

$$(2) E^\circ = E_{\text{ox}}^\circ \text{Zn} + E_{\text{red}}^\circ \text{H}^+ = +0.762 \text{ V}$$

(3) All that remains is to substitute for E , E_{tot}° , $[\text{Zn}^{2+}]$, P_{H_2} , and solve for $[\text{H}^+]$:

$$+0.560 \text{ V} = +0.762 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{1 \times 1}{[\text{H}^+]^2}$$

Solving

$$\ln \frac{1}{[\text{H}^+]^2} = \frac{2(+0.560 - 0.762)}{-0.0257} = 15.7$$

$$\frac{1}{[\text{H}^+]^2} = 7 \times 10^6 \quad [\text{H}^+] = 4 \times 10^{-4} \text{ M}$$

Reality Check Notice that the concentration of H^+ , a reactant, is much less than 1 M. That explains why the cell voltage, +0.560 V, is less than the standard voltage, +0.762 V.

As Example 18.7 implies, the $\text{Zn}|\text{Zn}^{2+}||[\text{H}^+]\text{H}_2|\text{Pt}$ cell can be used to measure the concentration of H^+ or pH of a solution. Indeed, cells of this type are commonly used to measure pH; Figure 18.7 shows a schematic diagram of a cell used with a pH meter. The pH meter, referred to in Chapter 13, is actually a high-resistance voltmeter calibrated to read pH rather than voltage. The cell connected to the pH meter consists of two half-cells. One of these is a reference half-cell of known voltage. The other half-cell contains a solution of known pH separated by a thin, fragile *glass electrode* from a solution whose pH is to be determined. The voltage of this cell is a linear function of the pH of the solution in the beaker.

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

The general approach illustrated by Example 18.7 is widely used to determine equilibrium constants for solution reactions. The pH meter in particular can be used to determine acid or base equilibrium constants by measuring the pH of solutions containing known concentrations of weak acids or bases. Specific ion electrodes are readily adapted to the determination of solubility product constants. For example, a chloride ion electrode can be used to find $[\text{Cl}^-]$ in equilibrium with $\text{AgCl}(\text{s})$ and a known $[\text{Ag}^+]$. From that information, K_{sp} of AgCl can be calculated.

18.5 ELECTROLYTIC CELLS

In an **electrolytic cell**, a nonspontaneous redox reaction is made to occur by pumping electrical energy into the system. A generalized diagram for such a cell is shown in Figure 18.8. The storage battery at the left provides a source of direct electric current. From the terminals of the battery, two wires lead to the electrolytic cell. This consists of two electrodes, A and C, dipping into a solution containing ions M^+ and X^- .

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

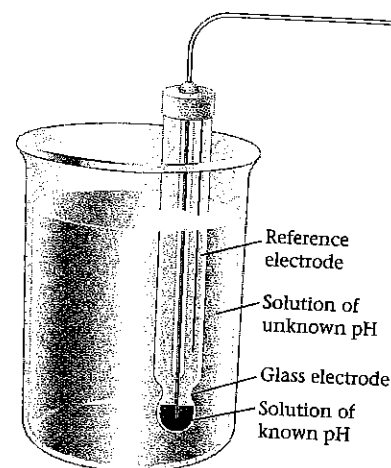


FIGURE 18.7 Electrode for a pH meter. The pH of a solution can be determined with the aid of a "glass electrode." The voltage between the glass electrode and the reference electrode is directly related to pH. The leads from the electrodes are connected to a pH meter. **OH!**

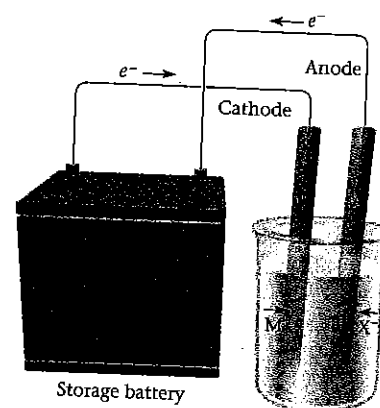


FIGURE 18.8 Diagram of an electrolytic cell. Electrons enter the cathode from an external source. Cations move to the cathode, where they are reduced, and anions move to the anode, where they are oxidized. **OH!**

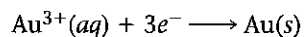
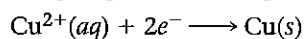
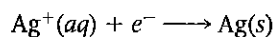
Oxidation occurs at the anode, reduction at the cathode, in both voltaic and electrolytic cells.

TABLE 18.3 Electrical Units

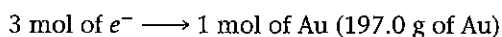
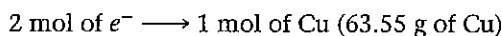
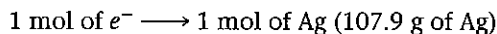
Quantity	Unit	Defining Relation	Conversion Factors
Charge	coulomb (C)	$1 \text{ C} = 1 \text{ A} \cdot \text{s} = 1 \text{ J/V}$	$1 \text{ mol } e^- = 9.648 \times 10^4 \text{ C}$
Current	ampere (A)	$1 \text{ A} = 1 \text{ C/s}$	
Potential	volt (V)	$1 \text{ V} = 1 \text{ J/C}$	
Power	watt (W)	$1 \text{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

Quantitative Relationships

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



you can deduce that



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

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

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

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

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

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

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

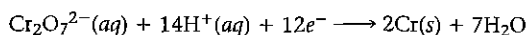
Your electric bill deals with a different unit of electrical energy called the kilowatt hour (kWh). The joule and the kilowatt hour are related through a simple conversion factor:

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

These relations and others are contained in Table 18.3.

EXAMPLE 18.8 Graded

Chromium metal can be electroplated from a water solution of potassium dichromate; the reduction half-reaction is



- (a) How many grams of chromium will be plated by 1.00×10^4 C?
 (b) How long will it take to plate one gram of chromium using a current of 6.00 A?
 (c) If the applied voltage is 4.5 V, how many kilowatt hours of electrical energy are required to plate 1.00 g of Cr?

Solution

- (a) Use a conversion factor approach: coulombs \rightarrow mol e^- \rightarrow mol Cr \rightarrow mass Cr

$$1.00 \times 10^4 \text{ C} \times \frac{1 \text{ mol } e^-}{9.648 \times 10^4 \text{ C}} \times \frac{2 \text{ mol Cr}}{12 \text{ mol } e^-} \times \frac{52.0 \text{ g Cr}}{1 \text{ mol Cr}} = 0.898 \text{ g Cr}$$

- (b) First find the number of coulombs:

$$1.00 \text{ g Cr} \times \frac{1 \text{ mol Cr}}{52.0 \text{ g Cr}} \times \frac{12 \text{ mol } e^-}{2 \text{ mol Cr}} \times \frac{9.648 \times 10^4 \text{ C}}{1 \text{ mol } e^-} = 1.11 \times 10^4 \text{ C}$$

Now find the time required:

$$t(\text{s}) = \frac{\text{charge(C)}}{\text{current(A)}} = \frac{1.11 \times 10^4 \text{ C}}{6.00 \text{ C/s}} = 1.85 \times 10^3 \text{ s (about a half-hour)}$$

- (c) In part (b) you found that 1.11×10^4 C was required to produce 1.00 g of Cr. To find the energy required in joules, multiply the voltage by the number of coulombs. Finally, convert joules to kilowatt hours.

$$\text{energy (J)} = \text{voltage (V)} \times \text{charge (C)} = (4.5 \text{ V})(1.11 \times 10^4 \text{ C}) = 5.0 \times 10^4 \text{ J}$$

$$\text{energy in kWh} = 5.0 \times 10^4 \text{ J} \times \frac{1 \text{ kWh}}{3.6 \times 10^6 \text{ J}} = 1.4 \times 10^{-2} \text{ kWh}$$

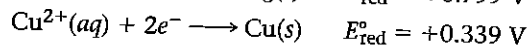
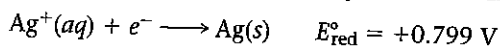
In working Example 18.8, we have in effect assumed that the electrolyses were 100% efficient in converting electrical energy into chemical energy. In practice, this is almost never the case. Some electrical energy is wasted in side reactions at the electrodes and in the form of heat. This means that the actual yield of products is less than the theoretical yield.

‡ Nobody is 100% efficient.

Cell Reactions (Water Solution)

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

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



This type of half-reaction is characteristic of electroplating processes, in which a metal object serves as the cathode (Figure 18.9, p. 492).

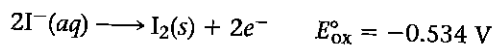
- the reduction of a water molecule to hydrogen gas



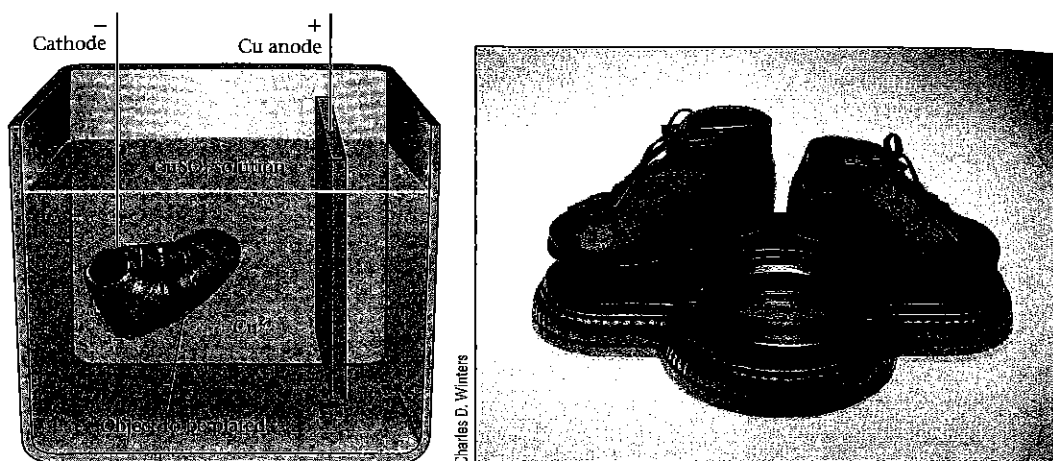
This half-reaction commonly occurs when the cation in solution is very difficult to reduce. For example, electrolysis of a solution containing K^+ ions ($E_{\text{red}}^\circ = -2.936 \text{ V}$) or Na^+ ions ($E_{\text{red}}^\circ = -2.714 \text{ V}$) yields hydrogen gas at the cathode (Table 18.4, p. 492).

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

- the oxidation of an anion to the corresponding nonmetal



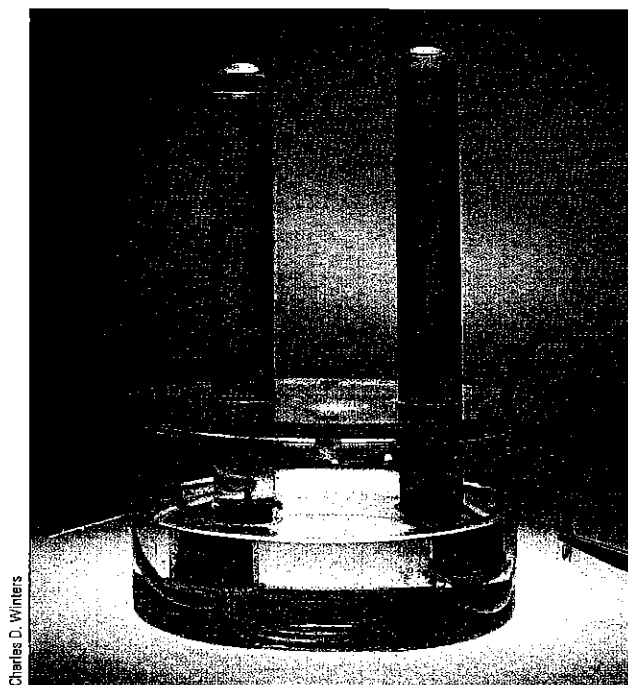
Electrolysis of a water solution of KI gives a saturated solution of iodine at the anode (see photo at bottom of page 492).

**FIGURE 18.9**

Electroplating. Copper metal can be plated onto a baby's shoe by electrolysis. The shoe's surface is coated with graphite to make it conduct electricity.

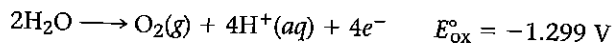
TABLE 18.4 Electrolysis of Water Solutions

Solution	Cathode Product	Anode Product
$\text{CuBr}_2(aq)$	$\text{Cu}(s)$	$\text{Br}_2(l)$
$\text{AgNO}_3(aq)$	$\text{Ag}(s)$	$\text{O}_2(g)$
$\text{KI}(aq)$	$\text{H}_2(g)$	$\text{I}_2(s)$
$\text{Na}_2\text{SO}_4(aq)$	$\text{H}_2(g)$	$\text{O}_2(g)$



Electrolysis of potassium iodide (KI) solution. The electrolysis of aqueous KI is similar to that of aqueous NaCl. The cathode reaction (*left*) is the reduction of water to $\text{H}_2(g)$ and OH^- , as shown by the pink color of phenolphthalein indicator in the water. The anode reaction (*right*) is the oxidation of $\text{I}^-(aq)$ to $\text{I}_2(aq)$, as shown by the brown color of the solution.

- the oxidation of a water molecule to oxygen gas



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

CHEMISTRY | The Human Side

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

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

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

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

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

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

Desper Collection in the History of Chemistry, University of Cincinnati



18.6 COMMERCIAL CELLS

To a chemist, electrochemical cells are of interest primarily for the information they yield concerning the spontaneity of redox reactions, the strengths of oxidizing and reducing agents, and the concentrations of trace species in solution. The viewpoint of an engineer is somewhat different; applications of electrolytic cells in

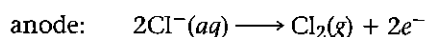
GENERAL
Chemistry Now™

Click Chemistry Interactive for the module Batteries.

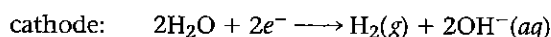
electroplating and electrosynthesis are of particular importance. To the non-scientist, electrochemistry is important primarily because of commercial voltaic cells, which supply the electrical energy for instruments ranging in size from pacemakers to automobiles.

Electrolysis of Aqueous NaCl

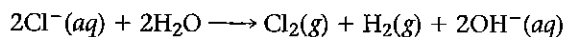
From a commercial standpoint, the most important electrolysis carried out in water solution is that of sodium chloride (Figure 18.10). At the anode, Cl^- ions are oxidized to chlorine gas:



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



The overall cell reaction is obtained by summing the half-reactions:



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

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

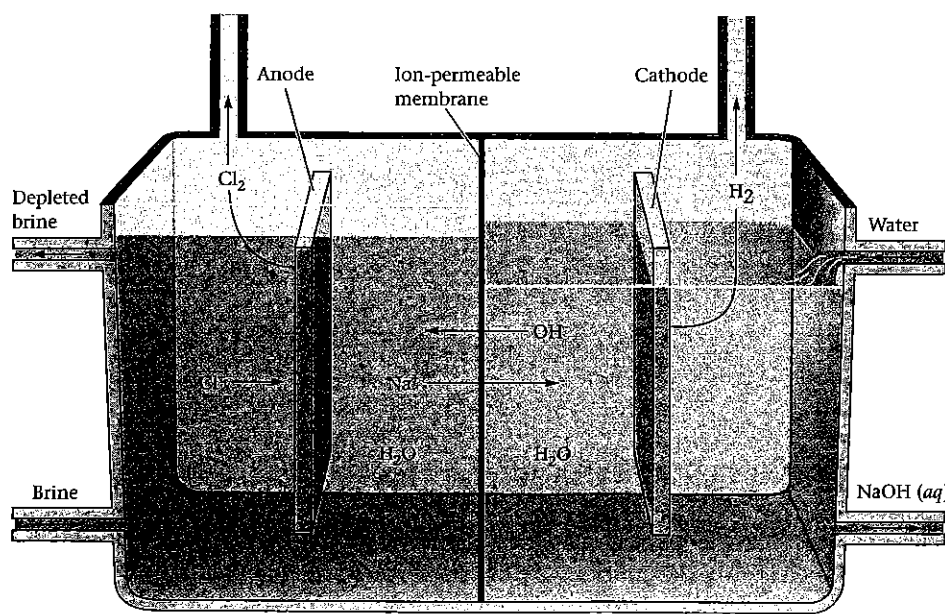
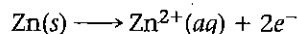


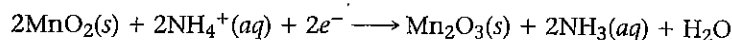
FIGURE 18.10
Electrolysis of aqueous NaCl (brine). The anode and cathode half-cells are separated by a membrane that is permeable to ions but not to water. Thus the flow of ions maintains charge balance. The products, $\text{NaOH}(aq)$, Cl_2 , and H_2 , are all valuable industrial chemicals.

Primary (Nonrechargeable) Voltaic Cells

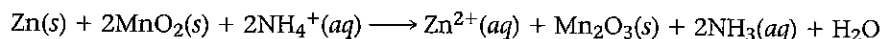
The construction of the ordinary dry cell (Leclanché cell) used in flashlights is shown in Figure 18.11. The zinc wall of the cell is the anode. The graphite rod through the center of the cell is the cathode. The space between the electrodes is filled with a moist paste. This contains MnO_2 , ZnCl_2 , and NH_4Cl . When the cell operates, the half-reaction at the anode is



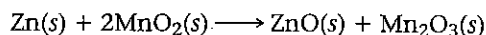
At the cathode, manganese dioxide is reduced to species in which Mn is in the +3 oxidation state, such as Mn_2O_3 :



The overall reaction occurring in this voltaic cell is

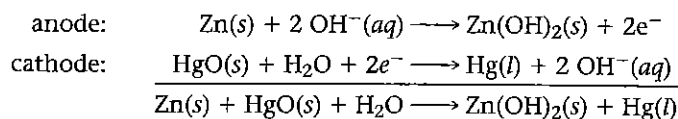


If too large a current is drawn from a Leclanché cell, the ammonia forms a gaseous insulating layer around the carbon cathode. When this happens, the voltage drops sharply and then returns slowly to its normal value of 1.5 V. This problem can be avoided by using an alkaline dry cell, in which the paste between the electrodes contains KOH rather than NH_4Cl . In this case the overall cell reaction is simply



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

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



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

Storage (Rechargeable) Voltaic Cells

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

The rechargeable 12-V lead storage battery used in automobiles consists of six voltaic cells of the type shown in Figure 18.12, p. 496. A group of lead plates, the grids of which are filled with spongy gray lead, forms the anode of the cell. The multiple cathode consists of another group of plates of similar design filled with lead(IV) oxide, PbO_2 . These two sets of plates alternate through the cell. They are immersed in a water solution of sulfuric acid, H_2SO_4 , which acts as the electrolyte.

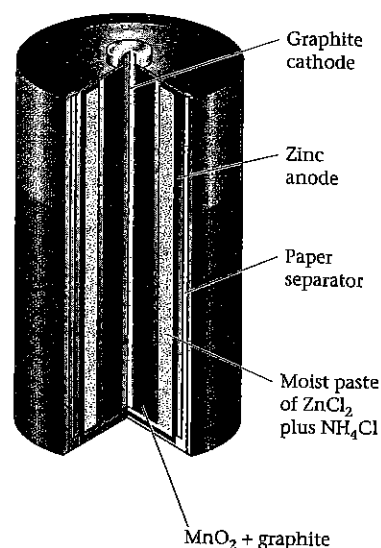


FIGURE 18.11
Zn- MnO_2 dry cell. This cell produces 1.5 V and will deliver a current of about half an ampere for six hours.

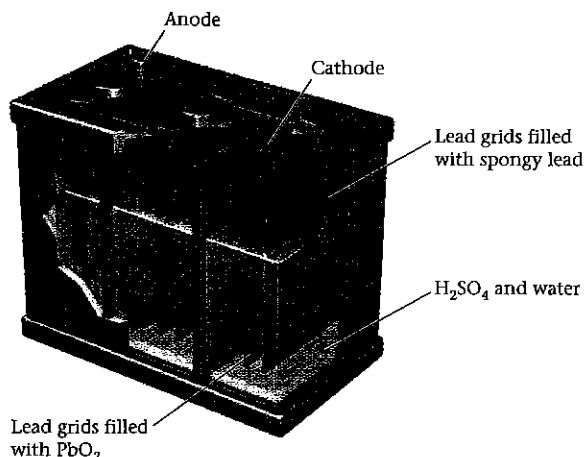
(OHT)

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

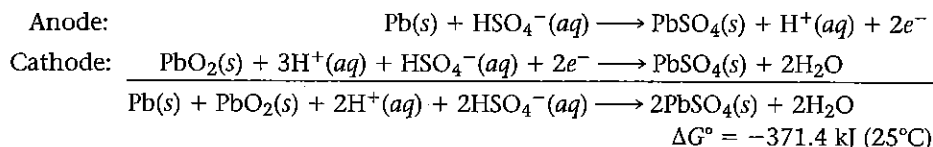
A 12-V storage battery can deliver 300 A for a minute or so.

FIGURE 18.12

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



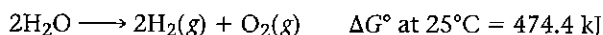
When a lead storage battery is supplying current, the lead in the anode grids is oxidized to Pb^{2+} ions, which precipitate as PbSO_4 . At the cathode, lead dioxide is reduced to Pb^{2+} ions, which also precipitate as PbSO_4 .



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

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

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

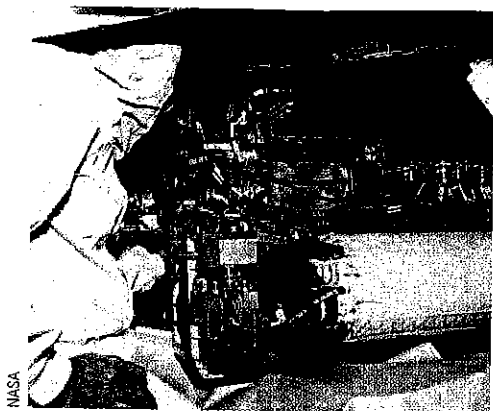


The hydrogen and oxygen produced create a safety hazard. Beyond that, they can cause Pb , PbO_2 , and PbSO_4 to flake off the plates. In a modern "maintenance-free" battery, the lead plates are alloyed with small amounts of calcium, which inhibits the electrolysis reaction.

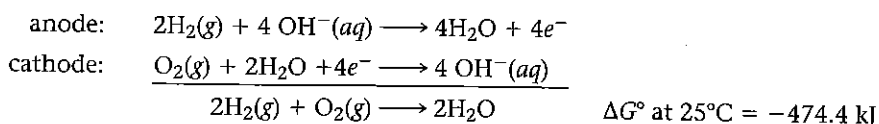
One of the advantages of the lead storage battery is that its voltage stays constant at 2 V per cell over a wide range of sulfuric acid concentrations. Only when the battery is nearly completely discharged does the voltage drop. It is also true that the cell voltage is virtually independent of temperature.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

Fuel Cells

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



A hydrogen-oxygen fuel cell used on U.S. space missions.



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

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

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

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

Fuel cells have been around for about 50 years.

CHEMISTRY

Beyond the Classroom



Andy Levin/Photo Researchers, Inc.

FIGURE A
The Statue of Liberty. The statue was erected in 1885. It is constructed of sheets of copper that have corroded over the years.

Corrosion of Metals

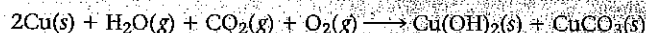
Most metals corrode when exposed to the atmosphere, reacting with oxygen, water vapor, or carbon dioxide. Gold and platinum are among the few metals that retain their shiny appearance indefinitely when exposed to air. These metals are very difficult to oxidize ($E_{\text{ox}}^{\circ} \text{Pt} = +1.20 \text{ V}$, $\text{Au} = +1.498 \text{ V}$).

Aluminum ($E_{\text{ox}}^{\circ} = +1.68 \text{ V}$) reacts readily with oxygen to form a thin



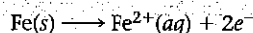
However, the Al_2O_3 coating, which is only about 10^{-8} m thick, adheres tightly to the surface of the metal. This prevents further corrosion and explains why aluminum cookware does not disintegrate on exposure to air.

Copper in moist air (Figure A) slowly acquires a dull green coating. The green material is a 1:1 mole mixture of $\text{Cu}(\text{OH})_2$ and CuCO_3 :

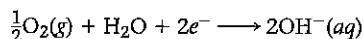


Several other elements, including zinc and lead, react similarly. The products, $\text{Zn}(\text{OH})_2 \cdot \text{ZnCO}_3$ and $\text{Pb}(\text{OH})_2 \cdot \text{PbCO}_3$, are white and adhere tightly to the metal, preventing further corrosion. In the case of lead, the protective coating dissolves in acetic acid, primarily because Pb^{2+} forms a very stable complex with the acetate ion. It has been suggested that the ancient Romans suffered from lead poisoning because they stored wine (containing some acetic acid) in pottery vessels glazed with lead compounds.

From an economic standpoint, the most important corrosion reaction is that involving iron and steel. About 20% of all the iron produced each year goes to replace products whose usefulness has been destroyed by rust. When a piece of iron is exposed to water containing dissolved oxygen, the half-reactions of oxidation



and reduction



occur at different locations. The surface of a piece of corroding iron consists of a series of tiny voltaic cells. At *anodic areas*, iron is oxidized to Fe^{2+} ions; at *cathodic areas*, elementary oxygen is reduced to OH^{-} ions. Electrons are transferred through the iron, which acts like the external conductor of an ordinary voltaic cell. The electrical circuit is completed by the flow of ions through the water solution or film covering the iron.

Many characteristics of corrosion are most readily explained in terms of an electrochemical mechanism. A perfectly dry metal surface is not attacked by oxygen; iron exposed to dry air does not corrode. This seems plausible if corrosion occurs through a voltaic cell, which requires a water solution through which ions can move to complete the circuit. The fact that corrosion occurs more readily in seawater than in fresh water has a similar explanation. The dissolved salts in seawater supply the ions necessary for the conduction of current.

The existence of discrete cathodic and anodic areas on a piece of corroding iron requires that adjacent surface areas differ from each other chemically. This can happen if there are differences in oxygen concentration along the metal surface, as when a drop of water adheres to the surface of a piece of iron exposed to the air (Figure B). The metal around the edges of the drop is in contact with water containing a high concentration of dissolved oxygen. The water touching the metal beneath the center of the drop is depleted in oxygen, because it is cut off from contact with air. As a result, the area around the edge of the drop, where the oxygen concentration is high, becomes cathodic; oxygen molecules are reduced there. Directly beneath the drop is an anodic area where the iron is oxidized. A particle of

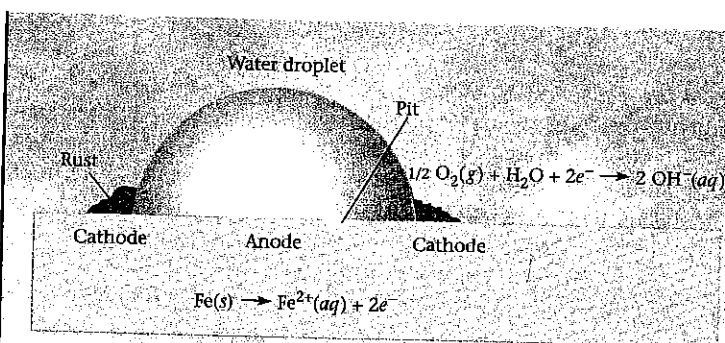


FIGURE B
Corrosion of iron under a drop of water. The Fe^{2+} ions migrate toward the edge of the drop, where they precipitate as $\text{Fe}(\text{OH})_2$, which later forms $\text{Fe}(\text{OH})_3 \cdot \text{O}(\text{H})_2$.

dirt on the surface of an iron object can act in much the same way as a drop of water to cut off the supply of oxygen to the area beneath it and thereby establish anodic and cathodic areas. This explains why garden tools left covered with soil are particularly susceptible to rusting.

CHAPTER HIGHLIGHTS

KEY CONCEPTS

1. Draw a diagram for a voltaic cell, labeling electrodes and direction of current flow.
(Example 18.1; Problems 3–6)
2. Use standard potentials (Table 18.1) to—
 - compare the relative strengths of different oxidizing agents; different reducing agents.
(Example 18.2; Problems 7–14)
 - calculate E° and/or reaction spontaneity.
(Examples 18.3, 18.4; Problems 15–32)
3. Relate E° to ΔG° and K .
(Example 18.5; Problems 33–42)
4. Use the Nernst equation to relate voltage to concentration.
(Examples 18.6, 18.7; Problems 43–56)
5. Relate mass of product to amount of electricity (coulombs) or amount of energy (joules) used in electrolysis reactions.
(Example 18.8; Problems 57–62)

KEY EQUATIONS

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

E° , ΔG° , K $E^\circ = \frac{-\Delta G^\circ}{nF} = \frac{RT \ln K}{nF} = \frac{0.0257 \text{ V} \ln K}{n}$ (at 25°C)

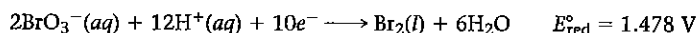
Nernst equation $E = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{(0.0257 \text{ V})}{n} \ln Q$ (at 25°C)

KEY TERMS

ampere	electrolysis	standard potential
anode	electrolytic cell	standard voltage
cathode	Faraday constant	volt
coulomb	half-cell	voltaic cell
E° , E°_{ox} , E°_{red}	salt bridge	

SUMMARY PROBLEM

A voltaic cell consists of two half-cells. One of the half-cells contains a platinum electrode surrounded by chromium(III) and dichromate ions. The other half-cell contains a platinum electrode surrounded by bromate ions and liquid bromine. Assume that the cell reaction, which produces a positive voltage, involves both chromium(III) and bromate ions. The cell is at 25°C. Information for the bromate reduction half reaction is as follows:



- Write the anode half-reaction, the cathode half-reaction, and the overall equation for the cell.
- Write the cell description in abbreviated notation.
- Calculate E° for the cell.
- For the redox reaction in (a), calculate K and ΔG° .
- Calculate the voltage of the cell when all ionic species except H^+ are at 0.1500 M and the pH is at -0.301 .

An electrolytic cell contains an aqueous solution of chromium(III) nitrate at 25°C. Assume that chromium plates out at one electrode and oxygen gas is evolved at the other electrode.

- Write the anode half-reaction, the cathode half-reaction, and the overall equation for the electrolysis.
- How many hours will it take to deposit 22.00 g of chromium metal, using a current of 5.4 A?
- A current of 3.75 A is passed through the cell for 45 minutes. Starting out with 1.25 L of 0.787 M $\text{Cr}(\text{NO}_3)_3$, what is $[\text{Cr}^{3+}]$ after electrolysis? What is the pH of the solution, neglecting the H^+ originally present? Assume 100% efficiency and no change in volume during electrolysis.

Answers

- anode: $2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O} \longrightarrow \text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6e^-$
cathode: $2\text{BrO}_3^-(aq) + 12\text{H}^+(aq) + 10e^- \longrightarrow \text{Br}_2(l) + 6\text{H}_2\text{O}$
overall: $10\text{Cr}^{3+}(aq) + 6\text{BrO}_3^-(aq) + 17\text{H}_2\text{O} \longrightarrow 5\text{Cr}_2\text{O}_7^{2-}(aq) + 3\text{Br}_2(l) + 34\text{H}^+(aq)$
- (Pt) | Cr^{3+} , $\text{Cr}_2\text{O}_7^{2-}$ || BrO_3^- | Br_2 | (Pt)
- 0.15 V
- $K = 1 \times 10^{75}$; $\Delta G^\circ = -4.3 \times 10^2 \text{ kJ}$
- 0.110 V
- anode: $2\text{H}_2\text{O} \longrightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^-$
cathode: $\text{Cr}^{3+}(aq) + 3e^- \longrightarrow \text{Cr}(s)$
overall: $4\text{Cr}^{3+}(aq) + 6\text{H}_2\text{O} \longrightarrow 4\text{Cr}(s) + 3\text{O}_2(g) + 12\text{H}^+(aq)$
- 6.3 h
- 0.759 M; 1.09

GENERAL
Chemistry Now™

Assess your understanding of this chapter's topics with additional quizzing and conceptual questions at <http://now.brookscole.com/masterton5e>

QUESTIONS & PROBLEMS

Problem numbers in blue indicate that the answer is available in Appendix 6 at the back of the book. **WEB** indicates that the solution is posted at <http://now.brookscole.com/masterton5e>

Voltaic Cells

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

- $\text{Mg} | \text{Mg}^{2+} || \text{Sc}^{3+} | \text{Sc}$
- $\text{Sn} | \text{Sn}^{2+} || \text{Pb}^{2+} | \text{Pb}$
- $\text{Pt} | \text{Cl}^-, \text{Cl}_2 || \text{NO}_3^-, \text{NO} | \text{Pt}$

WEB 2. Write a balanced chemical equation for the overall cell reaction represented as

- $\text{Ag} | \text{Ag}^+ || \text{Sn}^{4+}, \text{Sn}^{2+} | \text{Pt}$
- $\text{Al} | \text{Al}^{3+} || \text{Cu}^{2+} | \text{Cu}$
- $\text{Pt} | \text{Fe}^{2+}, \text{Fe}^{3+} || \text{MnO}_4^-, \text{Mn}^{2+} | \text{Pt}$

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

- $\text{Zn}(s) + \text{Cd}^{2+}(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{Cd}(s)$
- $2\text{AuCl}_4^-(aq) + 3\text{Cu}(s) \longrightarrow$
 $2\text{Au}(s) + 8\text{Cl}^-(aq) + 3\text{Cu}^{2+}(aq)$
- $\text{Fe}(s) + \text{Cu}(\text{OH})_2(s) \longrightarrow \text{Cu}(s) + \text{Fe}(\text{OH})_2(s)$

4. Follow the directions for Question 3 for the following reactions:

- $\text{Sn}(s) + 2\text{Ag}^+(aq) \longrightarrow \text{Sn}^{2+}(aq) + 2\text{Ag}(s)$
- $\text{H}_2(g) + \text{Hg}_2\text{Cl}_2(s) \longrightarrow 2\text{H}^+(aq) + 2\text{Cl}^-(aq) + 2\text{Hg}(l)$
- $\text{Pb}(s) + \text{PbO}_2(s) + 4\text{H}^+(aq) + 2\text{SO}_4^{2-}(aq) \longrightarrow$
 $2\text{PbSO}_4(s) + 2\text{H}_2\text{O}$

5. Consider a salt bridge cell in which the anode is a manganese rod immersed in an aqueous solution of manganese(II)