from the anode vessel) also migrate into the salt bridge.

Recall that in the zinc–copper cell the copper electrode is the *cathode;* now in the copper–silver cell the copper electrode is the *anode.*

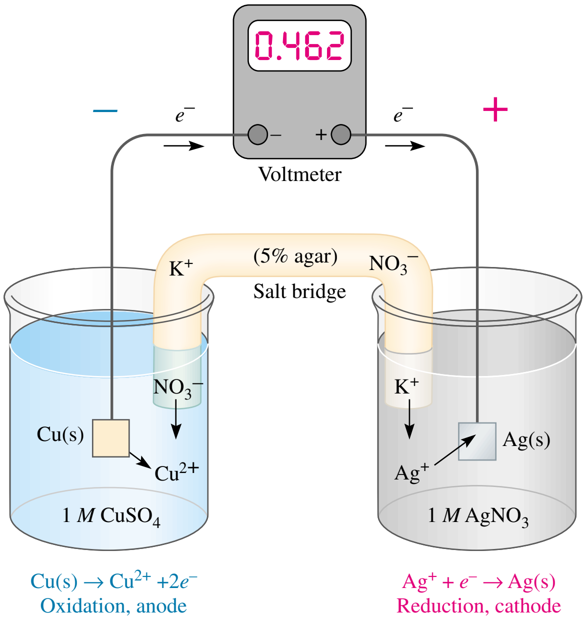


Figure 21-7 The copper–silver voltaic cell utilizes the reaction

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

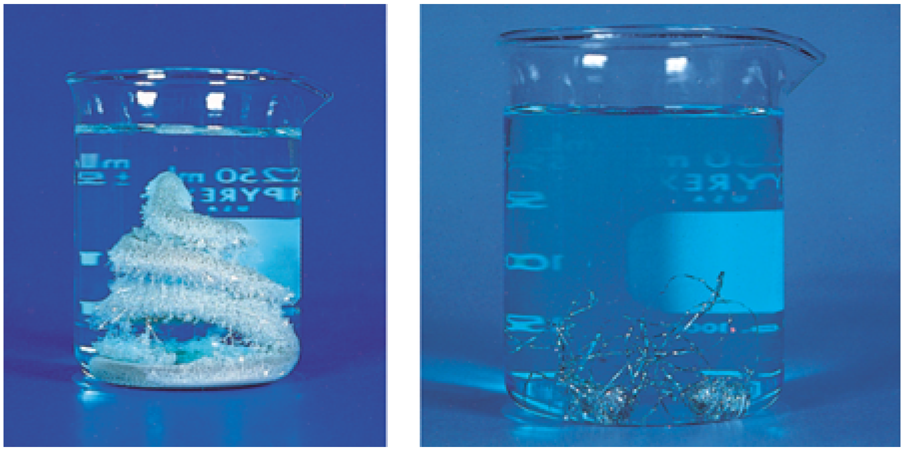
The standard potential of this cell is 0.462 volt. This standard cell can be represented as $\text{Cu}|\text{Cu}^{2+}(1\ M)||\text{Ag}^+(1\ M)|\text{Ag}$.

The standard $Cu|Cu^{2+}(1\ M)||Ag^+\ (1\ M)|Ag$ cell.

> Whether a particular electrode acts as an anode or a cathode in a voltaic cell depends on what the other electrode of the cell is.

The two cells we have described show that the Cu^{2+} ion is more easily reduced (is a stronger oxidizing agent) than Zn^{2+}, so Cu^{2+} oxidizes metallic zinc to Zn^{2+}. By contrast, Ag^+ ion is more easily reduced (is a stronger oxidizing agent) than Cu^{2+} ion, so Ag^+ oxidizes Cu atoms to Cu^{2+}. Conversely, metallic Zn is a stronger reducing agent than metallic Cu, and metallic Cu is a stronger reducing agent than metallic Ag. We can now arrange the species we have studied in order of increasing strength as oxidizing agents and as reducing agents.

$$\underset{\text{Increasing strength as oxidizing agents}}{\xrightarrow{Zn^{2+} < Cu^{2+} < Ag^+}} \qquad \underset{\text{Increasing strength as reducing agents}}{\xrightarrow{Ag < Cu < Zn}}$$



(*Left*) A spiral of copper wire was placed in a colorless solution of silver nitrate, $AgNO_3$. The silver has been displaced from solution and adheres to the wire. The resulting copper nitrate solution is blue. The same reaction occurs when the two half-reactions are separated in the copper–silver cell (see Figure 21-7). (*Right*) No reaction occurs when silver wire is placed in a blue copper sulfate solution. The reaction

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

is the *reverse* of the spontaneous reaction in Figure 21-7; it has a *negative* E^0_{cell} and is *nonspontaneous*.

STANDARD ELECTRODE POTENTIALS

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 21.5, Electrochemical Cells and Potentials.

The potentials of the standard zinc–copper and copper–silver voltaic cells are 1.100 volts and 0.462 volts, respectively. The magnitude of a cell's potential measures the spontaneity of its redox reaction. *Higher (more positive) cell potentials indicate greater driving force for the reaction as written.* Under standard conditions, the oxidation of metallic Zn by Cu^{2+} ions has a greater tendency to go toward completion than does the oxidation of metallic Cu by Ag^+ ions. It is convenient to separate the total cell potential into the individual contributions of the two half-reactions. This lets us determine the relative tendencies of particular oxidation or reduction half-reactions to occur. Such information gives us a quantitative basis for specifying strengths of oxidizing and reducing agents. In the next several sections we shall see how this is done for standard half-cells.

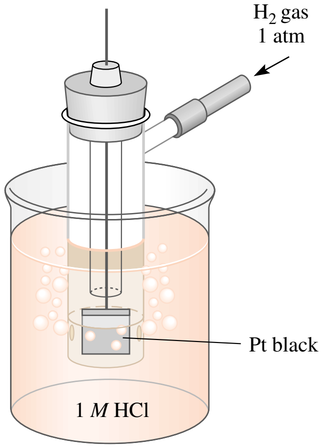


Figure 21-8 The standard hydrogen electrode (SHE). A molecular-level view of the operation of the SHE as a cathode is shown in Figure 21-9 and as an anode in Figure 21-10.

21-11 THE STANDARD HYDROGEN ELECTRODE

Every oxidation must be accompanied by a reduction (i.e., the electrons must have somewhere to go). So it is impossible to determine experimentally the potential of any *single* electrode. We therefore establish an arbitrary standard. The conventional reference electrode is the **standard hydrogen electrode (SHE).** This electrode contains a piece of metal electrolytically coated with a grainy black surface of inert platinum metal, immersed in a 1 M H^+ solution. Hydrogen, H_2, is bubbled at 1 atm pressure through a glass envelope over the platinized electrode (Figure 21-8).

> By international convention, the standard hydrogen electrode is arbitrarily assigned a potential of *exactly* 0.0000 . . . volt.

SHE Half-Reaction	E^0 (standard electrode potential)	
$H_2 \longrightarrow 2H^+ + 2e^-$	exactly 0.0000 . . . V	(SHE as anode)
$2H^+ + 2e^- \longrightarrow H_2$	exactly 0.0000 . . . V	(SHE as cathode)

The superscript in E^0 indicates thermodynamic standard-state conditions.

We then construct a standard cell consisting of a standard hydrogen electrode and some other standard electrode (half-cell). Because the defined electrode potential of the SHE contributes exactly 0 volt to the sum, the voltage of the overall cell then lets us determine the **standard electrode potential** of the other half-cell. This is its potential with respect to the standard hydrogen electrode, measured at 25°C when the concentration of each ion in the solution is 1 M and the pressure of any gas involved is 1 atm.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 21.6, Standard Potentials.

> By agreement, we always present the standard cell potential for each half-cell as a *reduction* process.

21-12 THE ZINC–SHE CELL

This cell consists of an SHE in one beaker and a strip of zinc immersed in 1 M zinc chloride solution in another beaker (Figure 21-9). A wire and a salt bridge complete the circuit. When the circuit is closed, the following observations can be made.

1. The initial potential of the cell is 0.763 volt.
2. As the cell operates, the mass of the zinc electrode decreases. The concentration of Zn^{2+} ions increases in the solution around the zinc electrode.
3. The H^+ concentration decreases in the SHE. Gaseous H_2 is produced.

We can conclude from these observations that the following half-reactions and cell reaction occur.

		E^0	
(oxidation, anode)	$Zn \longrightarrow Zn^{2+} + 2e^-$	0.763 V	
(reduction, cathode)	$2H^+ + 2e^- \longrightarrow H_2$	0.000 V	(by definition)
(cell reaction)	$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$	$E^0_{cell} = 0.763$ V	(measured)

The standard potential at the anode *plus* the standard potential at the cathode gives the standard cell potential. The potential of the SHE is 0.000 volt, and the standard cell potential is found to be 0.763 volt. So the standard potential of the zinc anode must be 0.763 volt. The $Zn|Zn^{2+}(1.0\ M)||H^+(1.0\ M), H_2(1\ atm)|Pt$ cell is depicted in Figure 21-9.

Note that in *this* cell the SHE is the *cathode*, and metallic zinc reduces H^+ to H_2. The zinc electrode is the *anode* in this cell.

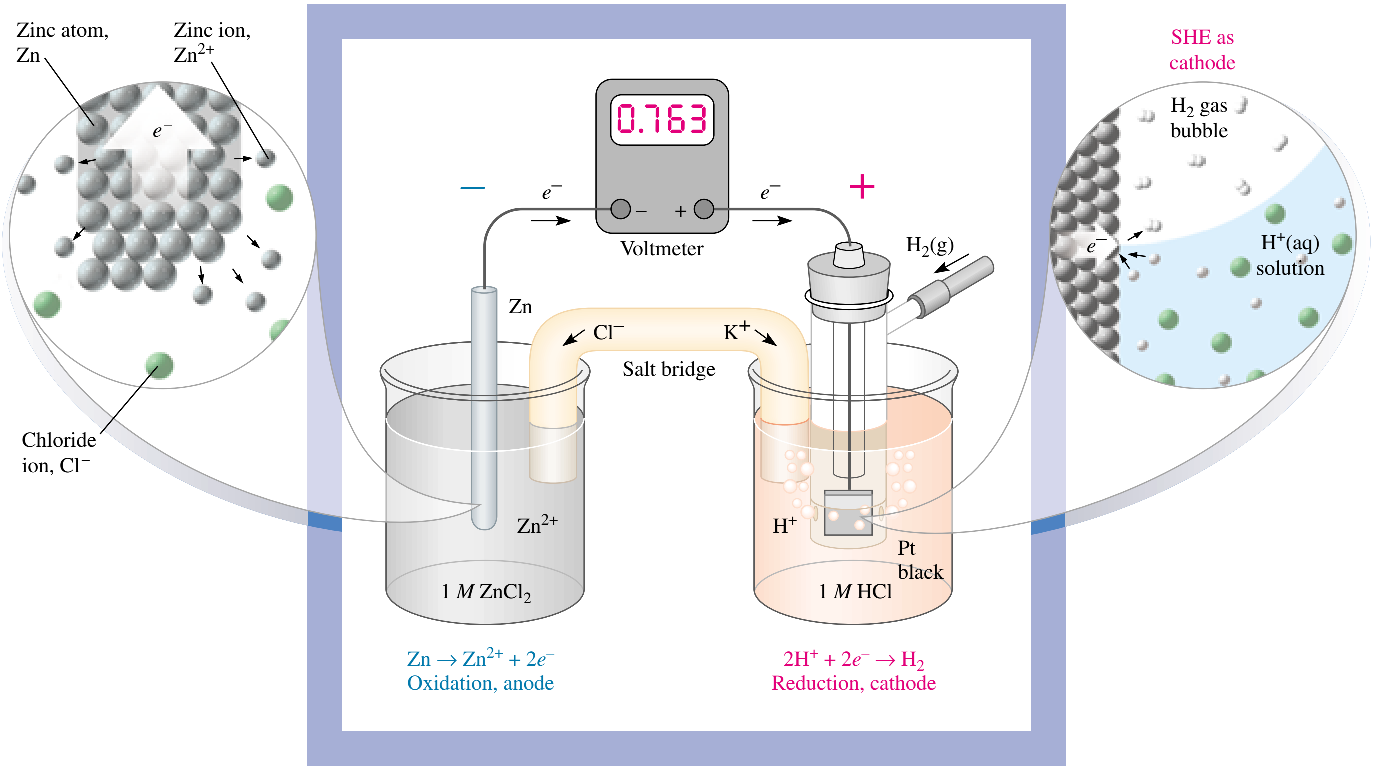


Figure 21-9 The $Zn|Zn^{2+}(1\ M)||H^+(1\ M); H_2(1\ atm)|Pt$ cell, in which the following net reaction occurs.

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

In this cell the standard hydrogen electrode functions as the cathode.

The idea of "electron pressure" helps to explain this process. The negative reduction potential for the half-reaction

$$\mathrm{Zn^{2+}} + 2e^- \longrightarrow \mathrm{Zn} \qquad E^0 = -0.763\ \mathrm{V}$$

says that this reaction is *less favorable* than the corresponding reduction to H_2,

$$2\mathrm{H^+} + 2e^- \longrightarrow \mathrm{H_2} \qquad E^0 = 0.000\ \mathrm{V}$$

What we have informally called "electron pressure" is the tendency to undergo oxidation. This is formally expressed as an *oxidation potential;* however, we usually tabulate reduction potentials (Table 21-2).

Before they are connected, each half-cell builds up a supply of electrons waiting to be released, thus generating an electron pressure. Let us compare these electron pressures by reversing the two half-reactions to show production of electrons (and changing the signs of their E^0 values).

$$\begin{aligned} \mathrm{Zn} &\longrightarrow \mathrm{Zn^{2+}} + 2e^- & E^0_{\text{oxidation}} &= +0.763\ \mathrm{V} \\ \mathrm{H_2} &\longrightarrow 2\mathrm{H^+} + 2e^- & E^0_{\text{oxidation}} &= 0.000\ \mathrm{V} \end{aligned}$$

The process with the more *positive* E^0 value is favored, so we reason that the electron pressure generated at the Zn electrode is greater than that at the H_2 electrode. As a result, when the cell is connected, the electrons released by the oxidation of Zn flow through the wire *from the Zn electrode to the H_2 electrode*, where they are consumed by the reduction of H^+ ions. Oxidation occurs at the zinc electrode (anode), and reduction occurs at the hydrogen electrode (cathode).

21-13 THE COPPER–SHE CELL

Another voltaic cell consists of an SHE in one beaker and a strip of Cu metal immersed in 1 *M* copper(II) sulfate solution in another beaker. A wire and a salt bridge complete the circuit. For this cell, we observe the following (Figure 21-10).

1. The initial cell potential is 0.337 volt.
2. Gaseous hydrogen is consumed. The H^+ concentration increases in the solution of the SHE.
3. The mass of the copper electrode increases. The concentration of Cu^{2+} ions decreases in the solution around the copper electrode.

Thus, the following half-reactions and cell reaction occur.

		E^0	
(oxidation, anode)	$\mathrm{H_2} \longrightarrow 2\mathrm{H^+} + 2e^-$	0.000 V	(by definition)
(reduction, cathode)	$\mathrm{Cu^{2+}} + 2e^- \longrightarrow \mathrm{Cu}$	0.337 V	
(cell reaction)	$\mathrm{H_2} + \mathrm{Cu^{2+}} \longrightarrow 2\mathrm{H^+} + \mathrm{Cu}$	$E^0_{\text{cell}} = 0.337\ \mathrm{V}$	(measured)

Recall that in the Zn–SHE cell the SHE was the *cathode.*

The SHE functions as the *anode* in this cell, and Cu^{2+} ions oxidize H_2 to H^+ ions. The standard electrode potential of the copper half-cell is 0.337 volt as a *cathode* in the Cu–SHE cell.

Again, we can think of $E^0_{\text{oxidation}}$ in the two half-cells as "electron pressures."

$$\begin{aligned} \mathrm{Cu} &\longrightarrow \mathrm{Cu^{2+}} + 2e^- & E^0_{\text{oxidation}} &= -0.337\ \mathrm{V} \\ \mathrm{H_2} &\longrightarrow 2\mathrm{H^+} + 2e^- & E^0_{\text{oxidation}} &= 0.000\ \mathrm{V} \end{aligned}$$

Now the hydrogen electrode has the higher electron pressure. When the cell is connected, electrons flow through the wire from the hydrogen electrode to the copper electrode. H_2 is oxidized to $2H^+$ (anode), and Cu^{2+} is reduced to Cu (cathode).

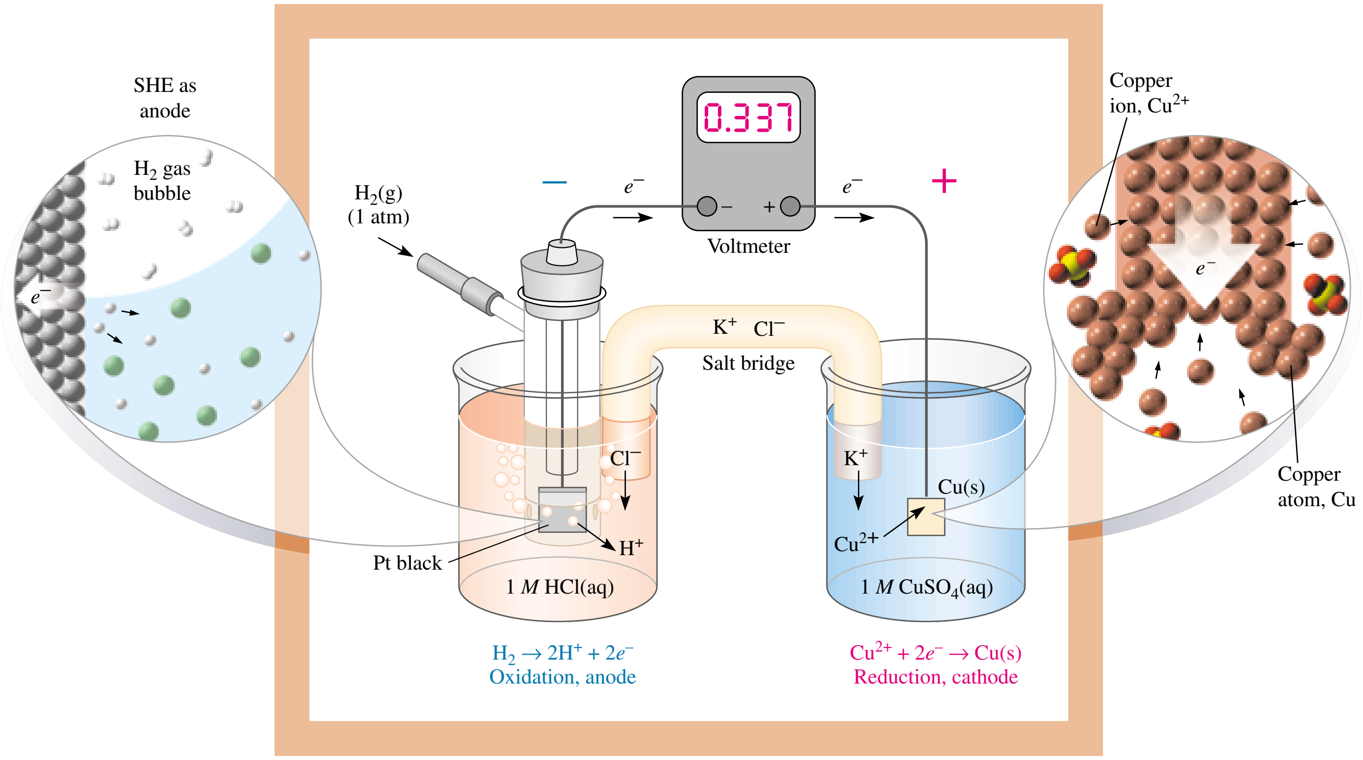


Figure 21-10 The standard copper–SHE cell,

$$\text{Pt}|\text{H}^+(1\ M);\ \text{H}_2(1\ \text{atm})||\text{Cu}^{2+}(1\ M)|\text{Cu}$$

In this cell, the standard hydrogen electrode functions as the anode. The net reaction is

$$\text{H}_2(\text{g}) + \text{Cu}^{2+}(\text{aq}) \longrightarrow 2\text{H}^+(\text{aq}) + \text{Cu(s)}$$

21-14 STANDARD ELECTRODE POTENTIALS

The activity series (Table 4-12) is based on standard electrode potentials.

We can develop a series of standard electrode potentials by measuring the potentials of other standard electrodes versus the SHE in the way we described for the standard Zn–SHE and standard Cu–SHE voltaic cells. Many electrodes involve metals or nonmetals in contact with their ions. We saw (Section 21-12) that the standard Zn electrode behaves as the anode versus the SHE and that the standard *oxidation* potential for the Zn half-cell is 0.763 volt.

		$E^0_{\text{oxidation}}$
(as anode)	$\text{Zn} \longrightarrow \text{Zn}^{2+} + 2e^-$	+0.763 V
	reduced form $\longrightarrow$ oxidized form + ne^-	(standard *oxidation* potential)

The *reduction* potential for the standard zinc electrode (to act as a *cathode* relative to the SHE) is therefore the negative of this, or −0.763 volt.

		$E^0_{\text{oxidation}}$
(as cathode)	$\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}$	−0.763 V
	oxidized form + ne^- $\longrightarrow$ reduced form	(standard *reduction* potential)

By international convention, the standard potentials of electrodes are tabulated for *reduction half-reactions.* These indicate the tendencies of the electrodes to behave as cathodes toward the SHE. Electrodes with positive E^0 values for reduction half-reactions act as *cathodes* versus the SHE. Those with negative E^0 values for reduction half-reactions act as anodes versus the SHE.

Electrodes with *Positive* $E^0_{\text{reduction}}$	**Electrodes with *Negative* $E^0_{\text{reduction}}$**
Reduction occurs *more readily* than the reduction of $2H^+$ to H_2. Electrode acts as a *cathode* versus the SHE.	Reduction is *more difficult* than the reduction of $2H^+$ to H_2. Electrode acts as an *anode* versus the SHE.

The more positive the E^0 value for a half-reaction, the greater the tendency for the half-reaction to occur in the forward direction as written. Conversely, the more negative the E^0 value for a half-reaction, the greater the tendency for the half-reaction to occur in the reverse direction as written.

Table 21-2 lists standard reduction potentials for a few elements.

The *oxidizing agent* is *reduced.*

1. The species on the *left* side are all cations of metals, hydrogen ions, or elemental nonmetals. These are all *oxidizing agents* (*oxidized forms* of the elements). Their strengths as oxidizing agents increase from top to bottom, that is, as the $E^0_{\text{reduction}}$ values become more positive. Fluorine, F_2, is the strongest oxidizing agent, and Li^+ is a very weak oxidizing agent.

The *reducing agent* is *oxidized.*

2. The species on the *right* side are free metals, hydrogen, or anions of nonmetals. These are all *reducing agents* (*reduced forms* of the elements). Their strengths as reducing agents increase from bottom to top, that is, as the $E^0_{\text{reduction}}$ values become more negative. Metallic Li is a very strong reducing agent, and F^- is a very weak reducing agent.

The more positive the reduction potential, the stronger the species on the left is as an oxidizing agent and the weaker the species on the right is as a reducing agent.

21-15 USES OF STANDARD ELECTRODE POTENTIALS

The most important application of electrode potentials is the prediction of the spontaneity of redox reactions. Standard electrode potentials can be used to determine the spontaneity of redox reactions in general, whether or not the reactions can take place in electrochemical cells.

Suppose we ask the question: At standard conditions, will Cu^{2+} ions oxidize metallic Zn to Zn^{2+} ions, or will Zn^{2+} ions oxidize metallic copper to Cu^{2+}? One of the two possible reactions is spontaneous, and the reverse reaction is nonspontaneous. We must determine which one is spontaneous. We already know the answer to this question from experimental results (see Section 21-9), but let us demonstrate the procedure for predicting the spontaneous reaction.

TABLE 21-2 *Standard Aqueous Reduction Potentials in Aqueous Solution at 25°C*

Element	Reduction Half-Reaction	Standard Reduction Potential E^0, volts	
Li	$Li^+ + e^- \longrightarrow Li$	−3.045	
K	$K^+ + e^- \longrightarrow K$	−2.925	
Ca	$Ca^{2+} + 2e^- \longrightarrow Ca$	−2.87	
Na	$Na^+ + e^- \longrightarrow Na$	−2.714	
Mg	$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.37	
Al	$Al^{3+} + 3e^- \longrightarrow Al$	−1.66	
Zn	$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.763	
Cr	$Cr^{3+} + 3e^- \longrightarrow Cr$	−0.74	
Fe	$Fe^{2+} + 2e^- \longrightarrow Fe$	−0.44	
Cd	$Cd^{2+} + 2e^- \longrightarrow Cd$	−0.403	
Ni	$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.25	
Sn	$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.14	
Pb	$Pb^{2} + 2e^- \longrightarrow Pb$	−0.126	
H_2	$2H^+ + 2e^- \longrightarrow H_2$	0.000	(reference electrode)
Cu	$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.337	
I_2	$I_2 + 2e^- \longrightarrow 2I^-$	+0.535	
Hg	$Hg^{2+} + 2e^- \longrightarrow Hg$	+0.789	
Ag	$Ag^+ + e^- \longrightarrow Ag$	+0.799	
Br_2	$Br_2 + 2e^- \longrightarrow 2Br^-$	+1.08	
Cl_2	$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+1.360	
Au	$Au^{3+} + 3e^- \longrightarrow Au$	+1.50	
F_2	$F_2 + 2e^- \longrightarrow 2F^-$	+2.87	

Increasing strength as oxidizing agent; increasing ease of reduction

Increasing strength as reducing agent; increasing ease of oxidation

1. Choose the appropriate half-reactions from a table of standard reduction potentials.
2. Write the equation for the half-reaction with the more positive (or less negative) E^0 value *for reduction* first, along with its potential.
3. Then write the equation for the other half-reaction *as an oxidation* and write its *oxidation potential*; to do this, reverse the tabulated reduction half-reaction, and change the sign of E^0. (Reversing a half-reaction or a complete reaction also changes the sign of its potential.)
4. Balance the electron transfer. *We do not multiply the potentials by the numbers used to balance the electron transfer!* The reason is that each potential represents a *tendency* for a reaction process to occur relative to the SHE; this does not depend on *how many times* it occurs. An electric potential is an *intensive property*.
5. Add the reduction and oxidation half-reactions, and add the reduction and oxidation potentials. E^0_{cell} will be *positive* for the resulting overall cell reaction. This indicates that the reaction as written is *product-favored (spontaneous)*. A *negative* E^0_{cell} value would indicate that the reaction is *reactant-favored (nonspontaneous)*.

For the cell described here, the Cu^{2+}/Cu couple has the more positive reduction potential, so we keep it as the reduction half-reaction and reverse the other half-reaction. Following the steps outlined, we obtain the equation for the spontaneous reaction.

$$\begin{array}{rcll}
Cu^{2+} + 2e^- & \longrightarrow & Cu & +0.337\text{ V} \longleftarrow \text{reduction potential} \\
Zn & \longrightarrow & Zn^{2+} + 2e^- & +0.763\text{ V} \longleftarrow \text{oxidation potential} \\
\hline
Cu^{2+} + Zn & \longrightarrow & Cu + Zn^{2+} & E^0_{cell} = +1.100\text{ V}
\end{array}$$

The positive E^0_{cell} value tells us that the forward reaction is spontaneous at standard conditions. So we conclude that copper(II) ions oxidize metallic zinc to Zn^{2+} ions as they are reduced to metallic copper. (Section 21-9 shows that the potential of the standard zinc–copper voltaic cell is 1.100 volts. This is the spontaneous reaction that occurs.)

The reverse reaction has a negative E^0 and is nonspontaneous.

$$\text{nonspontaneous reaction:} \qquad Cu + Zn^{2+} \longrightarrow Cu^{2+} + Zn \qquad E^0_{cell} = -1.100\text{ volts}$$

To make it occur, we would have to supply electrical energy with a potential difference greater than 1.100 volts. That is, this nonspontaneous reaction would have to be carried out in an *electrolytic cell.*

EXAMPLE 21-3 *Predicting the Direction of Reactions*

At standard conditions, will chromium(III) ions, Cr^{3+}, oxidize metallic copper to copper(II) ions, Cu^{2+}, or will Cu^{2+} oxidize metallic chromium to Cr^{3+} ions? Write the cell reaction, and calculate E^0_{cell} for the spontaneous reaction.

Plan

We refer to the table of standard reduction potentials and choose the two appropriate half-reactions.

Solution

The copper half-reaction has the more positive reduction potential, so we write it first. Then we write the chromium half-reaction as an oxidation, balance the electron transfer, and add the two half-reactions and their potentials.

$$\begin{array}{rclll}
 & & & & \mathbf{E^0} \\
3(Cu^{2+} + 2e^- & \longrightarrow & Cu) & \text{(reduction)} & +0.337\text{ V} \\
2(Cr & \longrightarrow & Cr^{3+} + 3e^-) & \text{(oxidation)} & +0.74\text{ V} \\
\hline
2Cr + 3Cu^{2+} & \longrightarrow & 2Cr^{3+} + 3Cu & & E^0_{cell} = +1.08\text{ V}
\end{array}$$

Because E^0_{cell} is positive, we know that the reaction is product-favored (spontaneous).

Cu^{2+} ions spontaneously oxidize metallic Cr to Cr^{3+} ions and are reduced to metallic Cu.

You should now work Exercise 54a.

Problem-Solving Tip: *The Sign of E^0 Indicates Spontaneity*

For a reaction that is spontaneous at *standard conditions*, E^0 must be positive. A negative value of E^0_{cell} indicates that the reverse of the reaction written would be spontaneous at standard conditions.

21-16 STANDARD ELECTRODE POTENTIALS FOR OTHER HALF-REACTIONS

In some half-cells, the oxidized and reduced species are both in solution as ions in contact with inert electrodes. For example, the standard iron(III) ion/iron(II) ion half-cell contains 1 *M* concentrations of the two ions. It involves the following half-reaction.

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad E^0 = +0.771\ V$$

Platinum metal is often used as the inert electrode material. These two standard half-cells could be shown in shorthand notation as

$Pt/Fe^{3+}(1\ M), Fe^{2+}(1\ M)$ and $Pt/Cr_2O_7^{2-}(1\ M), Cr^{3+}(1\ M)$

The standard dichromate ($Cr_2O_7^{2-}$) ion/chromium(III) ion half-cell consists of a 1 *M* concentration of each of the two ions in contact with an inert electrode. The balanced half-reaction in acidic solution (1.0 *M* H^+) is

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \qquad E^0 = +1.33\ V$$

Standard reduction potentials for some other reactions are given in Table 21-3 and in Appendix J. These potentials can be used like those of Table 21-2.

TABLE 21-3 *Standard Reduction Potential for Selected Half-Cells*

Reduction Half-Reaction			Standard Reduction Potential E^0 (volts)
$Zn(OH)_4^{2-} + 2e^-$	$\longrightarrow$	$Zn + 4OH^-$	−1.22
$Fe(OH)_2 + 2e^-$	$\longrightarrow$	$Fe + 2OH^-$	−0.877
$2H_2O + 2e^-$	$\longrightarrow$	$H_2 + 2OH^-$	−0.828
$PbSO_4 + 2e^-$	$\longrightarrow$	$Pb + SO_4^{2-}$	−0.356
$NO_3^- + H_2O + 2e^-$	$\longrightarrow$	$NO_2^- + 2OH^-$	+0.01
$Sn^{4+} + 2e^-$	$\longrightarrow$	Sn^{2+}	+0.15
$AgCl + e^-$	$\longrightarrow$	$Ag + Cl^-$	+0.222
$Hg_2Cl_2 + 2e^-$	$\longrightarrow$	$2Hg + 2Cl^-$	+0.27
$O_2 + 2H_2O + 4e^-$	$\longrightarrow$	$4OH^-$	+0.40
$NiO_2 + 2H_2O + 2e^-$	$\longrightarrow$	$Ni(OH)_2 + 2OH^-$	+0.49
$H_3AsO_4 + 2H^+ + 2e^-$	$\longrightarrow$	$H_3AsO_3 + H_2O$	+0.58
$Fe^{3+} + e^-$	$\longrightarrow$	Fe^{2+}	+0.771
$ClO^- + H_2O + 2e^-$	$\longrightarrow$	$Cl^- + 2OH^-$	+0.89
$NO_3^- + 4H^+ + 3e^-$	$\longrightarrow$	$NO + 2H_2O$	+0.96
$O_2 + 4H^+ + 4e^-$	$\longrightarrow$	$2H_2O$	+1.229
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\longrightarrow$	$2Cr^{3+} + 7H_2O$	+1.33
$MnO_4^- + 8H^+ + 5e^-$	$\longrightarrow$	$Mn^{2+} + 4H_2O$	+1.507
$Cl_2 + 2e^-$	$\longrightarrow$	$2Cl^-$	+1.360
$PbO_2 + HSO_4^{2-} + 3H^+ + 2e^-$	$\longrightarrow$	$PbSO_4 + 2H_2O$	+1.685

Increasing strength as oxidizing agent; increasing ease of reduction ↓

Increasing strength as reducing agent; increasing ease of oxidation ↑

EXAMPLE 21-4 *Predicting the Direction of Reactions*

In an acidic solution at standard conditions, will tin(IV) ions, Sn^{4+}, oxidize gaseous nitrogen oxide, NO, to nitrate ions, NO_3^-, or will NO_3^- oxidize Sn^{2+} to Sn^{4+} ions? Write the cell reaction and calculate E^0_{cell} for the spontaneous reaction.

Plan

We refer to the table of standard reduction potentials (see Table 21-3) and choose the appropriate half-reactions.

Solution

The NO_3^-/NO reduction half-reaction has the more positive E^0 value, so we write it first and write the Sn^{4+}/Sn^{2+} half-reaction as an oxidation. We balance the electron transfer and add the two half-reactions to obtain the equation for the *spontaneous* reaction. Then we add the half-reaction potentials to obtain the overall cell potential.

$$\begin{array}{rcllr}
 & & & & E^0 \\
2(NO_3^- + 4H^+ + 3e^- & \longrightarrow & NO + 2H_2O) & \text{(reduction)} & +0.96\ \text{V} \\
3(Sn^{2+} & \longrightarrow & Sn^{4+} + 2e^-) & \text{(oxidation)} & -0.15\ \text{V} \\
\hline
2NO_3^- + 8H+ + 3Sn^{2+} & \longrightarrow & 2NO + 4H_2O + 3Sn^{4+} & & E^0_{cell} = +0.81\ \text{V}
\end{array}$$

Because E^0_{cell} is positive for this reaction,

nitrate ions spontaneously oxidize tin(II) ions to tin(IV) ions and are reduced to nitrogen oxide in acidic solution.

You should now work Exercises 55 and 56.

✓ Problem-Solving Tip: *A Common Error in E^0_{cell} Calculations*

Remember the italicized warning in step 4 of the procedure set out in Section 21-15. *We do not multiply the potentials by the numbers used to balance the electron transfer!* This is a very common error.

✓ Problem-Solving Tip: *Remember What We Mean by Standard Conditions*

When we say that a reaction takes place at *standard conditions*, we mean the following:

1. The temperature is the standard thermodynamic temperature, 25°C, unless stated otherwise.
2. All reactants and products are at *unit activity*. This means that:
   - **a.** Any solution species that takes part in the reaction is at a concentration of exactly 1 *M*;
   - **b.** Any gas that takes part in the reaction is at a pressure of exactly 1 atm;
   - **c.** Any other substance that takes part in the reaction is *pure*.

(When we say "takes part in the reaction" we mean either as a reactant or a product.) These are the same conditions that were described as *standard conditions* for thermodynamic purposes (Section 15-6). When one or more of these conditions is not satisfied, we must adjust our calculations for nonstandard conditions. We shall learn how to do this in Section 21-19.

Now that we know how to use standard reduction potentials, let us use them to explain the reaction that occurs in the electrolysis of aqueous NaCl. The first two electrolytic cells we considered involved *molten* NaCl and *aqueous* NaCl (see Sections 21-3 and 21-4). There was no doubt that in molten NaCl, metallic Na would be produced by reduction of Na^+, and gaseous Cl_2 would be produced by oxidation of Cl^-. But we found that in aqueous NaCl, H_2O, rather than Na^+, was reduced. This is consistent with the less negative reduction potential of H_2O, compared with Na^+.

$$\begin{array}{lr} & \boldsymbol{E^0} \\ \hline 2H_2O + 2e^- \longrightarrow H_2 + 2OH^- & -0.828\text{ V} \\ Na^+ + e^- \longrightarrow Na & -2.714\text{ V} \end{array}$$

The more easily reduced species, H_2O, is reduced.

Electrode potentials measure only the relative *thermodynamic* likelihood for various half-reactions. In practice kinetic factors can complicate matters. For instance, sometimes the electrode process is limited by the rate of diffusion of dissolved species to or from the electrode surface. At some cathodes, the rate of electron transfer from the electrode to a reactant is the rate-limiting step, and a higher voltage (called *overvoltage*) must be applied to accomplish the reduction. As a result of these factors, a half-reaction that is *thermodynamically* more favorable than some other process still might not occur at a significant rate. In the electrolysis of NaCl(aq), Cl^- is oxidized to Cl_2 gas (−1.360 V), instead of H_2O being oxidized to form O_2 gas (−1.229 V), because of the overvoltage of O_2 on Pt, the inert electrode.

21-17 CORROSION

Ordinary **corrosion** is the redox process by which metals are oxidized by oxygen, O_2, in the presence of moisture. There are other kinds, but this is the most common. The problem of corrosion and its prevention are of both theoretical and practical interest. Corrosion is responsible for the loss of billions of dollars annually in metal products. The mechanism of corrosion has been studied extensively. It is now known that the oxidation of metals occurs most readily at points of strain (where the metals are most "active"). Thus, a steel nail, which is mostly iron (Section 22-7), first corrodes at the tip and head (Figure 21-11). A bent nail corrodes most readily at the bend.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 21.9, Corrosion.

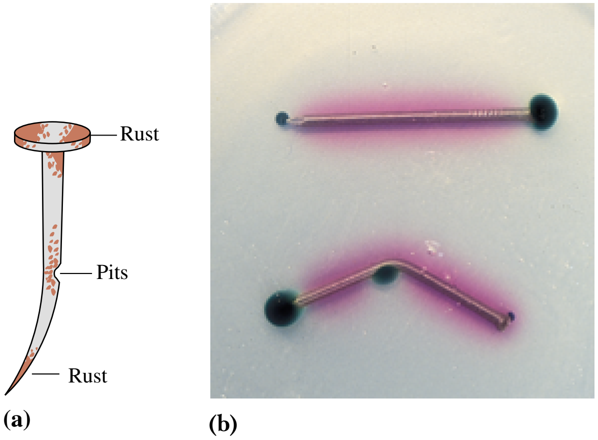


Figure 21-11 (a) A bent nail corrodes at points of strain and "active" metal atoms. (b) Two nails were placed in an agar gel that contained phenolphthalein and potassium ferricyanide, $K_3[Fe(CN)_6]$. As the nails corroded they produced Fe^{2+} ions at each end and at the bend. Fe^{2+} ions react with $[Fe(CN)_6]^{3-}$ ions to form $Fe_3[Fe(CN)_6]_2$, an intensely blue-colored compound. The rest of each nail is the cathode, at which water is reduced to H_2 and OH^- ions. The OH^- ions turn phenolphthalein pink.

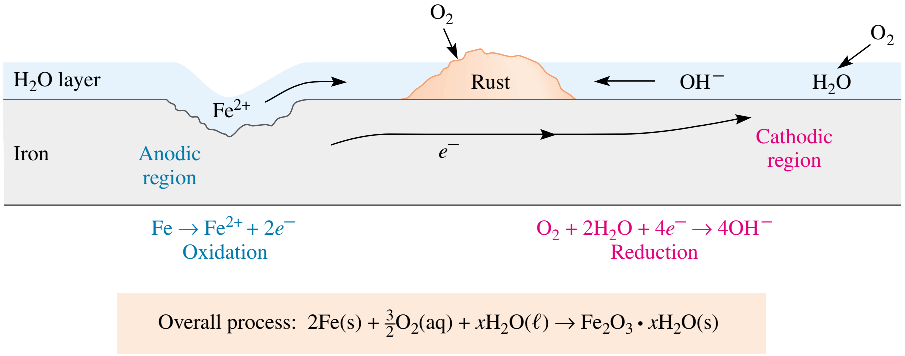


Figure 21-12 The corrosion of iron. Pitting appears at the anodic region, where iron metal is oxidized to Fe^{2+}. Rust appears at the cathodic region.

A point of strain in a steel object acts as an anode where the iron is oxidized to iron(II) ions, and pits are formed (Figure 21-12).

$$\text{Fe} \longrightarrow \text{Fe}^{2+} + 2e^- \qquad \text{(oxidation, anode)}$$

The electrons produced then flow through the nail to areas exposed to O_2. These act as cathodes where oxygen is reduced to hydroxide ions, OH^-.

$$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \longrightarrow 4\text{OH}^- \qquad \text{(reduction, cathode)}$$

At the same time, the Fe^{2+} ions migrate through the moisture on the surface. The overall reaction is obtained by balancing the electron transfer and adding the two half-reactions.

$$\begin{array}{rcll} 2(\text{Fe} & \longrightarrow & \text{Fe}^{2+} + 2e^-) & \text{(oxidation, anode)} \\ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- & \longrightarrow & 4\text{OH}^- & \text{(reduction, cathode)} \\ \hline 2\text{Fe} + \text{O}_2 + 2\text{H}_2\text{O} & \longrightarrow & 2\text{Fe}^{2+} + 4\text{OH}^- & \text{(net reaction)} \end{array}$$

The Fe^{2+} ions can migrate from the anode through the solution toward the cathode region, where they combine with OH^- ions to form iron(II) hydroxide. Iron is further oxidized by O_2 to the +3 oxidation state. The material we call rust is a complex hydrated form of iron(III) oxides and hydroxides with variable water composition; it can be represented as $Fe_2O_3 \cdot xH_2O$. The overall reaction for the rusting of iron is

$$2\text{Fe(s)} + \tfrac{3}{2}\text{O}_2\text{(aq)} + x\text{H}_2\text{O}(\ell) \longrightarrow \text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O(s)}$$

21-18 CORROSION PROTECTION

There are several methods for protecting metals against corrosion. The most widely used are

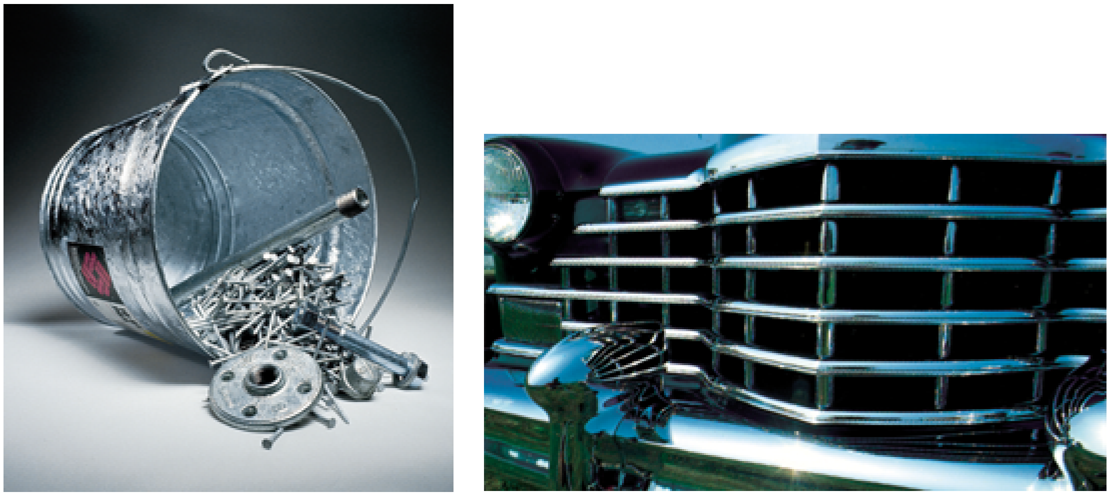
1. Plating the metal with a thin layer of a less easily oxidized metal
2. Connecting the metal directly to a "sacrificial anode," a piece of another metal that is more active and therefore preferentially oxidized
3. Allowing a protective film, such as a metal oxide, to form naturally on the surface of the metal
4. Galvanizing, or coating steel with zinc, a more active metal
5. Applying a protective coating, such as paint

Compare the potentials for the reduction half-reactions to see which metal is more easily oxidized. The more positive the reduction potential for a metal, the more stable the metal is as the free element and the harder it is to oxidize.

	$E^0_{\text{reduction}}$
$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.37 V
$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.763 V
$Fe^{2+} + 2e^- \longrightarrow Fe$	−0.44 V
$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.14 V
$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.337 V

Rust is a serious economic problem.

The thin layer of tin on tin-plated steel cans is less easily oxidized than iron, and it protects the steel underneath from corrosion. It is deposited either by dipping the can into molten tin or by electroplating. Copper is also less active than iron (see Table 21-2). It is sometimes deposited by electroplating to protect metals when food is not involved. Whenever the layer of tin or copper is breached, the iron beneath it corrodes even more rapidly than it would without the coating, because of the adverse electrochemical cell that is set up.



Protection against corrosion. (*Left*) Galvanized objects are steel coated with zinc. (*Right*) Steel is plated with chromium for appearance as well as protection against corrosion.

Figure 21-13a shows an iron pipe connected to a strip of magnesium, a more active metal, to protect the iron from oxidation. The magnesium is preferentially oxidized. It is called a "sacrificial anode." Similar methods are used to protect bridges and the hulls of ships from corrosion. Other active metals, such as zinc, are also used as sacrificial anodes. Galvanizing (coating the iron with zinc), combines these two approaches. Even if the zinc coating is broken so the iron is exposed, the iron is not oxidized as long as it is in contact with the more reactive zinc (Figure 21-13c).

Aluminum, a very active metal, reacts rapidly with O_2 from the air to form a surface layer of aluminum oxide, Al_2O_3, that is so thin that it is transparent. This very tough, hard substance is inert to oxygen, water, and most other corrosive agents in the environment. In this way, objects made of aluminum form their own protective layers and need not be treated further to inhibit corrosion.

Acid rain endangers structural aluminum by dissolving this Al_2O_3 coating.

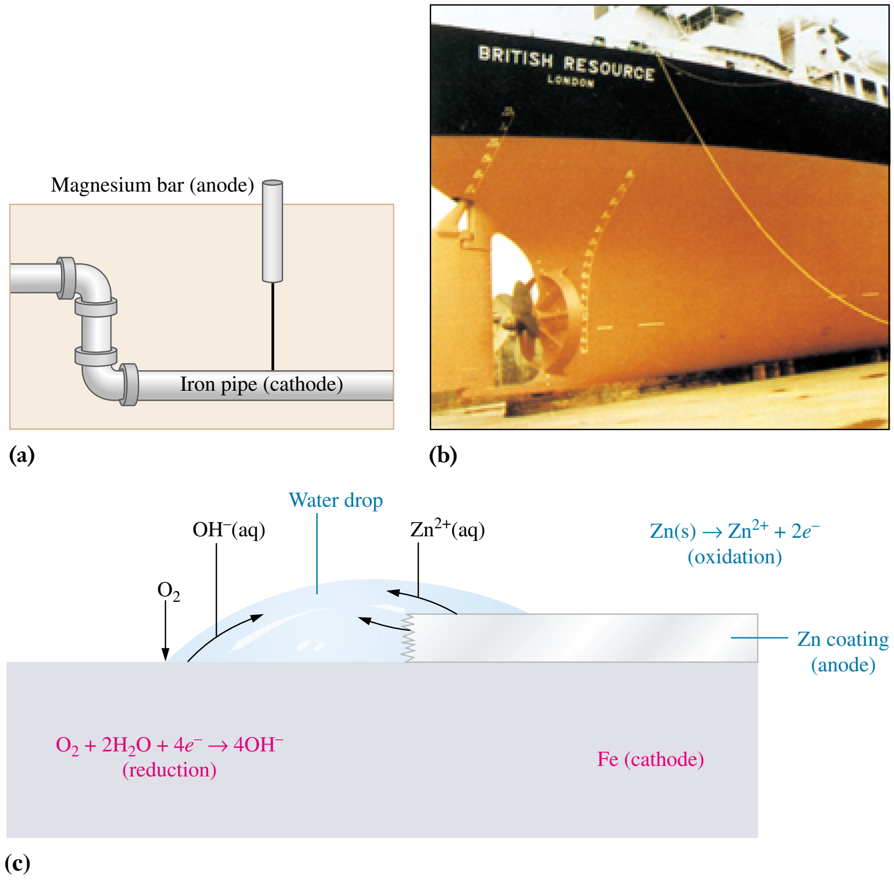


Figure 21-13 (a) Cathodic protection of buried iron pipe. A magnesium or zinc bar is oxidized instead of the iron. The "sacrificial" anode eventually must be replaced. (b) Cathodic protection of a ship's hull. The small yellow horizontal strips are blocks of titanium (coated with platinum) that are attached to the ship's hull. The hull is steel (mostly iron). When the ship is in salt water, the titanium blocks become the anode, and the hull the cathode, in a voltaic cell. Because oxidation always occurs at the anode, the ship's hull (the cathode) is protected from oxidation (corrosion). (c) Galvanizing is another method of corrosion protection. Even if the zinc coating is broken, it is still oxidized in preference to the less reactive iron as long as the two metals remain in contact.

EFFECT OF CONCENTRATIONS (OR PARTIAL PRESSURES) ON ELECTRODE POTENTIALS

21-19 THE NERNST EQUATION

Standard electrode potentials, designated E^0, refer to standard-state conditions. These standard-state conditions are one molar solutions for ions, one atmosphere pressure for gases, and all solids and liquids in their standard states at 25°C. (Remember that we refer to *thermodynamic* standard-state conditions, and not standard temperature and pressure as in gas law calculations.) As any of the standard cells described earlier operates, and concentrations or pressures of reactants change, the observed cell voltage drops. Similarly, cells constructed with solution concentrations different from one molar, or gas pressures different from one atmosphere, cause the corresponding potentials to deviate from standard electrode potentials.

The **Nernst equation** is used to calculate electrode potentials and cell potentials for concentrations and partial pressures other than standard-state values.

$$E = E^0 - \frac{2.303\ RT}{nF} \log Q$$

where

E = potential under the **nonstandard** conditions
E^0 = **standard** potential
R = gas constant, 8.314 J/mol·K
T = absolute temperature in K
n = number of moles of electrons transferred in the reaction or half-reaction
F = faraday, 96,485 C/mol $e^- \times 1$ J/(V·C) = 96,485 J/V·mol e^-
Q = reaction quotient

In this equation the expression following the minus sign represents how much the *nonstandard* conditions cause the electrode potential to deviate from its standard value, E^0. The Nernst equation is normally presented in terms of base-10 logarithms, as we will do in this text.

The reaction quotient, Q, was introduced in Section 17-4. It involves a ratio of concentrations or pressures of products to those of reactants, each raised to the power indicated by the coefficient in the balanced equation. The Q expression that is used in the Nernst equation is the thermodynamic reaction quotient; it can include *both* concentrations and pressures. Substituting these values into the Nernst equation at 25°C gives

$$E = E^0 - \frac{0.0592}{n} \log Q \qquad (\textit{Note:}\ \text{in terms of base-10 log})$$

At 25°C, the value of $\frac{2.303\ RT}{F}$ is 0.0592; at any other temperature, this term must be recalculated. Can you show that this term has the units V·mol?

In general, half-reactions for standard reduction potentials are written

$$x\ \text{Ox} + ne^- \longrightarrow y\ \text{Red}$$

"Ox" refers to the oxidized species and "Red" to the reduced species; x and y are their coefficients, respectively, in the balanced equation. The Nernst equation for any *cathode* half-cell (*reduction* half-reaction) is

$$E = E^0 - \frac{0.0592}{n} \log \frac{[\mathrm{Red}]^y}{[\mathrm{Ox}]^x} \qquad \text{(reduction half-reaction)}$$

For the familiar half-reaction involving metallic zinc and zinc ions,

$$\mathrm{Zn^{2+}} + 2e^- \longrightarrow \mathrm{Zn} \qquad E^0 = -0.763\ \mathrm{V}$$

the corresponding Nernst equation is

Metallic Zn is a pure solid, so its concentration does not appear in Q.

$$E = E^0 - \frac{0.0592}{2} \log \frac{1}{[\mathrm{Zn^{2+}}]} \qquad \text{(for reduction)}$$

We substitute the E^0 value into the equation to obtain

$$E = -0.763\ \mathrm{V} - \frac{0.0592}{2} \log \frac{1}{[\mathrm{Zn^{2+}}]}$$

EXAMPLE 21-5 *The Nernst Equation*

Calculate the potential, E, for the $\mathrm{Fe^{3+}/Fe^{2+}}$ electrode when the concentration of $\mathrm{Fe^{2+}}$ is exactly five times that of $\mathrm{Fe^{3+}}$.

Plan

The Nernst equation lets us calculate potentials for concentrations other than one molar. The tabulation of standard reduction potentials gives us the value of E^0 for the reduction half-reaction. We use the balanced half-reaction and the given concentration ratio to calculate the value of Q. Then we substitute this into the Nernst equation with n equal to the number of moles of electrons involved in the half-reaction.

Solution

The reduction half-reaction is

$$\mathrm{Fe^{3+}} + e^- \longrightarrow \mathrm{Fe^{2+}} \qquad E^0 = +0.771\ \mathrm{V}$$

We are told that the concentration of $\mathrm{Fe^{2+}}$ is five times that of $\mathrm{Fe^{3+}}$, or $[\mathrm{Fe^{2+}}] = 5[\mathrm{Fe^{3+}}]$. Calculating the value of Q,

$$Q = \frac{[\mathrm{Red}]^y}{[\mathrm{Ox}]^x} = \frac{[\mathrm{Fe^{2+}}]}{[\mathrm{Fe^{3+}}]} = \frac{5[\mathrm{Fe^{3+}}]}{[\mathrm{Fe^{3+}}]} = 5$$

The balanced half-reaction shows one mole of electrons, or $n = 1$. Putting values into the Nernst equation,

$$E = E^0 - \frac{0.0592}{n} \log Q = +0.771 - \frac{0.0592}{1} \log 5 = (+0.771 - 0.041)\ \mathrm{V}$$

$$= +0.730\ \mathrm{V}$$

You should now work Exercise 78.

The Nernst equation can be applied to balanced equations for redox reactions. One approach is to correct the reduction potential for each half-reaction to take into account the nonstandard concentrations or pressures.

EXAMPLE 21-6 *The Nernst Equation*

A cell is constructed at 25°C as follows. One half-cell consists of the Fe^{3+}/Fe^{2+} couple in which $[Fe^{3+}] = 1.00\ M$ and $[Fe^{2+}] = 0.100\ M$; the other involves the MnO_4^-/Mn^{2+} couple in acidic solution in which $[MnO_4^-] = 1.00 \times 10^{-2}\ M$, $[Mn^{2+}] = 1.00 \times 10^{-4}\ M$, and $[H^+] = 1.00 \times 10^{-3}\ M$. (a) Find the electrode potential for each half-cell with these concentrations, and (b) calculate the overall cell potential.

Plan

(a) We can apply the Nernst equation to find the reduction potential of each half-cell with the stated concentrations. (b) As in Section 21-15, we write the half-reaction with the more positive potential (*after* correction) along with its potential. We reverse the other half-reaction and change the sign of its E value. We balance the electron transfer and then add the half-reactions and their potentials to find the overall cell potential.

Solution

(a) For the MnO_4^-/Mn^{2+} half-cell *as a reduction*,

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + H_2O \qquad E^0 = +1.507\ V$$

$$\begin{aligned} E &= E^0 - \frac{0.0592}{n}\log\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8} \\ &= +1.507\ V - \frac{0.0592}{5}\log\frac{1.00\times10^{-4}}{(1.00\times10^{-2})(1.00\times10^{-3})^8} \\ &= +1.507\ V - \frac{0.0592}{5}\log(1.00\times10^{22}) = +1.507\ V - \frac{0.0592}{5}(22.0) \\ &= +1.246\ V \end{aligned}$$

(b) For the Fe^{3+}/Fe^{2+} half-cell *as a reduction*,

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad E^0 = +0.771\ V$$

$$\begin{aligned} E &= E^0 - \frac{0.0592}{n}\log\frac{[Fe^{2+}]}{[Fe^{3+}]} = +0.771\ V - \frac{0.0592}{1}\log\frac{0.100}{1.00} \\ &= +0.771\ V - \frac{0.0592}{1}\log(0.100) = +0.771\ V - \frac{0.0592}{1}(-1.00) \\ &= +0.830\ V \end{aligned}$$

The corrected potential for the MnO_4^-/Mn^{2+} half-cell is greater than that for the Fe^{3+}/Fe^{2+} half-cell, so we reverse the latter, balance the electron transfer, and add.

$$\begin{array}{rcl|c} & & & \textbf{E (corrected)} \\ MnO_4^- + 8H^+ + 5e^- & \longrightarrow & Mn^{2+} + 4H_2O & +1.246\ V \\ 5(Fe^{2+} & \longrightarrow & Fe^{3+} + e^-) & -0.830\ V \\ \hline MnO_4^- + 8H^+ + 5Fe^{2+} & \longrightarrow & Mn^{2+}\ 4H_2O + 5Fe^{3+} & E_{cell} = 0.416\ V \end{array}$$

The reaction in Example 21-6 is product-favored (spontaneous) under the stated conditions, with a potential of +0.416 volt *when the cell starts operation.* As the cell discharges and current flows, the product concentrations, $[Mn^{2+}]$ and $[Fe^{3+}]$, increase. At the same time, reactant concentrations, $[MnO_4^-]$, $[H^+]$, and $[Fe^{2+}]$, decrease. This increases

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 21.7, Electrochemical Cells at Nonstandard Conditions.

log Q_{cell}, so the correction factor becomes more negative. Thus, the overall E_{cell} *decreases* (the reaction becomes less favorable). Eventually the cell potential approaches zero (equilibrium), and the cell "runs down." The cell is completely run down ($E_{\text{cell}} = 0$) when the term $\frac{0.0592}{n}$ log Q_{cell} is equal in magnitude to E^0_{cell}.

We can also find the cell potential for a nonstandard cell by first finding E^0_{cell} or the overall standard cell reaction, and then using the Nernst equation to correct for nonstandard concentrations. The next example illustrates this approach.

EXAMPLE 21-7 *The Nernst Equation*

A cell is constructed at 25°C as follows. One half-cell consists of a chlorine/chloride, Cl_2/Cl^-, electrode with the partial pressure of $Cl_2 = 0.100$ atm and $[Cl^-] = 0.100\ M$. The other half-cell involves the MnO_4^-/Mn^{2+} couple in acidic solution with $[MnO_4^-] = 0.100\ M$, $[Mn^{2+}] = 0.100\ M$, and $[H^+] = 0.100\ M$. Apply the Nernst equation to the overall cell reaction to determine the cell potential for this cell.

Plan

First we determine the overall cell reaction and its *standard* cell potential, E^0_{cell}, as in Examples 21-3 and 21-4. Then we apply the Nernst equation to the overall cell.

Solution

The MnO_4^-/Mn^{2+} half-reaction has the more positive reduction potential, so we write it first. Then we write the Cl_2/Cl^- half-reaction as an oxidation, balance the electron transfer, and add the two half-reactions and their potentials to obtain the overall cell reaction and its E^0_{cell}.

$$\begin{array}{rcll} & & & \mathbf{E^0} \\ 2(MnO_4^- + 8H^+ + 5e^- & \longrightarrow & Mn^{2+} + 4H_2O) & +1.507\text{ V} \\ 5(2Cl^- & \longrightarrow & Cl_2 + 2e^-) & -1.360\text{ V} \\ \hline 2MnO_4^- + 16H^+ + 10Cl^- & \longrightarrow & 2Mn^{2+} + 8H_2O + 5Cl_2 & E^0_{\text{cell}} = +0.147\text{ V} \end{array}$$

In the overall reaction, $n = 10$. We then apply the Nernst equation to this overall reaction by substituting appropriate concentration and partial pressure values. Because Cl_2 is a gaseous component, its term in the Nernst equation involves its partial pressure, P_{Cl_2}.

$$\begin{aligned} E_{\text{cell}} = E^0_{\text{cell}} &- \frac{0.0592}{n} \log \frac{[Mn^{2+}]^2(P_{Cl_2})^5}{[MnO_4^-]^2[H^+]^{16}[Cl^-]^{10}} \\ &= 0.147\text{ V} - \frac{0.0592}{10} \log \frac{(0.100)^2(0.100)^5}{(0.100)^2(0.100)^{16}(0.100)^{10}} \\ &= 0.147\text{ V} - \frac{0.0592}{10} \log(1.00 \times 10^{21}) \\ &= 0.147\text{ V} - \frac{0.0592}{10}(21.00) = 0.017\text{ V} \end{aligned}$$

Remember that, in evaluating Q in the Nernst equation, (1) molar concentrations are used for dissolved species, and (2) partial pressures of gases are expressed in atmospheres.

You should now work Exercises 80 and 84.

Now solve Example 21-6 by applying the Nernst equation to the *overall* cell reaction to determine the cell potential.

The method illustrated in Example 21-7, applying the Nernst equation to the *overall* cell reaction, usually involves less calculation than correcting the separate half-reactions as in Example 21-6. We interpret our results as follows: The positive cell potentials in Examples 21-6 and 21-7 tell us that each of these cell reactions is spontaneous *in the direc-*

tion written, for the concentrations given. If the resulting cell potential were negative, the *reverse* reaction would be favored at those concentrations. We could then reverse the equation for the overall cell reaction and change the sign of its potential to describe the spontaneous operation of the cell.

✓ **Problem-Solving Tip:** ***Be Careful of the Value of n***

How do you know what value of n to use? Remember that n must be the number of moles of electrons transferred in the *balanced* equation for the process to which you apply the Nernst equation.

1. For a *half-reaction*, n represents the number of moles of electrons in that half-reaction. In Example 21-6 we applied the Nernst equation to each half-reaction separately, so we used $n = 5$ for the half-reaction

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

and we used $n = 1$ for the half-reaction

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

2. For an *overall reaction*, n represents the total number of moles of electrons transferred. In Example 21-7 we applied the Nernst equation to an *overall* reaction in which 10 moles of electrons was transferred from 10 moles of Cl^- to 2 moles of MnO_4^-, so we used the value $n = 10$.

21-20 USING ELECTROCHEMICAL CELLS TO DETERMINE CONCENTRATIONS

We can apply the ideas of the preceding section to *measure* the voltage of a cell and then use the Nernst equation to solve for an *unknown* concentration. The following example illustrates such an application.

A pH meter uses the voltage of a cell to measure the H^+ concentration in a solution. Each change of one pH unit causes a voltage change of 0.0592 volts.

EXAMPLE 21-8 *The Nernst Equation*

We construct an electrochemical cell at 25°C as follows. One half-cell is a standard Zn^{2+}/Zn cell, that is, a strip of zinc immersed in a 1.00 M Zn^{2+} solution; the other is a *nonstandard* hydrogen electrode in which a platinum electrode is immersed in a solution of *unknown* hydrogen ion concentration with gaseous hydrogen bubbling through it at a pressure of 1.000 atm. The observed cell voltage is 0.522 V. (a) Calculate the value of the reaction quotient Q. (b) Calculate $[H^+]$ in the second half-cell. (c) Determine the pH of the solution in the second half-cell.

This cell is similar to the zinc–hydrogen cell that we discussed in Section 21-12, except that the hydrogen concentration is not (necessarily) 1.00 M.

Plan

We saw in Section 21-12 that the zinc–hydrogen cell operated with oxidation at the zinc electrode and reduction at the hydrogen electrode, with a *standard* cell potential of 0.763 V.

$$\text{overall:} \quad Zn + 2H^+ \longrightarrow Zn^{2+} + H_2 \qquad E^0_{cell} = 0.763 \text{ V}$$

(a) We rearrange the Nernst equation to solve for the reaction quotient, Q, from the measured cell voltage and $n = 2$. (b) We substitute concentrations and partial pressures in the expression for Q. Then we can solve for the only unknown, $[H^+]$. (c) The pH can be determined from the $[H^+]$ determined in part (b).

Solution

(a)
$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.0592}{n}\log Q$$

Substituting and solving for Q,

$$0.522\text{ V} = 0.763\text{ V} - \frac{0.0592}{2}\log Q$$

$$\frac{0.0592\text{ V}}{2}\log Q = (0.763 - 0.522)\text{ V} = 0.241\text{ V}$$

$$\log Q = \frac{(2)(0.241\text{ V})}{0.0592\text{ V}} = 8.14$$

$$Q = 10^{8.14} = 1.4 \times 10^8$$

(b) We write the expression for Q from the balanced overall equation, and solve for $[H^+]$.

$$Q = \frac{[Zn^{2+}]P_{H_2}}{[H^+]^2}$$

$$[H^+]^2 = \frac{[Zn^{2+}]P_{H_2}}{Q} = \frac{(1.00)(1.00)}{1.4 \times 10^8} = 7.1 \times 10^{-9}$$

$$[H^+] = 8.4 \times 10^{-5}\ M$$

(c)
$$\text{pH} = -\log\,[H^+] = -\log\,(8.4 \times 10^{-5}) = 4.08$$

You should now work Exercises 81 and 82.

Microelectrodes have been developed to measure concentrations in very small volumes of solution.

Enrichment

Concentration Cells

As we have seen, different concentrations of ions in a half-cell result in different half-cell potentials. We can use this idea to construct a **concentration cell,** in which both half-cells are composed of the same species, but in different ion concentrations. Suppose we set up such a cell using the Cu^{2+}/Cu half-cell that we introduced in Section 21-9. We put copper electrodes into two aqueous solutions, one that is 0.10 M $CuSO_4$ and another that is 1.00 M $CuSO_4$. To complete the cell construction, we connect the two electrodes with a wire and join the two solutions with a salt bridge as usual (Figure 21-14). Now the relevant reduction half-reaction in either half-cell is

$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad E^0 = +0.337\text{ V}$$

Thus the Cu^{2+} ions in the more concentrated half-cell can be considered as the reactant, and those in the more dilute cell as the product.

$$Cu^{2+}(1.00\ M) \longrightarrow Cu^{2+}(0.10\ M)$$

The overall cell potential can be calculated by applying the Nernst equation to the overall cell reaction. We must first find E^0, the standard cell potential *at standard concentrations;* because the same electrode and the same type of ions are involved in both half-cells, this E^0 is always zero. Thus,

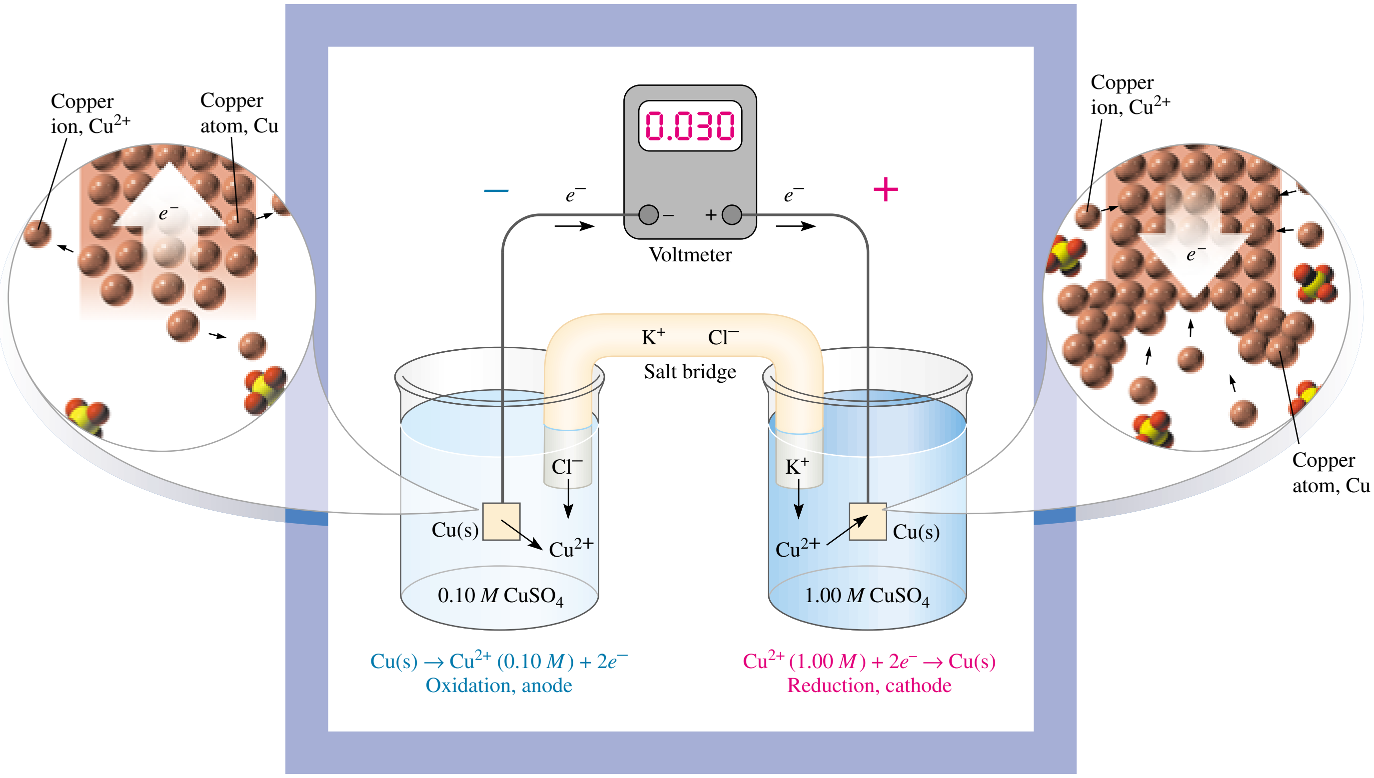


Figure 21-14 The concentration cell $Cu|Cu^{2+}(0.10\ M)||Cu^{2+}(1.00\ M)|Cu$. The overall reaction lowers the $[Cu^{2+}]$ concentration in the more concentrated solution and increases it in the more dilute solution.

$$E_{\text{cell}} = E^0 - \frac{0.0592}{n}\log\frac{[\text{dilute solution}]}{[\text{concentrated solution}]}$$

$$= 0 - \frac{0.0592}{2}\log\frac{0.10}{1.00} = +0.030\ \text{V}$$

The overall cell potential is positive; the reaction is spontaneous as written.

As the reaction proceeds, $[Cu^{2+}]$ decreases in the more concentrated half-cell and increases in the more dilute half-cell until the two concentrations are equal; at that point $E_{\text{cell}} = 0$, and equilibrium has been reached. This equilibrium $[Cu^{2+}]$ is the same concentration that would have been formed if we had just mixed the two solutions directly to obtain a solution of intermediate concentration.

In any concentration cell, the spontaneous reaction is always from the more concentrated solution to the more dilute solution.

Electrochemical procedures that use the principles illustrated here provide a convenient method for making many concentration measurements.

21-21 THE RELATIONSHIP OF E^0_{cell} TO ΔG^0 AND K

In Section 17-12 we studied the relationship between the standard Gibbs free energy change, ΔG^0, and the thermodynamic equilibrium constant, K.

$$\Delta G^0 = -RT \ln K$$

There is also a simple relationship between ΔG^0 and the standard cell potential, E^0_{cell}, for a redox reaction (reactants and products in standard states).

$$\Delta G^0 = -nFE^0_{\text{cell}}$$

ΔG^0 can be thought of as the *negative of the maximum electrical work* that can be obtained from a redox reaction. In this equation, n is the number of moles of electrons transferred in the overall process (mol e^-/mol rxn), and F is the faraday, 96,485 J/V·mol e^-.

Combining these relationships for ΔG^0 gives the relationship between E^0_{cell} values and equilibrium constants.

$$\underbrace{-nFE^0_{\text{cell}}}_{\Delta G^0} = \underbrace{-RT \ln K}_{\Delta G^0}$$

After multiplying by -1, we can rearrange.

$$nFE^0_{\text{cell}} = RT \ln K \quad \text{or} \quad E^0_{\text{cell}} = \frac{RT \ln K}{nF} \quad \text{or} \quad \ln K = \frac{nFE^0_{\text{cell}}}{RT}$$

If any one of the three quantities ΔG^0, K, and E^0_{cell} is known, the other two can be calculated using these equations. It is usually much easier to determine K for a redox reaction from electrochemical measurements than by measuring equilibrium concentrations directly, as described in Chapter 17. Keep in mind the following for all redox reactions at *standard conditions.*

Forward Reaction	ΔG^0	K	E^0_{cell}	
product-favored (spontaneous)	$-$	>1	$+$	(all substances at *standard conditions*)
at equilibrium	0	1	0	
reactant-favored (nonspontaneous)	$+$	<1	$-$	

Recall from Chapter 15 that ΔG^0 can be expressed in joules per *mole of reaction.* Here we ask for the number of joules of free energy change that corresponds to the reaction of 2 moles of chromium with 3 moles of tin(IV) to give 3 moles of tin(II) ions and 2 moles of chromium(III) ions.

EXAMPLE 21-9 *Calculation of ΔG^0 from Cell Potentials*

Calculate the standard Gibbs free energy change, ΔG^0, in J/mol at 25°C for the following reaction from standard electrode potentials.

$$3Sn^{4+} + 2Cr \longrightarrow 3Sn^{2+} + 2Cr^{3+}$$

Plan

We evaluate the standard cell potential as we have done before. Then we apply the relationship $\Delta G^0 = -nFE^0_{\text{cell}}$.

Solution

The standard reduction potential for the Sn^{4+}/Sn^{2+} couple is +0.15 volt; that for the Cr^{3+}/Cr couple is −0.74 volt. The equation for the reaction shows Cr being oxidized to Cr^{3+}, so the sign of the E^0 value for the Cr^{3+}/Cr couple is reversed. The overall reaction, the sum of the two half-reactions, has a cell potential equal to the sum of the two half-reaction potentials.

$$\begin{array}{rcl|r} & & & \textbf{E}^{\mathbf{0}} \\ 3(Sn^{4+} + 2e^- & \longrightarrow & Sn^{2+}) & +0.15\text{ V} \\ 2(Cr & \longrightarrow & Cr^{3+} + 3e^-) & -(-0.74\text{ V}) \\ \hline 3Sn^{4+} + 2Cr & \longrightarrow & 3Sn^{2+} + 2Cr^{3+} & E^0_{\text{cell}} = +0.89\text{ V} \end{array}$$

The positive value of E^0_{cell} indicates that the forward reaction is spontaneous.

$$\Delta G^0 = -nFE^0_{\text{cell}} = -\left(\frac{6\text{ mol }e^-}{\text{mol rxn}}\right)\left(\frac{9.65 \times 10^4\text{ J}}{\text{V}\cdot\text{mol }e^-}\right)(+0.89\text{ V})$$

$$= -5.2 \times 10^5\text{ J/mol rxn} \quad \text{or} \quad -5.2 \times 10^2\text{ kJ/mol rxn}$$

The quite negative value of ΔG^0 tells us that the reaction is product-favored. This tells us nothing about the speed with which the reaction would occur.

You should now work Exercise 95.

EXAMPLE 21-10 *Calculation of K from Cell Potentials*

Use the standard cell potential to calculate the value of the equilibrium constant, *K*, at 25°C for the following reaction.

$$2Cu + PtCl_6^{2-} \longrightarrow 2Cu^+ + PtCl_4^{2-} + 2Cl^-$$

Plan

We calculate E^0_{cell} for the reaction as written. Then we use it to calculate *K*.

Solution

First we find the appropriate half-reactions. Cu is oxidized to Cu^+, so we write the Cu^+/Cu couple as an oxidation and reverse the sign of its tabulated E^0 value. We balance the electron transfer and then add the half-reactions. The resulting E^0_{cell} value can be used to calculate the equilibrium constant, *K*, for the reaction *as written.*

As the problem is stated, we must keep the equation as written. We must therefore accept either a positive or a negative value of E^0_{cell}. A negative value of E^0_{cell} would lead to $K < 1$.

$$\begin{array}{rcll} 2(Cu & \longrightarrow & Cu^+ + e^-) & -(+0.521\text{ V}) \\ PtCl_6^{2-} + 2e^- & \longrightarrow & PtCl_4^{2-} + 2Cl^- & +0.68\text{ V} \\ \hline 2Cu + PtCl_6^{2-} & \longrightarrow & 2Cu^+ + PtCl_4^{2-} + 2Cl^- & E^0_{\text{cell}} = +0.16\text{ V} \end{array}$$

Then we calculate *K*.

$$\ln K = \frac{nFE^0_{\text{cell}}}{RT} = \frac{(2)(9.65 \times 10^4\text{ J/V}\cdot\text{mol})(+0.16\text{ V})}{(8.314\text{ J/mol}\cdot\text{K})(298\text{ K})} = 12.5$$

$$K = e^{12.5} = 2.7 \times 10^5$$

At equilibrium, $K = \dfrac{[Cu^+]^2[PtCl_4^{2-}][Cl^-]^2}{[PtCl_6^{2-}]} = 2.7 \times 10^5.$

The forward reaction is product-favored (spontaneous), and the equilibrium lies far to the right.

You should now work Exercises 96 and 98.

PRIMARY VOLTAIC CELLS

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 21.8, Batteries.

As any voltaic cell produces current **(discharges),** chemicals are consumed. **Primary voltaic cells** cannot be "recharged." Once the chemicals have been consumed, further chemical action is not possible. The electrolytes or electrodes (or both) cannot be regenerated by reversing the current flow through the cell using an external direct current source. The most familiar examples of primary voltaic cells are the ordinary "dry" cells that are used as energy sources in flashlights and other small appliances.

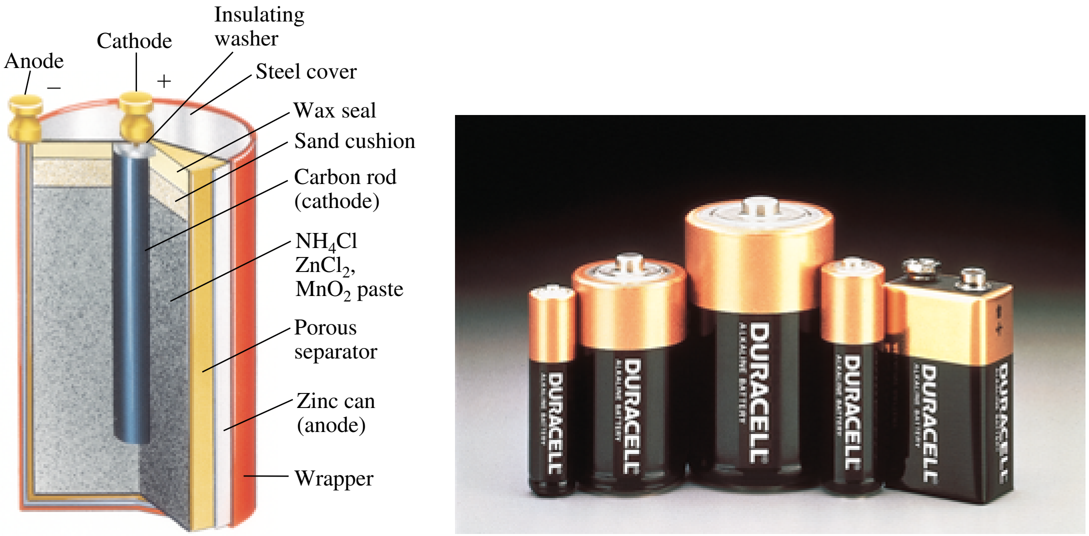
21-22 DRY CELLS

The first dry cell was patented by Georges Leclanché (1839–1882) in 1866. The container of this dry cell, made of zinc, also serves as one of the electrodes (Figure 21-15). The other electrode is a carbon rod in the center of the cell. The zinc container is lined with porous paper to separate it from the other materials of the cell. The rest of the cell is filled with a moist mixture (the cell is *not* really dry) of ammonium chloride (NH_4Cl), manganese(IV) oxide (MnO_2), zinc chloride ($ZnCl_2$), and a porous, inert filler. Dry cells are sealed to keep the moisture from evaporating. As the cell operates (the electrodes must be connected externally), the metallic Zn is oxidized to Zn^{2+}, and the liberated electrons flow along the container to the external circuit. Thus, the zinc electrode is the anode (negative electrode).

$$\mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+} + 2e^- \qquad \text{(oxidation, anode)}$$

The carbon rod is the cathode, at which ammonium ions are reduced.

$$2\mathrm{NH_4}^+ + 2e^- \longrightarrow 2\mathrm{NH_3} + \mathrm{H_2} \qquad \text{(reduction, cathode)}$$



(a) **(b)**

Figure 21-15 (a) The Leclanché cell is a dry cell that generates a potential difference of about 1.6 volts. (b) Some commercial alkaline dry cells.

Addition of the half-reactions gives the overall cell reaction

$$\mathrm{Zn} + 2\mathrm{NH_4}^+ \longrightarrow \mathrm{Zn}^{2+} + 2\mathrm{NH_3} + \mathrm{H_2} \qquad E_{\text{cell}} = 1.6\ \mathrm{V}$$

As H_2 is formed, it is oxidized by MnO_2 in the cell. This prevents collection of H_2 gas on the cathode, which would stop the reaction.

The buildup of reaction products at an electrode is called *polarization* of the electrode.

$$\mathrm{H_2} + 2\mathrm{MnO_2} \longrightarrow 2\mathrm{MnO(OH)}$$

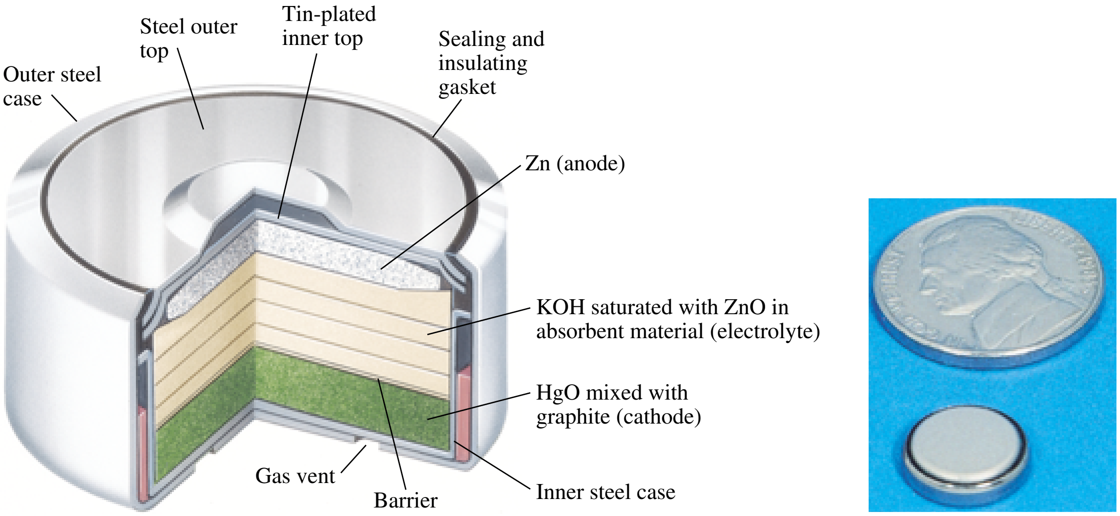
The ammonia produced at the cathode combines with zinc ions and forms a soluble compound containing the complex ions, $[Zn(NH_3)_4]^{2+}$.

$$\mathrm{Zn}^{2+} + 4\mathrm{NH_3} \longrightarrow [\mathrm{Zn(NH_3)_4}]^{2+}$$

This reaction prevents polarization due to the buildup of ammonia, and it prevents the concentration of Zn^{2+} from increasing substantially, which would decrease the cell potential.

Alkaline dry cells are similar to Leclanché dry cells except that (1) the electrolyte is basic (alkaline) because it contains KOH, and (2) the interior surface of the Zn container is rough; this gives a larger surface area. Alkaline cells have a longer shelf life than ordinary dry cells, and they stand up better under heavy use. The voltage of an alkaline cell is about 1.5 volts. During discharge, the alkaline dry cell reactions are

$$\begin{array}{rcll}
\mathrm{Zn(s)} + 2\mathrm{OH^-(aq)} & \longrightarrow & \mathrm{Zn(OH)_2(s)} + 2e^- & \text{(anode)} \\
2\mathrm{MnO_2(s)} + 2\mathrm{H_2O}(\ell) + 2e^- & \longrightarrow & 2\mathrm{MnO(OH)(s)} + 2\mathrm{OH^-(aq)} & \text{(cathode)} \\
\hline
\mathrm{Zn(s)} + 2\mathrm{MnO_2(s)} + 2\mathrm{H_2O}(\ell) & \longrightarrow & \mathrm{Zn(OH)_2(s)} + 2\mathrm{MnO(OH)(s)} & \text{(overall)}
\end{array}$$



The mercury battery of the type frequently used in watches, calculators, and hearing aids is a primary cell. Although mercury in the water supply is known to cause health problems, no conclusive evidence has been found that the disposal of household batteries contributes to such problems. Nevertheless, manufacturers are working to decrease the amount of mercury in batteries. In recent years, the amount of mercury in alkaline batteries decreased markedly; at the same time, the life of such batteries has increased dramatically.

SECONDARY VOLTAIC CELLS

In **secondary voltaic cells,** or *reversible cells*, the original reactants can be regenerated. This is done by passing a direct current through the cell in the direction opposite of the discharge current flow. This process is referred to as *charging*, or recharging, a cell or battery. The most common example of a secondary voltaic cell is the lead storage battery, used in most automobiles.

21-23 THE LEAD STORAGE BATTERY

The lead storage battery is depicted in Figure 21-16. One group of lead plates contains compressed spongy lead. These alternate with a group of lead plates that contain lead(IV) oxide, PbO_2. The electrodes are immersed in a solution of about 40% sulfuric acid. When the cell discharges, the spongy lead is oxidized to lead ions, and the lead plates accumulate a negative charge.

$$\mathrm{Pb} \longrightarrow \mathrm{Pb}^{2+} + 2e^- \qquad \text{(oxidation)}$$

The lead ions then react with hydrogen sulfate ions from the sulfuric acid to form insoluble lead(II) sulfate. This begins to coat the lead electrode.

$$\mathrm{Pb}^{2+} + \mathrm{HSO_4}^- \longrightarrow \mathrm{PbSO_4(s)} + \mathrm{H}^+ \qquad \text{(precipitation)}$$

Thus, the net process at the anode *during discharge* is

$$\mathrm{Pb} + \mathrm{HSO_4}^- \longrightarrow \mathrm{PbSO_4(s)} + \mathrm{H}^+ + 2e^- \qquad \text{(anode during discharge)}$$

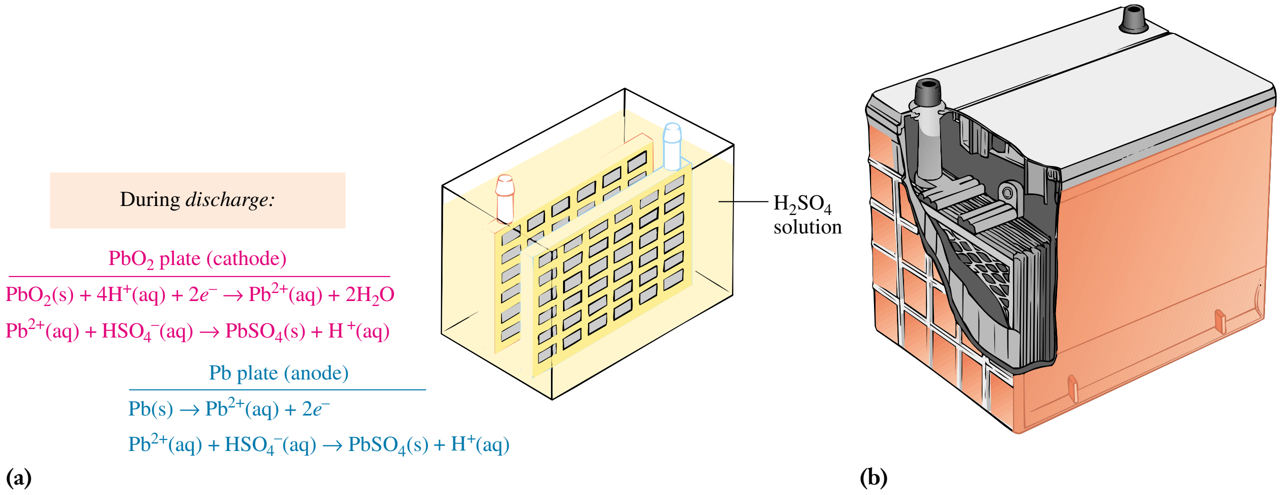


Figure 21-16 (a) A schematic representation of one cell of a lead storage battery. The reactions shown are those taking place during the *discharge* of the cell. Alternate lead grids are packed with spongy lead and lead(IV) oxide. The grids are immersed in a solution of sulfuric acid, which serves as the electrolyte. To provide a large reacting surface, each cell contains several connected grids of each type as in (b); for clarity, only one of each is shown in (a). Such a cell generates a voltage of about 2 volts. Six of these cells are connected together in series, so that their voltages add, to make a 12-volt battery.

The electrons travel through the external circuit and re-enter the cell at the PbO_2 electrode, which is the cathode during discharge. Here, in the presence of hydrogen ions, the lead(IV) oxide is reduced to lead(II) ions, Pb^{2+}. These ions also react with HSO_4^- ions from the H_2SO_4 to form an insoluble $PbSO_4$ coating on the lead(IV) oxide electrode.

$$\begin{array}{rcll}
PbO_2 + 4H^+ + 2e^- & \longrightarrow & Pb^{2+} + 2H_2O & \text{(reduction)} \\
Pb^{2+} + HSO_4^- & \longrightarrow & PbSO_4(s) + H^+ & \text{(precipitation)} \\
\hline
PbO_2 + 3H^+ + HSO_4^- + 2e^- & \longrightarrow & PbSO_4(s) + 2H_2O & \text{(cathode during discharge)}
\end{array}$$

The net cell reaction for discharge and its standard potential are obtained by adding the net anode and cathode half-reactions and their tabulated potentials. The tabulated E^0 value for the anode half-reaction is reversed in sign because it occurs as oxidation during discharge.

$$\begin{array}{rcll}
 & & & \mathbf{E^0} \\
Pb + HSO_4^- & \longrightarrow & PbSO_4(s) + H^+ + 2e^- & -(-0.356\text{ V}) \\
PbO_2 + 3H^+ + HSO_4^- + 2e^- & \longrightarrow & PbSO_4(s) + 2H_2O & +1.685\text{ V} \\
\hline
Pb + PbO_2 + \underbrace{2H^+ + 2HSO_4^-}_{2H_2SO_4} & \longrightarrow & 2PbSO_4(s) + 2H_2O & E^0_{cell} = +2.041\text{ V}
\end{array}$$

The decrease in the concentration of sulfuric acid provides an easy method for measuring the degree of discharge, because the density of the solution decreases accordingly. We simply measure the density of the solution with a hydrometer.

One cell creates a potential of about 2 volts. Automobile 12-volt batteries have six cells connected in series. The potential declines only slightly during use, because solid reagents are being consumed. As the cell is used, some H_2SO_4 is consumed, lowering its concentration.

When a potential slightly greater than the potential the battery can generate is imposed across the electrodes, the current flow can be reversed. The battery can then be recharged by reversal of all reactions. The alternator or generator applies this potential when the engine is in operation. The reactions that occur in a lead storage battery are summarized as follows.

$$Pb + PbO_2 + 2H^+ + 2HSO_4^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2PbSO_4(s) + 2H_2O$$

A *generator* supplies direct current (dc). An *alternator* supplies alternating current (ac), so a rectifier (an electronic device) is used to convert this to direct current for the battery.

During many repeated charge–discharge cycles, some of the $PbSO_4$ falls to the bottom of the container and the H_2SO_4 concentration becomes correspondingly low. Eventually the battery cannot be recharged fully. It can be traded in for a new one, and the lead can be recovered and reused to make new batteries.

This is one of the oldest and most successful examples of recycling.

21-24 THE NICKEL–CADMIUM (NICAD) CELL

The nickel–cadmium (nicad) cell has gained widespread popularity because it can be recharged. It thus has a much longer useful life than ordinary (Leclanché) dry cells. Nicad batteries are used in electronic wristwatches, calculators, and photographic equipment.

The anode is cadmium, and the cathode is nickel(IV) oxide. The electrolytic solution is basic. The "discharge" reactions that occur in a nicad battery are

$$\begin{array}{rcll}
Cd(s) + 2OH^-(aq) & \longrightarrow & Cd(OH)_2(s) + 2e^- & \text{(anode)} \\
NiO_2(s) + 2H_2O(\ell) + 2e^- & \longrightarrow & Ni(OH)_2(s) + 2OH^-(aq) & \text{(cathode)} \\
\hline
Cd(s) + NiO_2(s) + 2H_2O(\ell) & \longrightarrow & Cd(OH)_2(s) + Ni(OH)_2(s) & \text{(overall)}
\end{array}$$

To see why a nicad battery produces a constant voltage, write the Nernst equation for its reaction. Look at *Q*.

The solid reaction product at each electrode adheres to the electrode surface. Hence, a nicad battery can be recharged by an external source of electricity; that is, the electrode reactions can be reversed. Because no gases are produced by the reactions in a nicad battery, the unit can be sealed. The voltage of a nicad cell is about 1.4 volts, slightly less than that of a Leclanché cell.

Rechargeable nicad batteries are used to operate many electrical devices.

21-25 THE HYDROGEN–OXYGEN FUEL CELL

Fuel cells are voltaic cells in which the reactants are continuously supplied to the cell and the products are continuously removed. The hydrogen–oxygen fuel cell (Figure 21-17) already has many applications. It is used in spacecraft to supplement the energy obtained from solar cells. Liquid H_2 is carried on board as a propellant. The boiled-off H_2 vapor that ordinarily would be lost is used in a fuel cell to generate electrical power.

Hydrogen (the fuel) is supplied to the anode compartment. Oxygen is fed into the cathode compartment. The diffusion rates of the gases into the cell are carefully regulated for maximum efficiency. Oxygen is reduced at the cathode, which consists of porous carbon impregnated with a finely divided Pt or Pd catalyst.

$$O_2 + 2H_2O + 4e^- \xrightarrow{\text{catalyst}} 4OH^- \qquad \text{(cathode)}$$

The OH^- ions migrate through the electrolyte to the anode, an aqueous solution of a base. The anode is also porous carbon containing a small amount of catalyst (Pt, Ag, or CoO). Here H_2 is oxidized to H_2O.

$$H_2 + 2OH^- \longrightarrow 2H_2O + 2e^- \qquad \text{(anode)}$$

The net reaction is obtained from the two half-reactions.

$$\begin{array}{rcll} O_2 + 2H_2O + 4e^- & \longrightarrow & 4OH^- & \text{(cathode)} \\ 2(H_2 + 2OH^- & \longrightarrow & 2H_2O + 2e^-) & \text{(anode)} \\ \hline 2H_2 + O_2 & \longrightarrow & 2H_2O & \text{(net cell reaction)} \end{array}$$

The efficiency of energy conversion of the fuel cell operation is 60–70% of the theoretical maximum (based on ΔG). This represents about twice the efficiency that can be realized from burning hydrogen in a heat engine coupled to a generator.

The net reaction is the same as the burning of H_2 in O_2 to form H_2O, but combustion does not actually occur. Most of the chemical energy from the formation of H—O bonds is converted directly into electrical energy, rather than into heat energy as in combustion.

When the H_2/O_2 fuel cell is used aboard spacecraft, it is operated at a high enough temperature that the water evaporates at the same rate as it is produced. The vapor is then condensed to pure water.

Current research is aimed at modifying the design of fuel cells to lower their cost. Better catalysts would speed the reactions to allow more rapid generation of electricity and produce more power per unit volume. The H_2/O_2 cell is nonpolluting; the only substance released is H_2O. Catalysts have been developed that allow sunlight to decompose water into hydrogen and oxygen, which might be used to operate fuel cells, permitting the utilization of solar energy.

Fuel cells have also been constructed using fuels other than hydrogen, such as methane or methanol. Biomedical researchers envision the possibility of using tiny fuel cells to operate pacemakers. The disadvantage of other power supplies for pacemakers, which are primary voltaic cells, is that their reactants are eventually consumed so that they require periodic surgical replacement. As long as the fuel and oxidizer are supplied, a fuel cell can—in theory, at least—operate forever. Eventually, tiny pacemaker fuel cells might be operated by the oxidation of blood sugar (the fuel) by the body's oxygen at a metal electrode implanted just below the skin.

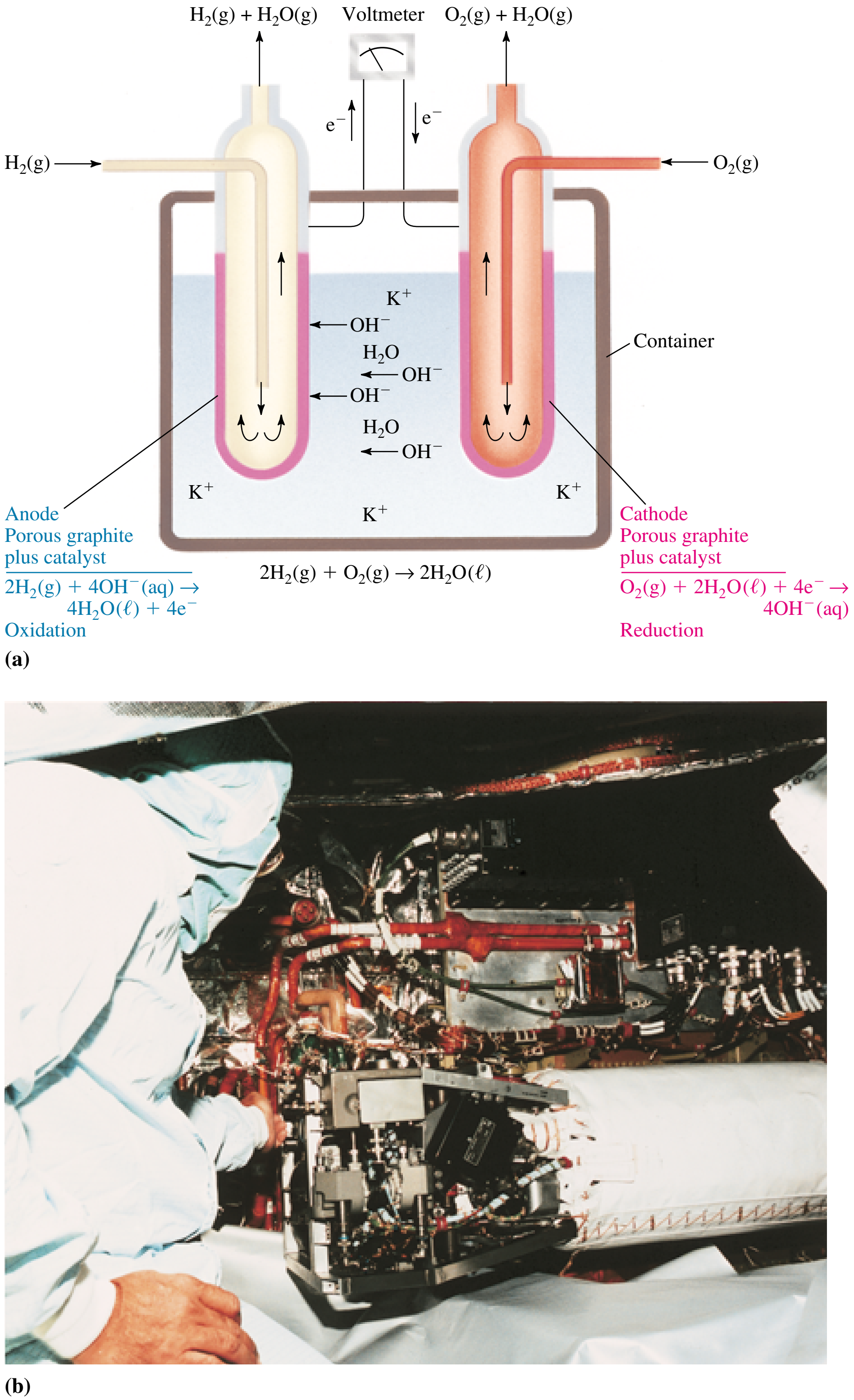


Figure 21-17 (a) Schematic drawing of a hydrogen–oxygen fuel cell. (b) A hydrogen–oxygen fuel cell that is used in spacecraft.

Key Terms

Alkaline cell A dry cell in which the electrolyte contains KOH.

Ampere Unit of electric current; 1 ampere equals 1 coulomb per second.

Anode The electrode at which oxidation occurs.

Cathode The electrode at which reduction occurs.

Cathode protection Protection of a metal against corrosion by making it a cathode (attaching it to a sacrificial anode of a more easily oxidized metal).

Cell potential Potential difference, E_{cell}, between reduction and oxidation half-cells; may be at *nonstandard* conditions.

Concentration cell A voltaic cell in which the two half-cells are composed of the same species but contain different ion concentrations.

Corrosion Oxidation of metals in the presence of air and moisture.

Coulomb Unit of electric charge; the amount of charge that passes a given point when 1 ampere of electric current flows for 1 second.

Downs cell An electrolytic cell for the commercial electrolysis of molten sodium chloride.

Dry cells Ordinary batteries (voltaic cells) for flashlights, radios, and so on; many are Leclanché cells.

Electrochemistry The study of the chemical changes produced by electric current and the production of electricity by chemical reactions.

Electrode potentials Potentials, *E*, of half-reactions as reductions versus the standard hydrogen electrode.

Electrodes Surfaces on which oxidation and reduction half-reactions occur in electrochemical cells.

Electrolysis The process that occurs in electrolytic cells.

Electrolytic cell An electrochemical cell in which electrical energy causes nonspontaneous redox reactions to occur.

Electrolytic conduction See *Ionic conduction.*

Electroplating Plating a metal onto a (cathodic) surface by electrolysis.

Faraday An amount of charge equal to 96,485 coulombs; corresponds to the charge on one mole of electrons, 6.022×10^{23} electrons.

Faraday's Law of Electrolysis The amount of substance that undergoes oxidation or reduction at each electrode during electrolysis is directly proportional to the amount of electricity that passes through the cell.

Fuel cell A voltaic cell in which the reactants (usually gases) are supplied continuously and products are removed continuously.

Galvanic cell See *Voltaic cell.*

Half-cell The compartment in a voltaic cell in which the oxidation or reduction half-reaction occurs.

Hydrogen–oxygen fuel cell A fuel cell in which hydrogen is the fuel (reducing agent) and oxygen is the oxidizing agent.

Ionic conduction Conduction of electric current by ions through a pure liquid or a solution.

Lead storage battery A secondary voltaic cell that is used in most automobiles.

Leclanché cell A common type of dry cell.

Metallic conduction Conduction of electric current through a metal or along a metallic surface.

Nernst equation An equation that corrects standard electrode potentials for nonstandard conditions.

Nickel–cadmium cell (nicad battery) A dry cell in which the anode is Cd, the cathode is NiO_2, and the electrolyte is basic.

Polarization of an electrode Buildup of a product of oxidation or reduction at an electrode, preventing further reaction.

Primary voltaic cell A voltaic cell that cannot be recharged; no further chemical reaction is possible once the reactants are consumed.

Sacrificial anode A more active metal that is attached to a less active metal to protect the less active metal cathode against corrosion.

Salt bridge A U-shaped tube containing an electrolyte that connects two half-cells of a voltaic cell.

Secondary voltaic cell A voltaic cell that can be recharged; the original reactants can be regenerated by reversing the direction of current flow.

Standard cell A cell in which all reactants and products are in their thermodynamic standard states (1 *M* for solution species and 1 atm partial pressure for gases).

Standard cell potential The potential difference, E^0_{cell}, between standard reduction and oxidation half-cells.

Standard electrochemical conditions 1 *M* concentration for solution species, 1 atm partial pressure for gases, and pure solids and liquids.

Standard electrode A half-cell in which the oxidized and reduced forms of a species are present at unit activity: 1 *M* solutions of dissolved species, 1 atm partial pressure of gases, and pure solids and liquids.

Standard electrode potential By convention, the potential (E^0) of a half-reaction as a reduction relative to the standard hydrogen electrode, when all species are present at unit activity.

Standard hydrogen electrode (SHE) An electrode consisting of a platinum electrode that is immersed in a 1 *M* H^+ solution and that has H_2 gas bubbled over it at 1 atm pressure; defined as the reference electrode, with a potential of *exactly* 0.0000 . . . volt.

Voltage Potential difference between two electrodes; a measure of the chemical potential for a redox reaction to occur.

Voltaic cell An electrochemical cell in which spontaneous chemical reactions produce electricity; also called a galvanic cell.

Exercises

Redox Review and General Concepts

1. (a) Define oxidation and reduction in terms of electron gain or loss. (b) What is the relationship between the numbers of electrons gained and lost in a redox reaction? (c) Do all electrochemical cells involve redox reactions?

2. Define and illustrate (a) oxidizing agent and (b) reducing agent.

3. For each of the following unbalanced equations, (i) write the half-reactions for oxidation and for reduction, and (ii) balance the overall equation in acidic solution using the half-reaction method.

(a) $Hg^{2+} + Cu \longrightarrow Hg + Cu^{2+}$

(b) $MnO_2 + Cl^- \longrightarrow Mn^{2+} + Cl_2$

(c) $Sn^{2+} + O_2 \longrightarrow Sn^{4+} + H_2O$

4. For each of the following unbalanced equations, (i) write the half-reactions for oxidation and reduction, and (ii) balance the overall equation using the half-reaction method.

(a) $FeS + NO_3^- \longrightarrow NO + SO_4^{2-} + Fe^{2+}$ (acidic solution)

(b) $Cr_2O_7^{2-} + Sn^{2+} \longrightarrow Cr^{3+} + Sn^{4+}$ (acidic solution)

(c) $S^{2-} + Cl_2 + OH^- \longrightarrow SO_4^{2-} + Cl^- + H_2O$ (basic solution)

5. (a) Compare and contrast ionic conduction and metallic conduction. (b) What is an electrode? (c) What is an inert electrode?

6. Support or refute each of the following statements: (a) In any electrochemical cell the positive electrode is the one toward which the electrons flow through the wire. (b) The cathode is the negative electrode in any electrochemical cell.

7. For each of the following unbalanced equations, (i) write the half-reactions for oxidation and reduction, (ii) identify the species that lose and the species that gain electrons, and (iii) write the balanced net ionic equation for the overall reaction.

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

(b) $NO_2^-(aq) + Cr_2O_7^{2-}(aq) \longrightarrow NO_3^-(aq) + Cr^{3+}(aq)$ (acidic solution)

(c) $N_2O_4(aq) + Br^-(aq) \longrightarrow NO_2^-(aq) + Br_3^-(aq)$ (basic solution)

8. For each of the following unbalanced equations, (i) write the half-reactions for oxidation and reduction, (ii) identify the species that lose and the species that gain electrons, and (iii) write the balanced net ionic equation for the overall reaction.

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

(b) $MnO_4^-(aq) + Cu(s) \longrightarrow Cu^{2+}(aq) + Mn^{2+}(aq)$ (acidic solution)

(c) $Cr(OH)_3(s) + IO_3^-(aq) \longrightarrow I^-(aq) + CrO_4^{2-}(aq)$ (basic solution)

Electrolytic Cells: General Concepts

9. (a) Solids such as potassium bromide, KBr, and sodium nitrate, $NaNO_3$, do not conduct electric current even though they are ionic. Why? Can these substances be electrolyzed as solids? (b) Support or refute the statement that the Gibbs free energy change, ΔG, is positive for any electrolysis reaction.

10. (a) Metallic magnesium cannot be obtained by electrolysis of aqueous magnesium chloride, $MgCl_2$. Why? (b) There are no sodium ions in the overall cell reaction for the electrolysis of aqueous sodium chloride. Why?

11. Consider the electrolysis of molten aluminum oxide, Al_2O_3, dissolved in cryolite, Na_3AlF_6, with inert electrodes. This is the Hall–Héroult process for commercial production of aluminum (Section 22-6). The following experimental observations can be made when current is supplied:

(i) Silvery metallic aluminum is produced at one electrode.

(ii) Oxygen, O_2, bubbles off at the other electrode.

Diagram the cell, indicating the anode, the cathode, the positive and negative electrodes, the half-reaction occurring at each electrode, the overall cell reaction, and the direction of electron flow through the wire.

12. Do the same as in Exercise 11 for the electrolysis of molten calcium chloride with inert electrodes. The observations are

(i) Bubbles of pale green chlorine gas, Cl_2, are produced at one electrode.

(ii) Silvery white molten metallic calcium is produced at the other electrode.

13. Do the same as in Exercise 11 for the electrolysis of aqueous potassium sulfate, K_2SO_4. The observations are

(i) Bubbles of gaseous hydrogen are produced at one electrode, and the solution becomes more basic around that electrode.

(ii) Bubbles of gaseous oxygen are produced at the other electrode, and the solution becomes more acidic around that electrode.

14. Do the same as in Exercise 11 for the electrolysis of an aqueous solution of copper(II) bromide, $CuBr_2$. The observations are

(i) One electrode becomes coated with copper metal, and the color of the solution around that electrode fades.

(ii) Around the other electrode, the solution turns brown, as bromine is formed and dissolves in water.

15. (a) Write the equation for the half-reaction when H_2O is reduced in an electrochemical cell. (b) Write the equation for the half-reaction when H_2O is oxidized in an electrochemical cell.

Faraday's Law

16. What are (a) a coulomb, (b) electric current, (c) an ampere, and (d) a faraday?

17. Calculate the number of electrons that have a total charge of 1 coulomb.

18. For each of the following cations, calculate (i) the number of faradays required to produce 1.00 mol of free metal and (ii) the number of coulombs required to produce 1.00 g of free metal. (a) Cr^{3+}, (b) Hg^{2+}, (c) $Hg_2{}^{2+}$.

19. For each of the following cations, calculate (i) the number of faradays required to produce 1.00 mol of free metal and (ii) the number of coulombs required to produce 1.00 g of free metal. (a) Mg^{2+}, (b) Al^{3+}, (c) K^+.

20. In 500. min 3.00 g of copper is obtained by electrolysis of a copper(I) nitrate solution. (a) How many amperes is required for this experiment? (b) Using the same current and time, what mass of copper would be obtained from a copper(II) nitrate solution?

21. A mass of 1.50 g of silver is plated from a silver nitrate solution in 1.5 h. Calculate the (a) coulombs, (b) faradays, and (c) amperes necessary for this process.

22. Rhodium is an element that has the appearance of silver, but does not tarnish like silver and, because it is very hard, does not become worn or scratched like silver. What mass of rhodium could be plated by electrolysis of a $Rh(NO_3)_3$ solution with a 0.75-A current for 10.0 min?

23. Hydrogen may be the fuel of the future for automobiles according to some experts. Hydrogen can be isolated from water by electrolysis. Calculate the mass of hydrogen that is released when 1.50 amperes is passed through salt water for 8 h.

24. The mass of silver deposited on a spoon during electroplating was 0.855 mg. How much electric charge passed through the cell?

25. What mass of platinum could be plated onto a ring from the electrolysis of a platinum(II) salt with a 0.385-A current for 125.0 s?

26. What mass of silver could be plated onto a spoon from electrolysis of silver nitrate with a 2.50-A current for 25.0 min?

***27.** We pass enough current through a solution to plate out *one* mole of nickel metal from a solution of $NiSO_4$. In other electrolysis cells, this same current plates out *two* moles of silver from $AgNO_3$ solution but liberates only *one-half* mole of O_2 gas. Explain these observations.

***28.** A current is passed through 500. mL of a solution of CaI_2. The following electrode reactions occur:

$$\begin{aligned} &\text{anode:} && 2I^- \longrightarrow I_2 + 2e^- \\ &\text{cathode:} && 2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \end{aligned}$$

After some time, analysis of the solution shows that 51.5 mmol of I_2 has been formed. (a) How many faradays of charge have passed through the solution? (b) How many coulombs? (c) What volume of dry H_2 at STP has been formed? (d) What is the pH of the solution?

29. The cells in an automobile battery were charged at a steady current of 5.0 A for exactly 4 h. What masses of Pb and PbO_2 were formed in each cell? The overall reaction is

$$2PbSO_4(s) + 2H_2O(\ell) \longrightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(aq)$$

***30.** The chemical equation for the electrolysis of a fairly concentrated brine solution is

$$2NaCl(aq) + 2H_2O(\ell) \longrightarrow Cl_2(g) + H_2(g) + 2NaOH(aq)$$

What volume of gaseous chlorine would be generated at 752 torr and 5°C if the process were 88% efficient and if a current of 1.5 A flowed for 5.0 h?

31. An electrolytic cell contains 40.0 mL of a 0.152 *M* solution of $FeCl_3$. A current of 0.620 A is passed through the cell, causing deposition of Fe(s) at the cathode. What is the concentration of $Fe^{3+}(aq)$ in the cell after this current has run for 20.0 min?

32. Suppose 250. mL of a 0.433 *M* solution of $CuCl_2$ is electrolyzed. How long will a current of 0.75 A have to run in order to reduce the concentration of Cu^{2+} to 0.167 *M*? What mass of Cu(s) will be deposited on the cathode during this time?

33. What is the charge on an ion of tin if 7.42 g of metallic tin is plated out by the passage of 24,125 C through a solution containing the ion?

***34.** Three electrolytic cells are connected in series; that is, the same current passes through all three, one after another. In the first cell, 1.20 g of Cd is oxidized to Cd^{2+}; in the second, Ag^+ is reduced to Ag; in the third, Fe^{2+} is oxidized to Fe^{3+}. (a) Find the number of faradays passed through the circuit. (b) What mass of Ag is deposited at the cathode in the second cell? (c) What mass of $Fe(NO_3)_3$ could be recovered from the solution in the third cell?

Voltaic Cells: General Concepts

35. What does voltage measure? How does it vary with time in a primary voltaic cell? Why?

36. (a) Why must the solutions in a voltaic cell be kept separate and not allowed to mix? (b) What are the functions of a salt bridge?

37. A voltaic cell containing a standard Fe^{3+}/Fe^{2+} electrode and a standard Ga^{3+}/Ga electrode is constructed, and the circuit is closed. Without consulting the table of standard reduction potentials, diagram and completely describe the cell from the following experimental observations. (i) The mass of the gallium electrode decreases, and the gallium ion concentration increases around that electrode. (ii) The ferrous ion, Fe^{2+}, concentration increases in the other electrode solution.

38. Repeat Exercise 37 for a voltaic cell that contains standard Co^{2+}/Co and Au^{3+}/Au electrodes. The observations are: (i) Metallic gold plates out on one electrode, and the gold ion concentration decreases around that electrode. (ii) The mass of the cobalt electrode decreases, and the cobalt(II) ion concentration increases around that electrode.

39. Appendix J lists selected reduction potentials in volts at 25°C. Why is it not necessary to list a mixture of reduction and oxidation potentials?

***40.** In Section 4-8 we learned how to predict from the activity series (Table 4-12) which metals replace which others from aqueous solutions. From that table, we predict that zinc will displace silver. The equation for this process is

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

Suppose we set up a voltaic cell based on this reaction. (a) What half-reaction would represent the reduction in this cell? (b) What half-reaction would represent the oxidation? (c) Which metal would be the anode? (d) Which metal would be the cathode? (e) Diagram this cell.

41. In a voltaic cell made with metal electrodes, is the more active metal more likely to be the anode or the cathode? Explain.

42. When metallic copper is placed into aqueous silver nitrate, a spontaneous redox reaction occurs. No electricity is produced. Why?

43. Assume that a voltaic cell utilizes the redox reaction

$$2Al(s) + 3Cu^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Cu(s) \qquad \text{(acidic solution)}$$

Potassium and nitrate ions may also be present. Draw this voltaic cell, and label the anode, cathode, electron flow, and ion flow.

44. Assume that a voltaic cell, proposed as a method for the purification of uranium, utilizes the redox reaction

$$3Mg(s) + 2U^{3+}(aq) \longrightarrow 3Mg^{2+}(aq) + 2U(s) \qquad \text{(acidic solution)}$$

Potassium and nitrate ions may also be present. Draw this voltaic cell, and label the anode, cathode, electron flow, and ion flow.

Standard Cell Potentials

45. (a) What are standard electrochemical conditions? (b) Why are we permitted to assign arbitrarily an electrode potential of exactly 0 V to the standard hydrogen electrode?

46. What does the sign of the standard reduction potential of a half-reaction indicate? What does the magnitude indicate?

47. (a) What are standard reduction potentials? (b) What information is contained in tables of standard reduction potentials (Tables 21-2 and 21-3, Appendix J)? How is the information in such tables arranged?

48. Standard reduction potentials are 2.9 V for $F_2(g)/F^-$, 0.8 V for $Ag^+/Ag(s)$, 0.5 V for $Cu^+/Cu(s)$, 0.3 V for $Cu^{2+}/Cu(s)$, −0.4 V for $Fe^{2+}/Fe(s)$, −2.7 V for $Na^+/Na(s)$, and −2.9 V for $K^+/K(s)$. (a) Arrange the oxidizing agents in order of increasing strength. (b) Which of these oxidizing agents will oxidize Cu under standard-state conditions?

49. Standard reduction potentials are 1.455 V for the $PbO_2(s)/Pb(s)$ couple, 1.360 V for $Cl_2(g)/Cl^-$, 3.06 V for $F_2(g)/HF(aq)$, and 1.77 V for $H_2O_2(aq)/H_2O(\ell)$. Under standard-state conditions, (a) which is the strongest oxidizing agent, (b) which oxidizing agent(s) could oxidize lead to lead(IV) oxide, and (c) which oxidizing agent(s) could oxidize fluoride ion in an acidic solution?

50. Arrange the following less commonly encountered metals in an activity series from the most active to the least active: radium [$Ra^{2+}/Ra(s)$, $E^0 = -2.9$ V], rhodium [$Rh^{3+}/Rh(s)$, $E^0 = 0.80$ V], europium [$Eu^{2+}/Eu(s)$, $E^0 = -3.4$ V]. How do these metals compare in reducing ability with the active metal lithium [$Li^+/Li(s)$, $E^0 = -3.0$ V], with hydrogen, and with gold [$Au^{3+}/Au(s)$, $E^0 = 1.5$ V], which is a noble metal and one of the least active of the metals?

51. Arrange the following metals in an activity series from the most active to the least active: nobelium [$No^{3+}/No(s)$, $E^0 = -2.5$ V], cobalt [$Co^{2+}/Co(s)$, $E^0 = -0.28$ V], gallium [$Ga^{3+}/Ga(s)$, $E^0 = -0.53$ V], thallium [$Tl^+/Tl(s)$, $E^0 = -0.34$ V], polonium [$Po^{2+}/Po(s)$, $E^0 = 0.65$ V].

52. Diagram the following cells. For each cell, write the balanced equation for the reaction that occurs spontaneously, and calculate the cell potential. Indicate the direction of electron flow, the anode, the cathode, and the polarity (+ or −) of each electrode. In each case, assume that the circuit is completed by a wire and a salt bridge.
(a) A strip of magnesium is immersed in a solution that is 1.0 *M* in Mg^{2+}, and a strip of silver is immersed in a solution that is 1.0 *M* in Ag^+.
(b) A strip of nickel is immersed in a solution that is 1.0 *M* in Ni^{2+}, and a strip of silver is immersed in a solution that is 1.0 *M* in Ag^+.

53. Repeat Exercise 52 for the following cells.
(a) A strip of chromium is immersed in a solution that is 1.0 *M* in Cr^{3+}, and a strip of gold is immersed in a solution that is 1.0 *M* in Au^{3+}.
(b) A strip of aluminum is immersed in a solution that is 1.0 *M* in Al^{3+}, and a strip of copper is immersed in a solution that is 1.0 *M* in Cu^{2+}.

In answering Exercises 54–73, justify each answer by appropriate calculations. Assume that each reaction occurs at standard electrochemical conditions.

54. (a) Will Fe^{3+} oxidize Sn^{2+} to Sn^{4+} in acidic solution? (b) Will dichromate ions oxidize fluoride ions to free fluorine in acidic solution?

55. (a) Will dichromate ions oxidize arsenous acid, H_3AsO_3, to arsenic acid, H_3AsO_4, in acid solution? (b) Will dichromate ions oxidize hydrogen peroxide, H_2O_2, to free oxygen, O_2, in acidic solution?

56. (a) Will permanganate ions oxidize Cr^{3+} to $Cr_2O_7{}^{2-}$ in acidic solution? (b) Will sulfate ions oxidize arsenous acid, H_3AsO_3, to arsenic acid, H_3AsO_4, in acid solution?

57. Calculate the standard cell potential, E^0_{cell} for the cell described in Exercise 37.

58. Calculate the standard cell potential, E^0_{cell}, for the cell described in Exercise 38.

59. (a) Write the equation for the oxidation of Zn(s) by $Br_2(\ell)$. (b) Calculate the potential of this reaction under standard-state conditions. (c) Is this a spontaneous reaction?

60. For each of the following cells, (i) write the net reaction in the direction consistent with the way the cell is written; (ii) write the half-reactions for the anode and cathode processes; (iii) find the standard cell potential, E^0_{cell}, at 25°C; and (iv) tell whether the standard cell reaction actually occurs as given or in the reverse direction.
(a) $Cr|Cr^{3+}||Sn^{2+}|Sn$
(b) $Ag|Ag^{+}||Cd^{2+}|Cd$

61. Repeat Exercise 60 for the following cells:
(a) $Al|Al^{3+}||Ce^{4+}, Ce^{3+}|Pt$
(b) $Zn|Zn^{2+}||Ni^{2+}|Ni$

62. Which of the following reactions are spontaneous in voltaic cells under standard conditions?
(a) $H_2(g) \longrightarrow H^+(aq) + H^-(aq)$
(b) $Zn(s) + 4CN^-(aq) + Ag_2CrO_4(s) \longrightarrow Zn(CN)_4{}^{2-}(aq) + 2Ag(s) + CrO_4{}^{2-}(aq)$
(c) $MnO_2(s) + 4H^+(aq) + Sr(s) \longrightarrow Mn^{2+}(aq) + 2H_2O(\ell) + Sr^{2+}(aq)$
(d) $Cl_2(g) + 2H_2O(\ell) + ZnS(s) \longrightarrow 2HOCl(aq) + H_2S(aq) + Zn(s)$

63. Consult a table of standard reduction potentials, and determine which of the following reactions are spontaneous under standard electrochemical conditions.
(a) $Mn(s) + 2H^+(aq) \longrightarrow H_2(g) + Mn^{2+}(aq)$
(b) $2Al^{3+}(aq) + 3H_2(g) \longrightarrow 2Al(s) + 6H^+(aq)$
(c) $2Cr(OH)_3(s) + 6F^-(aq) \longrightarrow 2Cr(s) + 6OH^-(aq) + 3F_2(g)$
(d) $Cl_2(g) + 2Br^-(aq) \longrightarrow Br_2(\ell) + 2Cl^-(aq)$

64. Which of each pair is the stronger reducing agent? (a) Ag or H_2, (b) Sn or Pb, (c) Hg or Au, (d) Cl^- in acidic solution or Cl^- in basic solution, (e) HCl or H_2S, (f) Ag or Au

65. Which of each pair is the stronger oxidizing agent? (a) Cu^+ or Ag^+, (b) Sn^{2+} or Sn^{4+}, (c) Fe^{2+} or Fe^{3+}, (d) I_2 or Br_2, (e) $MnO_4{}^-$ in acidic solution or $MnO_4{}^-$ in basic solution, (f) H^+ or Cl_2

***66.** The element ytterbium forms both 2+ and 3+ cations in aqueous solution. $E^0 = -2.797$ V for $Yb^{2+}/Yb(s)$, and -2.267 V for $Yb^{3+}/Yb(s)$. What is the standard-state reduction potential for the Yb^{3+}/Yb^{2+} couple?

***67.** The standard reduction potential for Cu^+ to Cu(s) is 0.521 V, and for Cu^{2+} to Cu(s) it is 0.337 V. Calculate the E^0 value for the Cu^{2+}/Cu^+ couple.

68. Consider a suggestion for purifying uranium without an outside energy source by setting up a voltaic cell with the reaction

$$3Mg(s) + 2U^{3+}(aq) \longrightarrow 3Mg^{2+}(aq) + 2U(s) \qquad \text{(acidic solution)}$$

The standard reduction potentials are −1.798 for the uranium half-reaction and −2.714 for the magnesium half-reaction. (a) Will this setup work spontaneously? (b) Calculate the voltage produced by this cell as written.

69. A reaction is proposed for a nickel–cadmium battery as

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

(a) Is the reaction spontaneous as written? (b) Calculate the voltage produced by this voltaic cell as written.

70. Selecting from half-reactions involving the following species, write the spontaneous reaction that will produce the voltaic cell with the highest voltage in an acidic solution: Li^+, Ba^{2+}, Ni^{2+}, H_2O_2, and F_2.

71. Propose the spontaneous reaction that will produce the voltaic cell with the highest voltage output by choosing from only reduction and oxidation potentials involving: $MnO_4{}^-$ and MnO_2, HgO and Hg, Ag_2O and Ag, S and S^{2-}, and $SO_4{}^{2-}$ and $SO_3{}^{2-}$.

72. Tarnished silver is coated with a layer of $Ag_2S(s)$. The coating can be removed by boiling the silverware in an aluminum pan, with some baking soda or salt added to make the solution conductive. Explain this from the point of view of electrochemistry.

***73.** Describe the process of corrosion. How can corrosion of an easily oxidizable metal be prevented if the metal must be exposed to the weather?

Concentration Effects; Nernst Equation

For cell voltage calculations, assume that the temperature is 25°C unless stated otherwise.

***74.** How is the Nernst equation of value in electrochemistry? How would the Nernst equation be modified if we wished to use natural logarithms, ln? What is the value of the constant in the following equation at 25°C?

$$E = E^0 - \frac{\text{constant}}{n} \ln Q$$

75. Identify all of the terms in the Nernst equation. What part of the Nernst equation represents the correction factor for nonstandard electrochemical conditions?

76. By putting the appropriate values into the Nernst equation, show that it predicts that the voltage of a standard half-cell is equal to E^0. Use the Zn^{2+}/Zn reduction half-cell as an illustration.

77. Calculate the potential associated with the following half-reaction when the concentration of the cobalt(II) ion is 1.0×10^{-3} *M*.

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

78. Calculate the reduction potential for hydrogen ion in a system having a perchloric acid concentration of 2.00×10^{-4} *M* and a hydrogen pressure of 2.50 atm. (Recall that $HClO_4$ is a strong acid in aqueous solution.)

79. The standard reduction potentials for the $H^+/H_2(g)$ and $O_2(g)$, $H^+/H_2O(\ell)$ couples are 0.0000 V and 1.229 V, respectively.

(a) Write the half-reactions and the overall reaction, and calculate E^0 for the reaction

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

(b) Calculate *E* for the cell when the pressure of H_2 is 3.00 atm and that of O_2 is 1.30 atm.

80. Consider the cell represented by the notation

$$Zn(s)|ZnCl_2(aq)||Cl_2(g,\ 1\ atm);\ Cl^-(aq)|C$$

Calculate (a) E^0 and (b) *E* for the cell when the concentration of the $ZnCl_2$ is 0.25 mol/L.

81. What is the concentration of Ag^+ in a half-cell if the reduction potential of the Ag^+/Ag couple is observed to be 0.45 V?

82. What must be the pressure of fluorine gas to produce a reduction potential of 2.75 V in a solution that contains 0.38 *M* F^-?

83. Calculate the cell potential of each of the following electrochemical cells at 25°C.

(a) $Sn(s)|Sn^{2+}(4.5 \times 10^{-3}\ M)||Ag^+(0.110\ M)|Ag(s)$

(b) $Zn(s)|Zn^{2+}(0.500\ M)||$ $Fe^{3+}\ (7.2 \times 10^{-6}\ M),\ Fe^{2+}(0.15\ M)|Pt$

(c) $Pt|H_2(1\ atm)|HCl(0.00880\ M)|Cl_2(1\ atm)|Pt$

84. Calculate the cell potential of each of the following electrochemical cells at 25°C.

(a) $Pt|H_2(10.0\ atm),\ H^+(1.00 \times 10^{-3}\ M)||$ $Ag^+(0.00549\ M)|Ag(s)$

(b) $Pt|H_2(1.00\ atm),\ H^+(pH = 5.97)||$ $H^+(pH = 3.47),\ H_2(1.00\ atm)|Pt$

(c) $Pt|H_2(0.0361\ atm),\ H^+(0.0100\ M)||$ $H^+(0.0100\ M),\ H_2(5.98 \times 10^{-4}\ atm)|Pt$

***85.** Find the potential of the cell in which identical iron electrodes are placed into solutions of $FeSO_4$ of concentration 1.5 mol/L and 0.15 mol/L.

***86.** We construct a cell in which identical copper electrodes are placed in two solutions. Solution A contains 0.75 *M* Cu^{2+}. Solution B contains Cu^{2+} at some concentration known to be lower than that in solution A. The potential of the cell is observed to be 0.040 V. What is $[Cu^{2+}]$ in solution B?

***87.** We construct a standard copper–cadmium cell, close the circuit, and allow the cell to operate. At some later time, the cell voltage reaches zero, and the cell is "run down." (a) What will be the ratio of $[Cd^{2+}]$ to $[Cu^{2+}]$ at that time? (b) What will be the concentrations?

***88.** Repeat Exercise 87 for a standard zinc–nickel cell.

***89.** The cell potential for the cell

$$Zn(s) + 2H^+(\underline{?}\ M) \longrightarrow Zn^{2+}\ (3.0\ M) + H_2(g)\ (5.0\ atm)$$

is observed to be 0.445 V. What is the pH in the H^+/H_2 half-cell?

90. We wish to produce a 0.375-volt concentration cell using two hydrogen electrodes, both with hydrogen at a pressure of one atmosphere. One of the solutions has a pH of 1.5. Calculate the required pH of the other solution.

91. A concentration cell prepared using two hydrogen electrodes, both with the partial pressure of hydrogen being one atmosphere, produces 0.450 volts. The pH of one hydrogen electrode is 1.65; what is the pH of the other?

Relationships Among ΔG^0, E^0_{cell}, and *K*

92. How are the signs and magnitudes of E^0_{cell}, ΔG^0, and *K* related for a particular reaction? Why is the equilibrium constant *K* related only to E^0_{cell} and not to E_{cell}?

93. In light of your answer to Exercise 92, how do you explain the fact that ΔG^0 for a redox reaction *does* depend on the number of electrons transferred, according to the equation $\Delta G^0 = -nFE^0_{cell}$?

94. Calculate E^0_{cell} from the tabulated standard reduction potentials for each of the following reactions in aqueous solution. Then calculate ΔG^0 and *K* at 25°C from E^0_{cell}. Which reactions are spontaneous as written?

(a) $MnO_4^- + 5Fe^{2+} \longrightarrow Mn^{2} + 5Fe^{3+}$ (acidic solution)

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

(c) $3Zn(s) + 2MnO_4^- + 4H_2O \longrightarrow 2MnO_2(s) + 3Zn(OH)_2(s) + 2OH^-$

95. Calculate ΔG^0 (overall) and ΔG^0 per mole of metal for each of the following reactions from E^0 values.

(a) Zinc dissolves in dilute hydrochloric acid to produce a solution that contains Zn^{2+}, and hydrogen gas is evolved.

(b) Chromium dissolves in dilute hydrochloric acid to produce a solution that contains Cr^{3+}, and hydrogen gas is evolved.
(c) Silver dissolves in dilute nitric acid to form a solution that contains Ag^+, and NO is liberated as a gas.
(d) Lead dissolves in dilute nitric acid to form a solution that contains Pb^{2+}, and NO is liberated as a gas.

96. Use tabulated reduction potentials to calculate the value of the equilibrium constant for the reaction

$$Sn^{4+} + 2Fe^{2+} \rightleftharpoons Sn^{2+} + 2Fe^{3+}$$

97. Use tabulated reduction potentials to calculate the equilibrium constant for the reaction

$$2I^- + Cl_2(g) \rightleftharpoons I_2(s) + 2Cl^-$$

98. Using the following half-reactions and E^0 data at 25°C:

$$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4{}^{2-} \quad E^0 = -0.356\text{ V}$$
$$PbI_2(s) + 2e^- \longrightarrow Pb(s) + 2I^- \quad E^0 = -0.365\text{ V}$$

calculate the equilibrium constant for the reaction

$$PbSO_4(s) + 2I^- \rightleftharpoons PbI_2(s) + SO_4{}^{2-}$$

Practical Aspects of Electrochemistry

99. Distinguish among (a) primary voltaic cells, (b) secondary voltaic cells, and (c) fuel cells.

100. Sketch and describe the operation of (a) the Leclanché dry cell, (b) the lead storage battery, and (c) the hydrogen–oxygen fuel cell.

101. Why is the dry cell designed so that Zn and MnO_2 do not come into contact? What reaction might occur if they were in contact? How would this reaction affect the usefulness of the cell?

***102.** People sometimes try to recharge dry cells, with limited success. (a) What reaction would you expect at the zinc electrode of a Leclanché cell in an attempt to recharge it? (b) What difficulties would arise from the attempt?

103. Briefly describe how a storage cell operates.

104. How does a fuel cell differ from a dry cell or a storage cell?

105. Does the physical size of a commercial cell govern the potential that it will deliver? What does the size affect?

Mixed Exercises

106. Consider the electrochemical cell represented by $Mg(s)|Mg^{2+}||Fe^{3+}|Fe(s)$. (a) Write the ion–electron equations for the half-reactions and the overall cell equation. (b) The standard reduction potential for $Fe^{3+}/Fe(s)$ is -0.036 V at 25°C. Determine the standard potential for the reaction. (c) Determine E for the cell when the concentration of Fe^{3+} is 10.0 mol/L and that of Mg^{2+} is 1.00×10^{-3} mol/L. (d) If 150 mA is to be drawn from this cell for a period of 20.0 min, what is the minimum mass for the magnesium electrode?

107. A sample of Al_2O_3 dissolved in a molten fluoride bath is electrolyzed using a current of 1.20 A. (a) What is the rate of production of Al in g/h? (b) The oxygen liberated at the positive carbon electrode reacts with the carbon to form CO_2. What mass of CO_2 is produced per hour?

***108.** The "life" of a certain voltaic cell is limited by the amount of Cu^{2+} in solution available to be reduced. If the cell contains 30.0 mL of 0.165 M $CuSO_4$, what is the maximum amount of electric charge this cell could generate?

109. A magnesium bar weighing 5.0 kg is attached to a buried iron pipe to protect the pipe from corrosion. An average current of 0.025 A flows between the bar and the pipe. (a) What reaction occurs at the surface of the bar? of the pipe? In which direction do electrons flow? (b) How many years will be required for the Mg bar to be entirely consumed (1 year = 3.16×10^7 s)? (c) What reaction(s) will occur if the bar is not replaced after the time calculated in part (b)?

110. (a) Calculate the ratio of ion concentrations of Mn^{2+} and Fe^{2+} necessary to produce a voltaic cell of 1.56 volts. The electrodes are solid manganese and iron. (b) Draw this voltaic cell. Indicate which electrode is the anode and which is the cathode, as well as the direction of electron flow.

111. (a) Calculate the ratio of ion concentrations of Mg^{2+} and Cu^{2+} necessary to produce a voltaic cell of 2.67 volts. The electrodes are solid magnesium and solid copper. (b) Draw this voltaic cell. Indicate which electrode is the anode and which is the cathode, as well as the direction of electron flow.

112. The production of uranium metal from purified uranium dioxide ore consists of the following steps:

$$UO_2(s) + 4HF(g) \longrightarrow UF_4(s) + 2H_2O(\ell)$$
$$UF_4(s) + 2Mg(s) \xrightarrow{\text{heat}} U(s) + 2MgF_2(s)$$

What is the oxidation number of U in (a) UO_2, (b) UF_4, and (c) U? Identify (d) the reducing agent and (e) the substance reduced. (f) What current could the second reaction produce if 0.500 g of UF_4 reacted each minute? (g) What volume of HF(g) at 25°C and 10.0 atm would be required to produce 0.500 g of U? (h) Would 0.500 g of Mg be enough to produce 0.500 g of U?

113. Which of each pair is the stronger oxidizing agent? (a) H^+ or Cl_2, (b) Ni^{2+} or Se in contact with acidic solution, (c) $Cr_2O_7{}^{2-}$ or Br_2 (acidic solution).

114. (a) Describe the process of electroplating. (b) Sketch and label an apparatus that a jeweler might use for electroplating silver onto jewelry. (c) A jeweler purchases highly purified silver to use as the anode in an electroplating operation. Is this a wise purchase? Why?

115. The same quantity of electric charge that deposited 0.612 g of silver was passed through a solution of a gold salt, and 0.373 g of gold was deposited. What is the oxidation state of gold in this salt?

CONCEPTUAL EXERCISES

116. Household electricity is an alternating current of 60 cycles per second. Can a redox reaction be used to provide an alternating current? Explain.

117. Electroplating is performed by using a source of direct current. (a) Why can't an alternating current be used? (b) What would happen if an alternating current were used for electroplating?

118. Figure 21-5 is a schematic diagram of the electrolytic cell used to separate copper from the impurities, that is, zinc, iron, silver, gold, and platinum. Can this process be used to separate the metals left after the copper has been removed? Explain.

119. A zinc–copper cell like that shown in Figure 21-7 is constructed, except that an inert platinum wire is used instead of the salt bridge. Will the cell still produce a potential?

BUILDING YOUR KNOWLEDGE

120. An electrochemical cell was needed in which hydrogen and oxygen would react to form water. (a) Using the following standard reduction potentials for the couples given, determine which combination of half-reactions gives the maximum output potential:

$E^0 = -0.828$ V for $H_2O(\ell)/H_2(g), OH^-$

$E^0 = 0.0000$ V for $H^+/H_2(g)$

$E^0 = 1.229$ V for $O_2(g), H^+/H_2O(\ell)$

$E^0 = 0.401$ V for $O_2(g), H_2O(\ell)/OH^-$

(b) Write the balanced equation for the overall reaction in (a).

121. (a) Given the following E^0 values at 25°C, calculate K_{sp} for cadmium sulfide, CdS.

$$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s) \qquad E^0 = -0.403\text{ V}$$

$$CdS(s) + 2e^- \longrightarrow Cd(s) + S^{2-}(aq) \qquad E^0 = -1.21\text{ V}$$

(b) Evaluate ΔG^0 at 25°C for the process

$$CdS(s) \rightleftharpoons Cd^{2+}(aq) + S^{2-}(aq)$$

122. Refer to tabulated reduction potentials. (a) Calculate K_{sp} for AgBr(s). (b) Calculate ΔG^0 for the reaction

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$$

***123.** Under standard-state conditions, the following reaction is not spontaneous:

$$Br^- + 2MnO_4^- + H_2O(\ell) \longrightarrow BrO_3^- + 2MnO_2(s) + 2OH^- \qquad E^0 = -0.022\text{ V}$$

The reaction conditions are adjusted so that $E = 0.120$ V by making $[Br^-] = [MnO_4^-] = 1.60$ mol/L and $[BrO_3^-] = 0.60$ mol/L. (a) What is the concentration of hydroxide ions in this cell? (b) What is the pH of the solution in the cell?

124. Show by calculation that $E^0 = -1.662$ V for the reduction of Al^{3+} to Al(s), regardless of whether the equation for the reaction is written

(i) $\frac{1}{3}Al^{3+} + e^- \longrightarrow \frac{1}{3}Al(s) \qquad \Delta G^0 = 160.4$ kJ/mol

or

(ii) $Al^{3+} + 3e^- \longrightarrow Al(s) \qquad \Delta G^0 = 481.2$ kJ/mol

125. We wish to fill a balloon with H_2 at a pressure of 1.05 atm and a temperature of 25°C. The volume of the balloon, when filled, is 750 mL. How long must a current of 2.25 A be passed through the cell in order to produce this amount of H_2 by electrolysis of water?