14 | Fundamentals of Electrochemistry

LITHIUM-ION BATTERY

$Li_{1-x}CoO_2$

$LiCoO_2$

Li$^+$ layer

CoO$_2$ layer

discharge

charge

- Co
- O
- Li

C_6Li

C_6Li_{1-x}

Graphite
C layer

Li layer

discharge

charge

Top view of
C_6Li structure

Li

Graphite is a hexagonal
sheet of carbon atoms

Lithium-ion
battery

- Graphite layer
- Porous separator plus Li$^+$ salt in organic solvent
- Cobalt oxide layer

QCA

e$^-$

e$^-$

Direction of electron flow from lithium battery
to laptop computer.
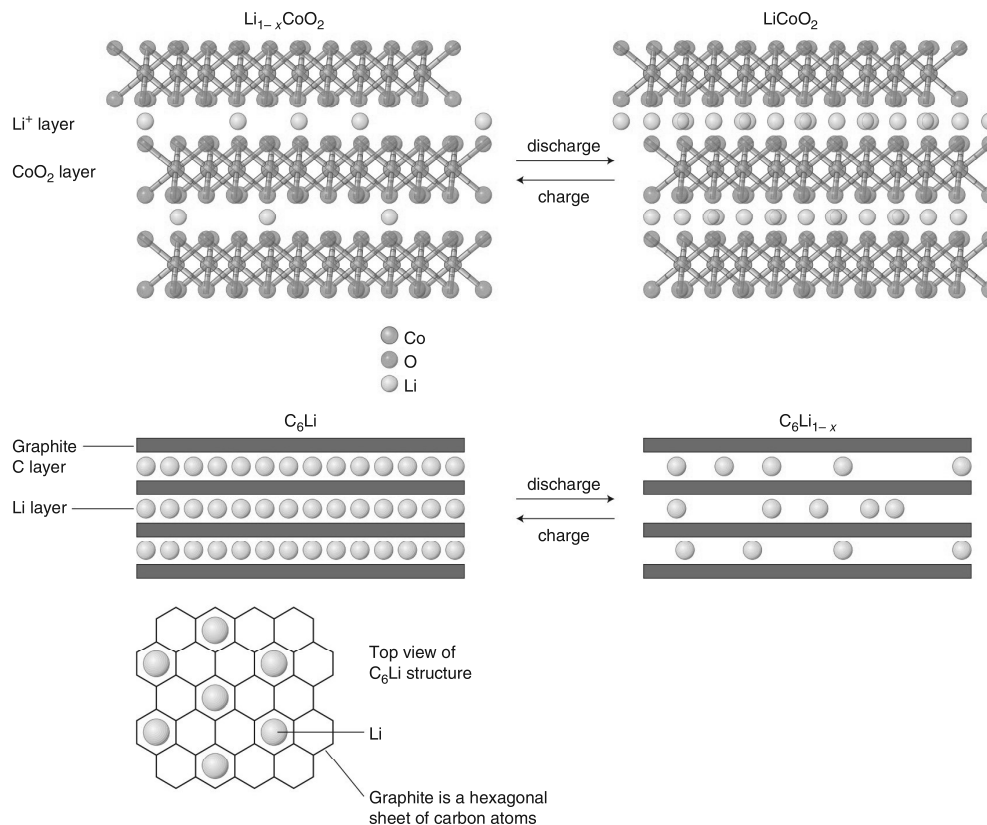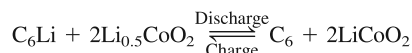
High-capacity, rechargeable lithium-ion batteries, such as those in cell phones and laptop computers, are a shining example of the fruits of materials chemistry research. The approximate chemistry is

$$C_6Li + 2Li_{0.5}CoO_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} C_6 + 2LiCoO_2$$

In C_6Li, lithium atoms reside between layers of carbon in graphite. Atoms or molecules located between layers of a structure are said to be *intercalated*. During operation of the battery, lithium ions migrate from graphite to cobalt oxide. Lithium atoms leave electrons behind in the graphite, and the resulting Li$^+$ ions become intercalated between CoO$_2$ layers. To go from graphite to cobalt oxide, Li$^+$ passes through an electrolyte consisting of a lithium salt dissolved in a high-boiling organic solvent. A porous polymer separator between graphite and cobalt oxide is an electrical insulator that permits Li$^+$ ions to pass. Electrons travel from graphite through the external circuit to reach the cobalt oxide and maintain electroneutrality. During recharging, Li$^+$ goes from LiCoO$_2$ to graphite under the influence of an externally applied electric field.
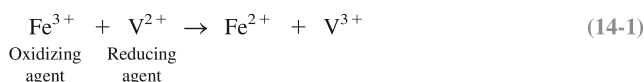
Batteries are *galvanic cells*, which are the subject of this chapter. A galvanic cell uses a favorable chemical reaction to produce electricity. A single-cell lithium-ion battery produces ~3.7 volts. These batteries store twice as much energy per unit mass as the nickel-metal hydride batteries they replaced. Ongoing research is aimed at improved materials and high-area microstructures for the electrodes and the separator layer. Goals include higher energy density, longer life, and safer operation. In 2013, two fires from lithium batteries grounded the fleet of Boeing 787 jet aircraft for four months. Though these were rare incidents, safe operation on an airplane is imperative.
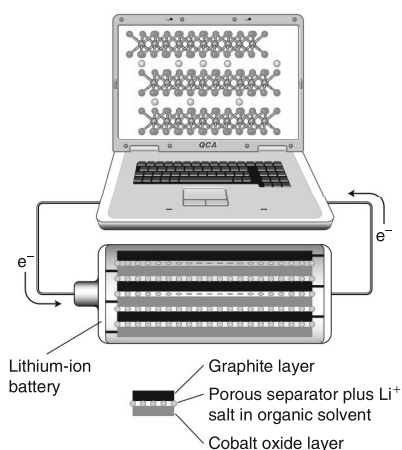
Electrochemistry is a major branch of analytical chemistry that uses electrical measurements of chemical systems for analytical purposes.[1] For example, the opening of Chapter 1 showed an electrode being used to measure neurotransmitter molecules released by a nerve cell. Electrochemistry also refers to the use of electricity to drive a chemical reaction or to the use of a chemical reaction to produce electricity.

14-1 Basic Concepts

A **redox reaction** involves transfer of electrons from one species to another. A species is said to be **oxidized** when it *loses electrons*. It is **reduced** when it *gains electrons*. An **oxidizing agent,** also called an **oxidant,** takes electrons from another substance and becomes reduced. A **reducing agent,** also called a **reductant,** gives electrons to another substance and is oxidized in the process. In the reaction

$$Fe^{3+} + V^{2+} \rightarrow Fe^{2+} + V^{3+} \qquad (14\text{-}1)$$

$$\underset{\substack{\text{Oxidizing} \\ \text{agent}}}{}\qquad \underset{\substack{\text{Reducing} \\ \text{agent}}}{}$$

Fe^{3+} is the oxidizing agent because it takes an electron from V^{2+}. V^{2+} is the reducing agent because it gives an electron to Fe^{3+}. Fe^{3+} is reduced, and V^{2+} is oxidized as the reaction proceeds from left to right. Appendix D reviews oxidation numbers and balancing of redox equations.

Oxidation: loss of electrons
Reduction: gain of electrons

Oxidizing agent: takes electrons
Reducing agent: gives electrons

$Fe^{3+} + e^- \rightarrow Fe^{2+}$
$V^{2+} \rightarrow V^{3+} + e^-$

Chemistry and Electricity

When electrons from a redox reaction flow through an electric circuit, we can learn something about the reaction by measuring current and voltage. Electric current is proportional to the rate of reaction, and the cell voltage is proportional to the free energy change for the electrochemical reaction.

Electric Charge

Electric charge (q) is measured in **coulombs** (C). The magnitude of the charge of a single electron or proton is 1.602×10^{-19} C, so a mole of electrons or protons has a charge of (1.602×10^{-19} C)(6.022×10^{23} mol^{-1}) = 9.649×10^4 C, which is called the **Faraday constant,** F. For N moles of a species with n charges per molecule, the moles of charge are nN. For example, for Fe^{3+}, $n = 3$ because each ion carries three units of charge. The electric charge in coulombs is

Relation between charge and moles:

$$q \quad = \quad n \quad \cdot \quad N \quad \cdot \quad F \qquad (14\text{-}2)$$

| Coulombs | Unit charges per molecule | Moles | $\dfrac{\text{Coulombs}}{\text{mole e}^-}$ |

The units work because the number of unit charges per molecule, n, is dimensionless. The charge on one mole of Fe^{3+} is $q = nNF = (3)(1 \text{ mol})(9.649 \times 10^4 \text{ C/mol}) = 2.89 \times 10^5$ C.

> **EXAMPLE** Relating Coulombs to Quantity of Reaction
>
> If 5.585 g of Fe^{3+} were reduced in Reaction 14-1, how many coulombs of charge must have been transferred from V^{2+} to Fe^{3+}?
>
> **Solution** The moles of iron reduced are (5.585 g)/(55.845 g/mol) = 0.100 0 mol Fe^{3+}. Each Fe^{3+} ion requires $n = 1$ electron in Reaction 14-1. Using the Faraday constant, we find that 0.100 0 mol of electrons corresponds to
>
> $$q = nNF = (1)(0.100 \text{ 0 mol e}^-)\left(9.649 \times 10^4 \frac{\text{C}}{\text{mol e}^-}\right) = 9.649 \times 10^3 \text{ C}$$
>
> **TEST YOURSELF** How many moles of Sn^{4+} are reduced to Sn^{2+} by 1.00 C of electric charge? (*Answer:* 5.18 μmol)
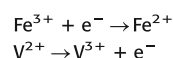
Electric Current

Electric **current** is the quantity of charge flowing each second through a circuit. The unit of current is the **ampere,** abbreviated A. A current of 1 ampere represents a charge of 1 coulomb per second flowing past a point in a circuit.

Michael Faraday (1791–1867) was a self-educated English "natural philosopher" (the old term for "scientist") who discovered that the extent of an electrochemical reaction is proportional to the electric charge passing through a cell. Faraday discovered many fundamental laws of electromagnetism. He gave us the electric motor, electric generator, and electric transformer, as well as the terms *ion, cation, anion, electrode, cathode, anode,* and *electrolyte.* His gift for lecturing is best remembered from his Christmas lecture demonstrations for children at the Royal Institution. Faraday "took great delight in talking to [children], and easily won their confidence…. They felt as if he belonged to them; and indeed he sometimes, in his joyous enthusiasm, appeared like an inspired child."[2]
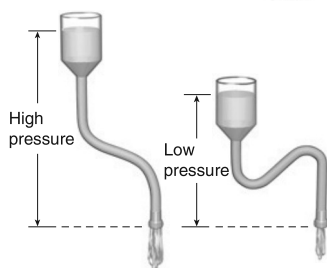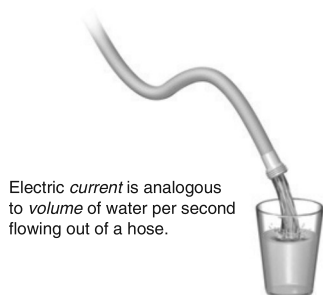
[Science Source.]

1 A = 1 C/s
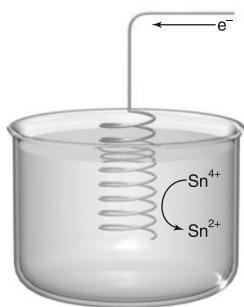
FIGURE 14-1 Electrons flowing into a coil of Pt wire at which Sn^{4+} ions in solution are reduced to Sn^{2+}. This process could not happen by itself, because there is no complete circuit. If Sn^{4+} is to be reduced at this Pt electrode, some other species must be oxidized at some other place.

EXAMPLE Relating Current to Rate of Reaction

Suppose that electrons are forced into a platinum wire immersed in a solution containing Sn^{4+} (Figure 14-1), which is reduced to Sn^{2+} at a constant rate of 4.24 mmol/h. How much current passes through the solution?

Solution *Two* electrons are required to reduce *one* Sn^{4+} ion:

$$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$$
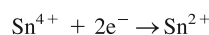
Electrons flow at a rate of (2 mmol e^-/mmol Sn^{4+})(4.24 mmol Sn^{4+}/h) = 8.48 mmol e^-/h, which corresponds to

$$\frac{8.48 \text{ mmol } e^-/h}{3\,600 \text{ s/h}} = 2.356 \times 10^{-3} \frac{\text{mmol } e^-}{s} = 2.356 \times 10^{-6} \frac{\text{mol } e^-}{s}$$

To find the current, we convert moles of electrons per second into coulombs per second:

$$\text{Current} = \frac{\text{charge}}{\text{time}} = \frac{\text{coulombs}}{\text{second}} = \frac{\text{moles } e^-}{\text{second}} \cdot \frac{\text{coulombs}}{\text{mole}}$$

$$= \left(2.356 \times 10^{-6} \frac{\text{mol}}{s}\right)\left(9.649 \times 10^4 \frac{C}{\text{mol}}\right)$$

$$= 0.227 \text{ C/s} = 0.227 \text{ A} = 227 \text{ mA}$$

TEST YOURSELF What current reduces Sn^{4+} at a rate of 1.00 mmol/h? (*Answer:* 53.6 mA)

In Figure 14-1, we encountered a Pt **electrode,** which conducts electrons into or out of a chemical species in the redox reaction. Platinum is a common *inert* electrode. It does not participate in the redox chemistry except as a conductor of electrons.

Voltage, Work, and Free Energy

Positive and negative charges attract each other. Positive charges repel other positive charges; negative charges repel other negative charges. The presence of electric charge creates an **electric potential** that attracts or repels charged particles. The electric *potential difference*, E, between two points is the work per unit charge that is needed or can be done when charge moves from one point to the other. *Potential difference* is measured in **volts** (V). The greater the potential difference between two points, the more work is required or can be done when a charged particle travels between those points.

A good analogy for understanding current and potential is to think of water flowing through a garden hose (Figure 14-2). Current is the electric charge flowing past a point in a wire each second. Current is analogous to the volume of water flowing past a point in the hose each second. The potential difference is analogous to the pressure on the water in the hose. The greater the pressure, the faster the water flows.

When a charge, q, moves through a potential difference, E, the work done is

Relation between work and voltage:

$$\boxed{\text{Work} = E \cdot q} \qquad (14\text{-}3)$$

Joules   Volts   Coulombs

Work has the dimensions of energy, whose units are **joules** (J). One *joule* of energy is gained or lost when 1 *coulomb* of charge moves between points whose potentials differ by 1 *volt*. Equation 14-3 tells us that the dimensions of volts are joules per coulomb.

It takes work to move like charges toward one another. Work can be done when opposite charges move toward one another.

Electric *current* is analogous to *volume* of water per second flowing out of a hose.

High pressure   Low pressure

Electric *potential difference* is analogous to the hydrostatic *pressure* pushing water through a hose. High pressure gives high flow.

FIGURE 14-2 Analogy between the flow of water through a hose and the flow of electricity through a wire.

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

EXAMPLE Electrical Work

How much work can be done if 2.4 mmol of electrons fall through a potential difference of 0.27 V?

Solution To use Equation 14-3, we must convert moles of electrons into coulombs of charge. Each electron has one unit of charge ($n = 1$), so

$$q = nNF = (1)(2.4 \times 10^{-3} \text{ mol})(9.649 \times 10^4 \text{ C/mol}) = 2.3 \times 10^2 \text{ C}$$

The work that could be done is

$$\text{Work} = E \cdot q = (0.27 \text{ V})(2.3 \times 10^2 \text{ C}) = 62 \text{ J}$$

TEST YOURSELF What must be the potential drop (V) for 1.00 μmol e^- to do 1.00 J of work? (**Answer:** 10.4 V)

In the garden hose analogy, suppose that one end of a hose is raised 1 m above the other end and a volume of 1 L of water flows through the hose. The flowing water goes through a mechanical device to do a certain amount of work. If one end of the hose is raised 2 m above the other, the amount of work that can be done by the falling water is twice as great. The elevation difference between the ends of the hose is analogous to electric potential difference and the volume of water is analogous to electric charge. The greater the electric potential difference between two points in a circuit, the more work can be done by the charge flowing between those two points.

The free energy change, ΔG, for a chemical reaction conducted reversibly at constant temperature and pressure equals the maximum possible electrical work that can be done by the reaction on its surroundings:

Section 6-2 gave a brief discussion of ΔG.

$$\text{Work done on surroundings} = -\Delta G \qquad (14\text{-}4)$$

The negative sign in Equation 14-4 indicates that the free energy of a system decreases when the work is done on the surroundings.

Combining Equations 14-2, 14-3, and 14-4 produces a relation of utmost importance:

$$\Delta G = -\text{work} = -E \cdot q$$

Relation between free energy difference and electric potential difference:

ΔG	$=$	$-n$	$\cdot$	N	$\cdot$	F	$\cdot$	E	(14-5)
Joules (J)		Unit charges per molecule		Moles		C/mol		Volts (V)	

$q = nNF$

Equation 14-5 relates the free energy change of a chemical reaction to the electric potential difference (that is, the voltage) that can be generated by the reaction. Recall that n is the dimensionless number of charges per molecule and N is the number of moles, so nN is the moles of charge transferred in the reaction.

Ohm's Law

Ohm's law states that current, I, is directly proportional to the potential difference (voltage) across a circuit and inversely proportional to the **resistance, R,** of the circuit.

Ohm's law:

$$I = \frac{E}{R} \qquad (14\text{-}6)$$

The greater the voltage, the more current will flow. The greater the resistance, the less current will flow.

Units of resistance are **ohms,** assigned the Greek symbol Ω (omega). A current of 1 ampere flows through a circuit with a potential difference of 1 volt if the resistance is 1 ohm. From Equation 14-6, the unit ampere (A) is equivalent to V/Ω.

Box 14-1 shows measurements of the resistance of single molecules by measuring current and voltage and applying Ohm's law.

Power

Power, P, is the work done per unit time. The SI unit of power is J/s, better known as the **watt** (W).

$$P = \frac{\text{work}}{\text{s}} = \frac{E \cdot q}{\text{s}} = E \cdot \frac{q}{\text{s}} \qquad (14\text{-}7)$$

Because q/s is the current, I, we can write

$$P = E \cdot I \qquad (14\text{-}8)$$

power (watts) = work per second
$P = E \cdot I = (IR) \cdot I = I^2R$

A cell capable of delivering 1 ampere at a potential difference of 1 volt has a power output of 1 watt.

Ohm's Law, Conductance, and Molecular Wire[3]

The electrical conductance of a single molecule suspended between two gold electrodes is known from measurement of voltage and current by applying Ohm's law. Conductance is 1/resistance, so it has the units 1/ohm ≡ siemens (S).

To make molecular junctions, the sharp gold tip of a scanning tunneling microscope was moved in and out of contact with a flat gold substrate in the presence of a solution containing a test molecule terminated by thiol (—SH) groups. Thiols spontaneously bind to gold, forming bridges such as that shown here. Nanoampere currents were observed with a potential difference of 0.1 V between the gold surfaces.
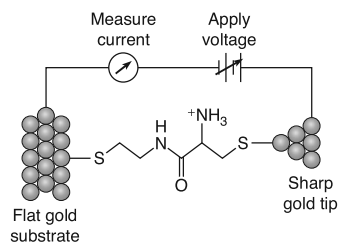
The graph shows four observations of conductance as the scanning tunneling microscope tip was pulled away from the Au substrate. Plateaus are observed at multiples of 19 nS. An interpretation is that a single molecule connecting two Au surfaces has a conductance of 19 nS (or a resistance of 50 MΩ). If two molecules form parallel bridges, conductance increases to 38 nS. Three molecules give a conductance of 57 nS. If there are three bridges and the electrodes are pulled apart, one of the bridges breaks and conductance drops to 38 nS. When the second bridge breaks, conductance drops to 19 nS. The exact conductance varies because the environment of each molecule on the Au surface is not identical. A histogram of >500 observations in the inset shows peaks at 19, 38, and 57 nS.
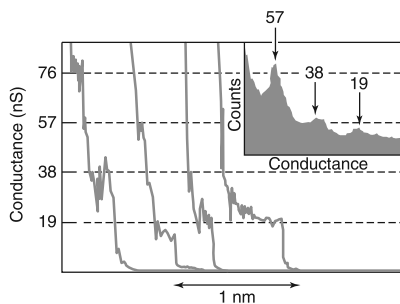

Change in conductance as Au scanning tunneling microscope tip immersed in dithiol solution is withdrawn from Au substrate. [Data from X. Xiao, B. Xu, and N. Tao, "Conductance Titration of Single-Peptide Molecules," *J. Am. Chem. Soc.* **2004,** *126,* 5370.]

Alkane hydrocarbons can be thought of as prototypical electrical insulators. The conductance of alkane dithiols decreases exponentially as chain length increases:[4]

$HS(CH_2)_8SH$ conductance = 16.1 nS

$HS(CH_2)_{10}SH$ conductance = 1.37 nS

$HS(CH_2)_{12}SH$ conductance = 0.35 nS
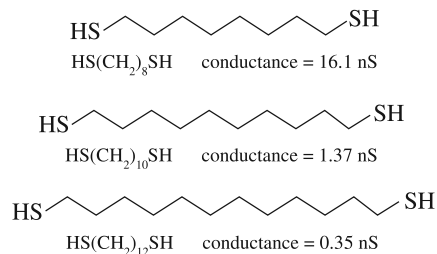
The conductance of conjugated aromatic bipyridines shown below is orders of magnitude greater than that of saturated hydrocarbons of a similar length. In fact, the conductance of 2.9 nS for the compound with six repeating units and length of 11 nm is almost three orders of magnitude higher than that reported for aromatic molecular wires of comparable length containing only carbon atoms.
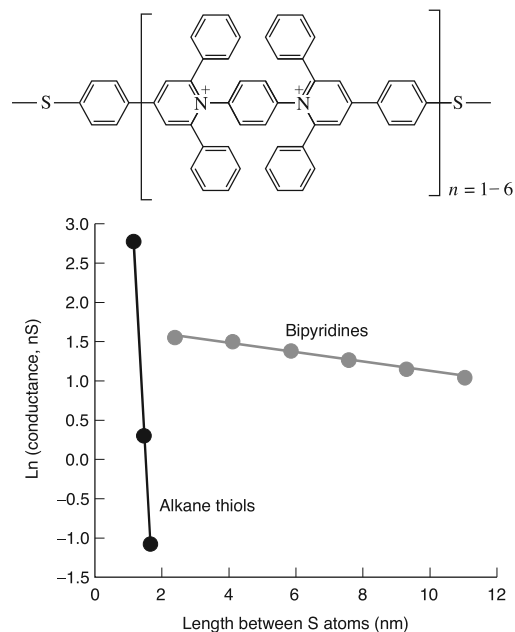
Dependence of conductivity on chain length from sulfur to sulfur. [Data for bipyridines from V. Kolivoška et al., "Single-Molecule Conductance in a Series of Extended Viologen Molecules," *J. Phys. Chem. Lett,* **2013,** *4,* 589.]

Using Ohm's Law

In the circuit in Figure 14-3, the battery generates a potential difference of 3.0 V, and the resistor has a resistance of 100 Ω. The wire connecting the battery and the resistor has negligible resistance. Find the current and power delivered by the battery.

Solution The current is

$$I = \frac{E}{R} = \frac{3.0 \text{ V}}{100 \text{ Ω}} = 0.030 \text{ A} = 30 \text{ mA}$$

The power produced by the battery is

$$P = E \cdot I = (3.0 \text{ V})(0.030 \text{ A}) = 90 \text{ mW}$$

TEST YOURSELF What voltage is required to produce 180 mW of power? (*Answer:* 4.24 V)

What happens to the power generated by the circuit? *The energy appears as heat in the resistor.* The power (90 mW) equals the rate at which heat is produced in the resistor.

Here is a summary of symbols, units, and relations from the last few pages:

Relation between charge and moles:

$$q = n \cdot N \cdot F$$
Charge   Unit charges   Moles   C/mol
(coulombs, C)   per molecule   (Faraday constant)

Relation between work and voltage:

$$\text{Work} = E \cdot q \qquad \textbf{(Units: J/C = V)}$$
Joules   Volts   Coulombs
(J)   (V)   (C)

Relation between free energy difference and electric potential difference:

$$\Delta G = -n \cdot N \cdot F \cdot E$$
Joules   Unit charges   Moles   C/mol   Volts
(J)   per molecule   (V)

Ohm's law:

$$I = E / R$$
Current   Volts   Resistance
(A)   (V)   (ohms, Ω)

Electric power:

$$P = \frac{\text{work}}{\text{s}} = E \cdot I$$
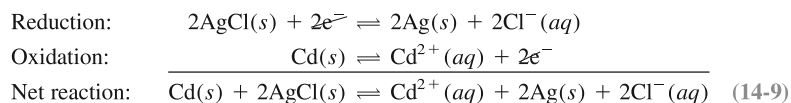Power   J/s   Volts   Amperes
(watts, W)

14-2 Galvanic Cells

A **galvanic cell** (also called a *voltaic cell*) uses a *spontaneous* chemical reaction to generate electricity. To accomplish this, one reagent must be oxidized and another must be reduced. The two cannot be in contact, or electrons would flow directly from the reducing agent to the oxidizing agent. Instead, oxidizing and reducing agents are physically separated, and electrons are forced to flow through a wire to go from one reactant to the other.

A Cell in Action

Figure 14-4 shows a galvanic cell with two electrodes suspended in a solution of $CdCl_2$. One electrode is cadmium; the other is metallic silver coated with solid AgCl. The reactions are

Reduction: $2AgCl(s) + 2e^- \rightleftharpoons 2Ag(s) + 2Cl^-(aq)$

Oxidation: $Cd(s) \rightleftharpoons Cd^{2+}(aq) + 2e^-$

Net reaction: $Cd(s) + 2AgCl(s) \rightleftharpoons Cd^{2+}(aq) + 2Ag(s) + 2Cl^-(aq)$ (14-9)

The net reaction is composed of a reduction and an oxidation, each of which is called a **half-reaction.** The two half-reactions are written with equal numbers of electrons so that their sum includes no free electrons.

The **potentiometer** in the circuit measures the difference in electric potential (voltage) between the two metal electrodes. The measured voltage is the difference $E_{\text{measured}} = E_+ - E_-$, where E_+ is the potential of the electrode attached to the positive terminal of the potentiometer and E_- is the potential of the electrode attached to the negative terminal. If electrons flow into the negative terminal, as in this illustration, the voltage is positive. The potentiometer has high electrical resistance so that little current flows through the meter. Ideally, no current would flow through the meter and we would say that the measured potential difference is the *open-circuit potential*, which is the hypothetical potential difference that would be observed if the electrodes were not connected to each other.

Oxidation of Cd metal to $Cd^{2+}(aq)$ provides electrons that flow through the circuit to the Ag electrode in Figure 14-4. At the Ag surface, Ag^+ (from AgCl) is reduced to $Ag(s)$.
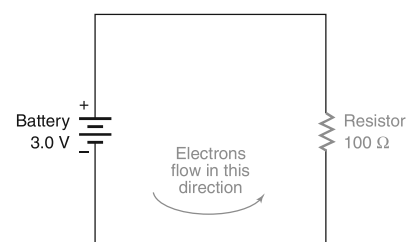
FIGURE 14-3 A circuit with a battery and a resistor. Benjamin Franklin investigated static electricity in the 1740s.[5] He thought electricity was a fluid that flows from a silk cloth to a glass rod when the rod is rubbed with the cloth. We now know that electrons flow from glass to silk. However, Franklin's convention for the direction of electric current has been retained, so we say that current flows from positive to negative—in the opposite direction of electron flow.
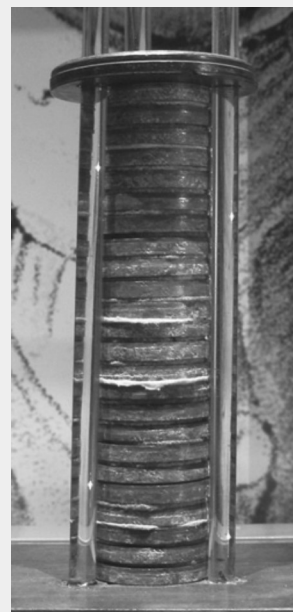
The battery invented by Alessandro Volta (1745–1827) in 1799 consisted of layers of Zn and Ag separated by cardboard soaked in brine. The "voltaic pile" on display at the Royal Institution in London was given by Volta to Humphry Davy and Michael Faraday when they visited Italy in 1814. Using electrolysis, Davy was the first to isolate Na, K, Mg, Ca, Sr, and Ba. Faraday used piles to discover laws of electricity and magnetism. [Courtesy Daniel Harris.]

FIGURE 14-4 A simple galvanic cell.

FIGURE 14-4 A simple galvanic cell.
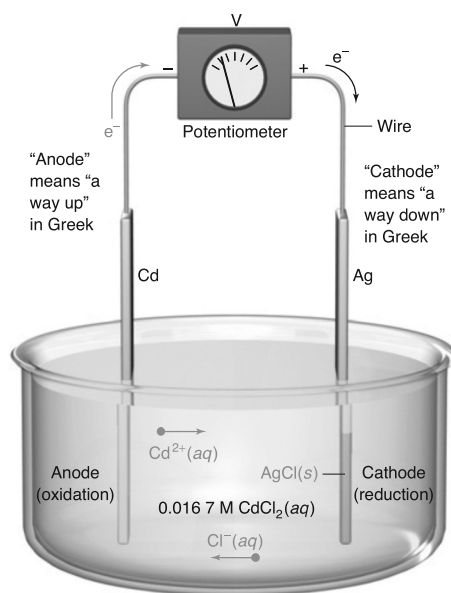
Recall that ΔG is *negative* for a spontaneous reaction.

Chloride from AgCl goes into solution. The free energy change for the net reaction, -150 kJ per mole of Cd, provides the driving force that pushes electrons through the circuit.

> **EXAMPLE** Voltage Produced by a Chemical Reaction
>
> Calculate the voltage that would be measured by the potentiometer in Figure 14-4.
>
> **Solution** Because $\Delta G = -150$ kJ per mol of Cd, we can use Equation 14-5 (where n is moles of electrons transferred in the balanced net reaction) to write
>
> $$E = -\frac{\Delta G}{nNF} = -\frac{-150 \times 10^3 \text{ J}}{\left(2\dfrac{\text{electrons}}{\text{atom}}\right)(1 \text{ mol Cd})\left(9.649 \times 10^4 \dfrac{\text{C}}{\text{mol}}\right)}$$
>
> $$= +0.777 \text{ J/C} = +0.777 \text{ V}$$
>
> A spontaneous chemical reaction (negative ΔG) produces a *positive voltage*.
>
> **TEST YOURSELF** Find E if $\Delta G = +150$ kJ and $n = 1$ e$^-$/atom. (***Answer:*** -1.55 V)

Reminder: 1 J/C = 1 volt

$n =$ e$^-$/atom is dimensionless

Cathode: where reduction occurs
**Anode:** where oxidation occurs

Michael Faraday wanted to describe his discoveries with terms that would "advance the general cause of science" and not "retard its progress." He sought the aid of William Whewell in Cambridge, who coined words such as "anode" and "cathode," meaning "a way up" and "a way down" (Figure 14-4).

Chemists define the electrode at which *reduction* occurs as the **cathode.** The **anode** is the electrode at which *oxidation* occurs. In Figure 14-4, Ag is the cathode because reduction takes place at its surface ($2AgCl + 2e^- \rightarrow 2Ag + 2Cl^-$). Cd is the anode because it is oxidized ($Cd \rightarrow Cd^{2+} + 2e^-$).

Electrons Move Toward More Positive Electric Potential

Being negatively charged, *electrons move toward more positive electric potential*. In Figure 14-4, the Ag electrode is positive with respect to the Cd electrode. Therefore, electrons move from Cd to Ag through the circuit. When we study the Nernst equation, you will learn how to find the electrode potentials and, therefore, to predict the direction of electron flow.
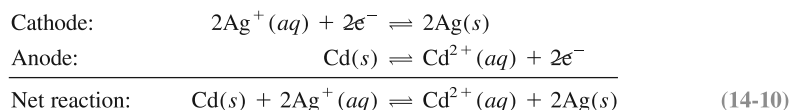
Electrons are not readily conducted through a solution. They must move through the wire. Ions are not conducted through a wire. They must move through the solution. Electroneutrality is maintained by a balance between the flow of electrons and the flow of ions so there is no significant buildup of charge in any region.
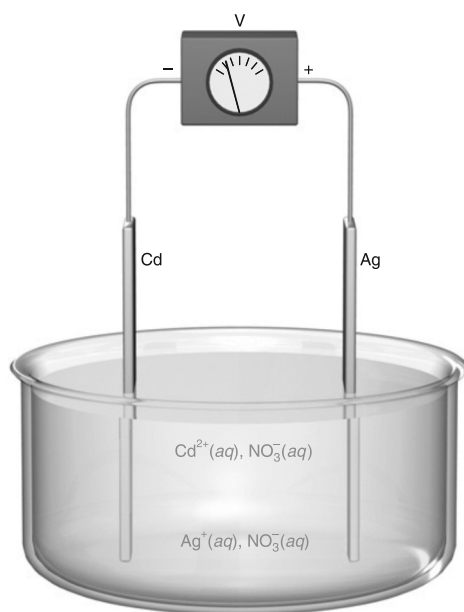
Salt Bridge

Consider the cell in Figure 14-5, in which the reactions are intended to be

Cathode:	$2Ag^+(aq) + 2e^- \rightleftharpoons 2Ag(s)$
Anode:	$Cd(s) \rightleftharpoons Cd^{2+}(aq) + 2e^-$

|		
Net reaction:	$Cd(s) + 2Ag^+(aq) \rightleftharpoons Cd^{2+}(aq) + 2Ag(s)$	(14-10)

The net reaction is spontaneous, but little current flows through the circuit because Ag^+ is not forced to be reduced at the Ag electrode. Aqueous Ag^+ can react directly at the $Cd(s)$ surface, giving the same net reaction with no flow of electrons through the external circuit.

The cell in Figure 14-5 is *short-circuited*.

We can separate the reactants into two *half-cells*[8] if we connect the two halves with a **salt bridge,** as shown in Figure 14-6. The salt bridge is a U-shaped tube filled with a gel containing a high concentration of KNO_3 (or other electrolyte that does not affect the cell reaction). The ends of the bridge are porous glass disks that allow ions to diffuse but minimize mixing of solutions inside and outside the bridge. When the galvanic cell is operating, K^+ from the bridge migrates into the cathode compartment and a small amount of NO_3^- migrates from the cathode into the bridge. Ion migration offsets the charge buildup that would otherwise occur as electrons flow into the silver electrode. In the absence of a salt bridge, negligible reaction can occur because of charge buildup. The migration of ions out of the bridge is greater than the migration of ions into the bridge because the salt concentration in the bridge

A salt bridge maintains electroneutrality (no charge buildup) throughout the cell. See Demonstration 14-1.
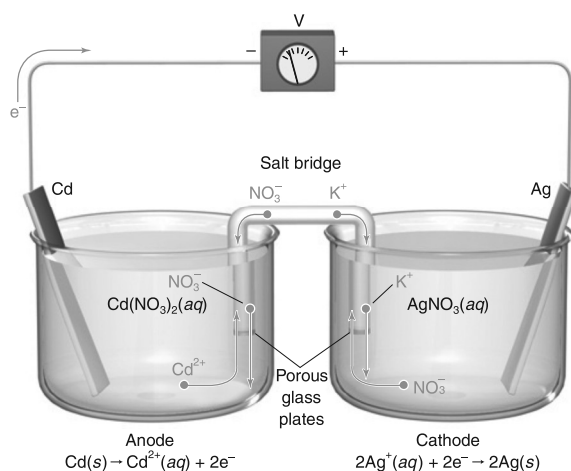
FIGURE 14-6 A cell that works—thanks to the salt bridge!

A salt bridge is an ionic medium with a *semipermeable* barrier on each end. Small molecules and ions can cross a semipermeable barrier, but large molecules cannot. Demonstrate a "proper" salt bridge by filling a U-tube with agar and KCl as described in the text and construct the cell shown here.
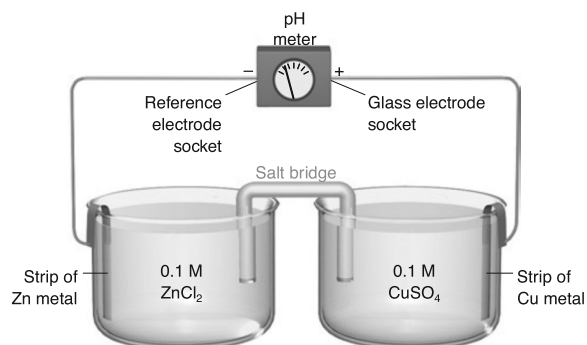
The pH meter is a potentiometer whose negative terminal is the reference electrode socket.

Write the half-reactions for this cell and use the Nernst equation to calculate the theoretical voltage. Measure the voltage with a conventional salt bridge. Then replace the salt bridge with filter paper soaked in NaCl solution and measure the voltage again. Finally, replace the filter-paper salt bridge with two fingers and measure the voltage again. A human is just a bag of salt housed in a semipermeable membrane. Small differences in voltage observed when the salt bridge is replaced can be attributed to the junction potential discussed in Section 15-3. To prove that it is hard to distinguish a chemistry instructor from a hot dog, use a hot dog as a salt bridge[6] and measure the voltage again.

Challenge   One hundred eighty students at Virginia Tech made a salt bridge by holding hands.[7] Their resistance was lowered from $10^6 \ \Omega$ per student to $10^4 \ \Omega$ per student by wetting everyone's hands. Can your class beat this record?

is much higher than the salt concentration in the half-cells. At the left side of the salt bridge, NO_3^- migrates into the anode compartment and a little Cd^{2+} migrates into the bridge to prevent buildup of positive charge.
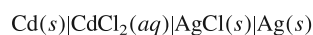
For reactions that do not involve Ag^+ or other species that react with Cl^-, the salt bridge usually contains KCl electrolyte. A typical salt bridge is prepared by heating 3 g of agar with 30 g of KCl in 100 mL of water until a clear solution is obtained. The solution is poured into the U-tube and allowed to gel. The bridge is stored in saturated aqueous KCl.

Line Notation

Electrochemical cells are described by a notation employing just two symbols:
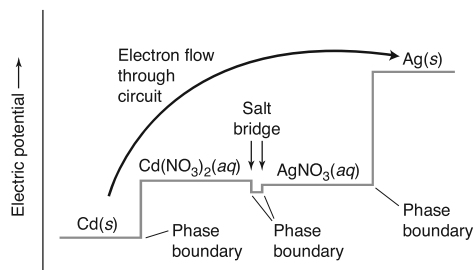
$$| \ \text{phase boundary} \qquad \| \ \text{salt bridge}$$

The salt bridge symbol ‖ represents the two phase boundaries on either side of the bridge.

The cell in Figure 14-4 is represented by the *line diagram*

$$Cd(s)|CdCl_2(aq)|AgCl(s)|Ag(s)$$

Each phase boundary is indicated by a vertical line. The electrodes are shown at the extreme left- and right-hand sides of the line diagram. The cell in Figure 14-6 is

$$Cd(s)|Cd(NO_3)_2(aq)\|AgNO_3(aq)|Ag(s)$$
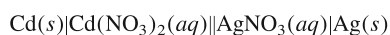
There is a change in electric potential at most phase boundaries in an electrochemical cell. The potential increase from Cd to Ag occurs principally at the $Cd(s) \ | \ Cd(NO_3)_2(aq)$ and $AgNO_3(aq) \ | \ Ag(s)$ phase boundaries, as shown in Figure 14-7 for the case of negligible


FIGURE 14-7 Schematic illustration of change in electric potential at each phase boundary of the cell in Figure 14-6 if there is negligible current flow. The potential step at the Cd | Cd(NO$_3$)$_2$(aq) phase boundary is given by the *Nernst equation* (Section 14-4) for the Cd | Cd^{2+} half-cell. The potential step at the Ag | AgNO$_3$(aq) phase boundary is given by the Nernst equation for the Ag | Ag$^+$ half-cell. *Junction potentials* at each end of the salt bridge are explained in Section 15-3.

BOX 14-2 **Hydrogen-Oxygen Fuel Cell**
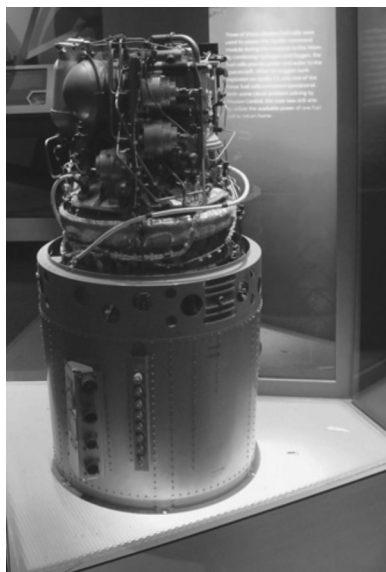
1.5 kW *Apollo* fuel cell. Apollo used two of these units. [© DaffodilPhotography/Alamy.]
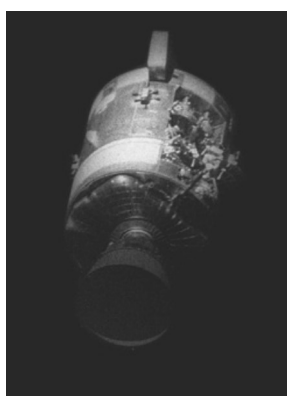

Ruptured *Apollo 13* service module observed by the crew after separation from the command module before re-entry into earth's atmosphere. [NASA.]

"Houston, we've had a problem." With these words, Commander Jim Lovell informed Mission Control that *Apollo 13* was in trouble on the second day of its trip to the moon in 1970. A tank holding liquid oxygen for the spacecraft's fuel cells had exploded. These fuel cells were developed in the 1960s as the most efficient method to provide electricity in space. As a result of the explosion, three astronauts were forced to use their lunar module as a "lifeboat" with almost no power or water for nearly four days as they flew to the moon and back to splash down in the Pacific Ocean. One of many technical highlights of the journey was adapting a LiOH canister from the command module to remove CO_2 from the atmosphere of the lunar module so the astronauts could survive $(2LiOH(s) + CO_2(g) \rightarrow Li_2CO_3(s) + H_2O(g))$. A billion people on

Earth, transfixed on the fate of three people, burst into cheers when the crew was safely recovered.

A modern H_2–O_2 polymer electrolyte fuel cell derives its energy from the net combination of H_2 and O_2 to make H_2O. *Fuel*, $H_2(g)$, flows into the cell at the left through a 10-μm-thick electrically conductive porous carbon sheet to the anode, which contains 2-nm catalytic particles of Pt (<0.5 mg/cm^2). H_2 dissociates to give Pt-bound H atoms, which go on to make H^+ and electrons. Electrons are conducted through the porous carbon into a circuit where they can do useful work. H^+ is conducted through the Nafion® polymer electrolyte membrane. Hydrated sulfonic acid groups of the polymer transport H^+ from one sulfonic acid group to another.
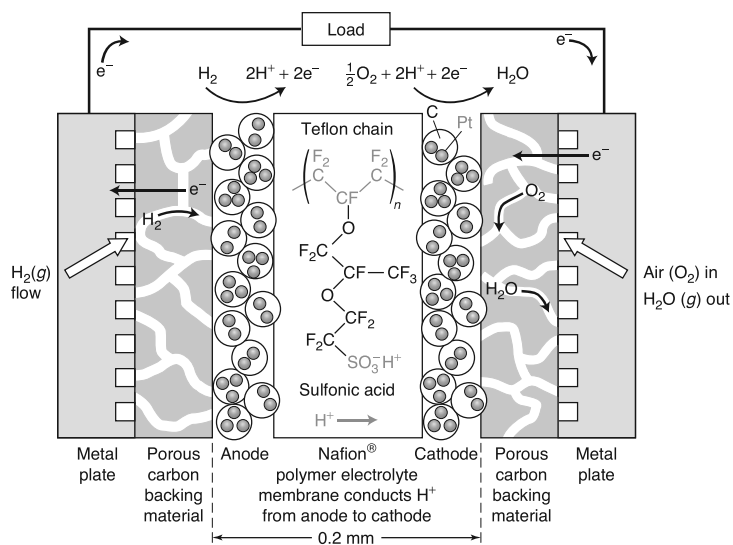
Schematic cross section of polymer electrolyte membrane hydrogen-oxygen fuel cell. [Information from S. Thomas and M. Zalbowitz, *Fuel Cells: Green Power* (Los Alamos National Laboratory, New Mexico, 1999), http://www.lanl.gov/orgs/mpa/mpa11/Green%20Power.pdf.]

When H^+ reaches the cathode, it combines on Pt catalyst particles with O_2 and electrons to make H_2O. O_2 is provided by air pumped in at the right. $H_2O(g)$ produced at the cathode exits the cell in the airstream. A key feature enabling the fuel cell to produce electricity is that the polymer electrolyte membrane conducts H^+ but not electrons.
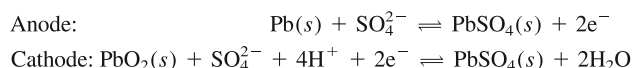
An ideal cell would produce 1.16 V at 80°C if no current were flowing. The operating voltage is typically ~0.7 V when current flows and the cell does useful work. The cell is 60% (= 0.7 V/1.16 V) efficient at converting chemical energy into electrical energy. The other 40% of energy is converted to heat that is removed by air flowing through the cathode to maintain a temperature of 80°C. The cell produces an impressive ~0.5 A per square centimeter of its area. High voltage can be produced by stacking cells in series.

Other H_2–O_2 fuel cells with different electrolytes operate at higher temperature. Some cells are capable of generating megawatts of power with 85% efficiency. For comparison, automobiles with internal combustion engines convert ~20% of the energy content of gasoline into motion of the car. Some fuel cells extract hydrogen from natural gas (methane) and use catalytic ceramic oxides in place of expensive noble metals.

A 12-V lead-acid battery consists of six cells that each deliver 2 V.[10] Invented in 1859 by the French physicist Gaston Planté at the age of 25, this was the first rechargeable battery. Its electrodes are metallic lead grids with a large surface area. Solid PbO_2 is pressed onto the cathode. The cell is filled with aqueous H_2SO_4, which is ~35 wt% $H_2SO_4 \approx 5.5$ m (molal) (~4.4 M) when fully charged. During discharge (when the battery is producing electricity), Pb is oxidized to $PbSO_4(s)$ at the anode. At the cathode, PbO_2 is reduced to $PbSO_4(s)$. As the cell discharges, both electrodes become coated with $PbSO_4(s)$. Both reactions consume H_2SO_4, whose concentration can fall to ~22 wt% ≈ 2.9 m during discharge.

Anode: $Pb(s) + SO_4^{2-} \rightleftharpoons PbSO_4(s) + 2e^-$

Cathode: $PbO_2(s) + SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O$

Batteries and fuel cells are examples of galvanic cells, which make electricity from a chemical reaction. A battery has a compartment filled with reactants that are consumed as the battery discharges. In a fuel cell, fresh reactants flow past the electrodes and products are continuously flushed from the cell. The most common rechargeable batteries that you use are the lithium battery in computers
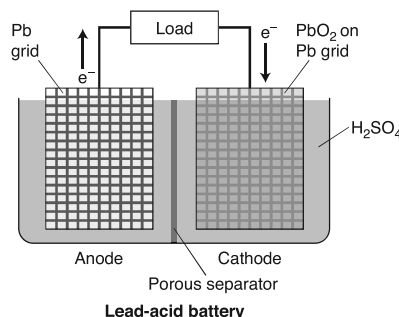
Lead-acid battery

and mobile telephones and the lead-acid battery in a car. One reason why we use lead-acid batteries is that they can deliver several hundred amperes of current for a short time to start the engine. Alkaline batteries used in flashlights and toys are not rechargeable. Alkaline and lithium batteries should be discarded as hazardous waste when they no longer work. Lead-acid batteries are recycled by dealers who sell them.

---

current flow. There is also a small change in potential, called the *junction potential*, at each end of the salt bridge. Saturated KCl or saturated KNO_3 is often used in a salt bridge to reduce the junction potential to a few millivolts or less, as discussed in Section 15-3.

Batteries[9, 10] and fuel cells[11–13] are galvanic cells that consume their reactants to generate electricity. A *battery* has a static compartment filled with reactants. In a *fuel cell*, fresh reactants flow past the electrodes and products are continuously flushed from the cell. Boxes 14-2 and 14-3 describe important fuel cells and batteries.
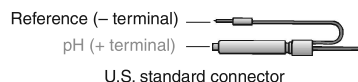
14-3 Standard Potentials

The voltage measured in Figure 14-6 is the difference in electric potential between the Ag electrode on the right and the Cd electrode on the left. Voltage tells us how much work can be done by electrons flowing from one side to the other (Equation 14-3). The potentiometer (voltmeter) indicates a positive voltage when electrons flow into the negative terminal, as in Figure 14-6. If electrons flow the other way, the voltage is negative.

Sometimes the negative terminal of a voltmeter is labeled "common." It may be colored black and the positive terminal red. When a pH meter with a BNC socket is used as a potentiometer, the center wire is the positive input and the outer connection is the negative input. In older pH meters, the negative terminal is the narrow receptacle to which the reference electrode is connected.

Positive terminal is the wire at the center inside connector

BNC connector

Reference (− terminal)
pH (+ terminal)

U.S. standard connector

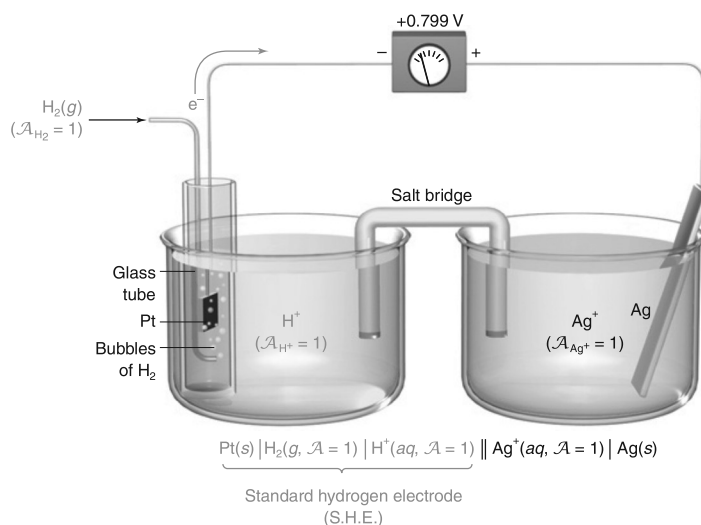### In General, We Will Write All Half-Reactions as Reductions

From now on, *we will generally write all half-reactions as reductions*. The Nernst equation in the next section enables us to find the electrode potentials for each half-reaction and, therefore, to predict the direction of electron flow. Electrons flow through the wire from the more negative electrode to the more positive electrode.

Measuring the Standard Reduction Potential

Each half-reaction is assigned a **standard reduction potential**, $E°$, measured by an experiment shown in an idealized form in Figure 14-8. The half-reaction of interest is

$$Ag^+ + e^- \rightleftharpoons Ag(s) \qquad (14\text{-}11)$$

which occurs in the half-cell at the right connected to the *positive* terminal of the potentiometer. *Standard* means that activities of all species are unity. For Reaction 14-11 under standard conditions, $\mathcal{A}_{Ag^+} = 1$ and, by definition, the activity of Ag(s) also is unity.

+0.799 V

H$_2$(g)
($\mathcal{A}_{H_2} = 1$)

e$^-$

Salt bridge

Glass tube

Pt

Bubbles of H$_2$

H$^+$
($\mathcal{A}_{H^+} = 1$)

Ag$^+$ Ag
($\mathcal{A}_{Ag^+} = 1$)

$Pt(s) | H_2(g, \mathcal{A} = 1) | H^+(aq, \mathcal{A} = 1) \, \| \, Ag^+(aq, \mathcal{A} = 1) | Ag(s)$

Standard hydrogen electrode
(S.H.E.)

The potentiometer measures the difference in potential of the electrode attached to the positive terminal of the meter minus the potential of the electrode attached to the negative terminal of the meter:

$E = E_+ - E_-$

The left half-cell, connected to the *negative* terminal of the potentiometer, is called the **standard hydrogen electrode** (S.H.E.). It consists of a catalytic Pt surface[14] in contact with an acidic solution in which $\mathcal{A}_{H^+} = 1$. A stream of H$_2$(g) bubbled through the electrode saturates the solution with H$_2$(aq). The activity of H$_2$(g) is unity if the pressure of H$_2$(g) is 1 bar. We describe the reaction that comes to equilibrium at the surface of the Pt electrode as

S.H.E. half-reaction: $\qquad H^+(aq, \mathcal{A} = 1) + e^- \rightleftharpoons \frac{1}{2}H_2(g, \mathcal{A} = 1)$ $\qquad$ (14-12)
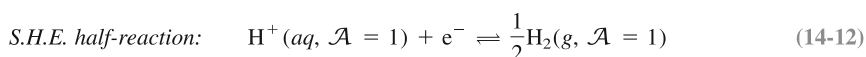
H$_2$(g) dissolves to give H$_2$(aq), which is in equilibrium with H$^+$(aq) on the Pt surface.

We *arbitrarily* assign a potential of 0 to the standard hydrogen electrode at 25°C. The voltage measured by the meter in Figure 14-8 can therefore be *assigned* to Reaction 14-11, which occurs in the right half-cell. The measured value $E° = +0.799$ V is the standard reduction potential for Reaction 14-11. The positive sign tells us that electrons flow from Pt to Ag through the meter.

We arbitrarily *assign* a potential to Reaction 14-12 and then use the reaction as a reference point to measure other half-cell potentials. An analogy is the assignment of 0°C to the freezing point of water and 100°C to the boiling point of water at 1 atmosphere pressure. On this scale, hexane boils at 69° and benzene boils at 80°. The difference between boiling points is $80° - 69° = 11°$. If we were to assign the freezing point of water to be 200°C and the boiling point to be 300°C, hexane would boil at 269° and benzene would boil at 280°. The difference is still 11°. Regardless of where we set zero on the scale, differences between benzene and hexane remains constant.

The line notation for the cell in Figure 14-8 is

$$\underbrace{Pt(s) | H_2(g, \mathcal{A} = 1) | H^+(aq, \mathcal{A} = 1)}_{S.H.E.} \, \| \, Ag^+(aq, \mathcal{A} = 1) | Ag(s)$$
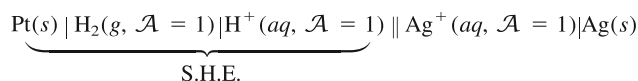
The standard reduction potential is the *difference* between the potential of the reaction of interest on the right and the potential of S.H.E on the left, which we have arbitrarily set to 0.

To measure the standard reduction potential of the half-reaction

$$Cd^{2+} + 2e^- \rightleftharpoons Cd(s) \qquad (14-13)$$

we construct the cell

$$S.H.E. \, \| \, Cd^{2+}(aq, \mathcal{A} = 1) | Cd(s)$$
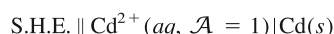
with the cadmium half-cell connected to the positive terminal of the potentiometer. In this case, we observe a *negative* voltage of -0.402 V. The negative sign means that electrons flow from Cd to Pt, a direction opposite that of the cell in Figure 14-8.

Appendix H contains standard reduction potentials arranged alphabetically by element. If the half-reactions were arranged according to descending value of $E°$ (as in Table 14-1), we would find the strongest oxidizing agents at the upper left and the strongest reducing agents

By convention, $E° = 0$ for S.H.E. Walther Nernst appears to have been the first to assign the potential of the hydrogen electrode as 0 in 1897.[15]

TABLE 14-1	**Ordered standard reduction potentials**	
Oxidizing agent	Reducing agent	$E°(V)$
$F_2(g) + 2e^- \rightleftharpoons 2F^-$		2.890
$O_3(g) + 2H^+ + 2e^- \rightleftharpoons O_2(g) + H_2O$		2.075
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$		1.507
$Ag^+ + e^- \rightleftharpoons Ag(s)$		0.799
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$		0.339
$2H^+ + 2e^- \rightleftharpoons H_2(g)$		0.000
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$		-0.402
$K^+ + e^- \rightleftharpoons K(s)$		-2.936
$Li^+ + e^- \rightleftharpoons Li(s)$		-3.040

Oxidizing power increases ↑ · Reducing power increases ↓

at the lower right. If we connected the two half-cells represented by Reactions 14-11 and 14-13, Ag^+ would be reduced to $Ag(s)$ as $Cd(s)$ is oxidized to Cd^{2+}.

14-4 Nernst Equation

Le Châtelier's principle tells us that increasing reactant concentrations drives a reaction to the right and increasing the product concentrations drives a reaction to the left. The net driving force for a redox reaction is expressed by the **Nernst equation,** whose two terms include the driving force under standard conditions ($E°$, which applies when all activities are unity) and a term showing the dependence on reagent concentrations.

Nernst Equation for a Half-Reaction

For the half-reaction

$$aA + ne^- \rightleftharpoons bB$$
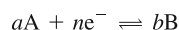
the Nernst equation giving the half-cell potential, E, is

Nernst equation:
$$E = E° - \frac{RT}{nF} \ln \frac{\mathcal{A}_B^b}{\mathcal{A}_A^a} \qquad (14\text{-}14)$$

A reaction is spontaneous if ΔG is negative and E is positive. $\Delta G°$ and $E°$ refer to the free energy change and potential when the activities of reactants and products are unity.
$$\Delta G° = -nNFE°$$

Challenge Show that Le Châtelier's principle requires a negative sign in front of the reaction quotient term in the Nernst equation. *Hint:* The more favorable a reaction, the more positive is E.

where $E°$ = standard reduction potential ($\mathcal{A}_A = \mathcal{A}_B = 1$)

R = gas constant (8.314 J/(K · mol) = 8.314 (V · C)/(K · mol))
T = temperature (K)
n = number of electrons in the half-reaction
F = Faraday constant (9.649×10^4 C/mol)
$\mathcal{A}_i$ = activity of species i

The logarithmic term in the Nernst equation is the **reaction quotient, Q.**

$$Q = \mathcal{A}_B^b / \mathcal{A}_A^a \qquad (14\text{-}15)$$

Q has the same form as the equilibrium constant, but the activities need not have their equilibrium values. Pure solids, pure liquids, and solvents are omitted from Q because their activities are unity (or close to unity). Concentrations of solutes are expressed as moles per liter and concentrations of gases are expressed as pressures in bars. When all activities are unity, $Q = 1$ and $\ln Q = 0$, thus giving $E = E°$.

Converting the natural logarithm in Equation 14-14 into the base 10 logarithm and inserting $T = 298.15$ K ($25.00°$C) gives the most useful form of the Nernst equation:

Appendix A shows that $\log x = (\ln x)/(\ln 10) = (\ln x)/2.303$.
The number 0.059 16 in the Nernst equation is $(RT \ln 10)/F$, which changes with temperature.

Nernst equation at 25°C:
$$E = E° - \frac{0.059\ 16\ \text{V}}{n} \log \frac{\mathcal{A}_B^b}{\mathcal{A}_A^a} \qquad (14\text{-}16)$$

The potential changes by $59.16/n$ mV for each factor-of-10 change in Q at 25°C.

EXAMPLE **Writing the Nernst Equation for a Half-Reaction**

Let's write the Nernst equation for the reduction of white phosphorus to phosphine gas:

$$\frac{1}{4}P_4(s, \text{white}) + 3H^+ + 3e^- \rightleftharpoons PH_3(g) \qquad E° = -0.046 \text{ V}$$
$$\text{Phosphine}$$
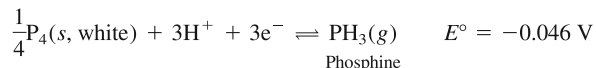
Solution We omit solids from the reaction quotient, and the concentration of a gas is expressed as the pressure of the gas. Therefore, the Nernst equation is

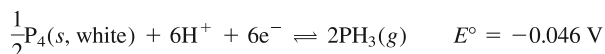$$E = -0.046 - \frac{0.059\ 16}{3}\log\frac{P_{PH_3}}{[H^+]^3}$$

TEST YOURSELF With $E°$ from Appendix H, write the Nernst equation for $ZnS(s) + 2e^- \rightleftharpoons Zn(s) + S^{2-}$. (*Answer:* $E = -1.405 - \dfrac{0.059\ 16}{2}\log[S^{2-}]$)

Phosphine is a highly poisonous gas with the odor of decaying fish. Solid white phosphorus glows faintly in the dark from spontaneous oxidation by O_2 in air.

Phosphine

White phosphorus consists of tetrahedral P_4 molecules
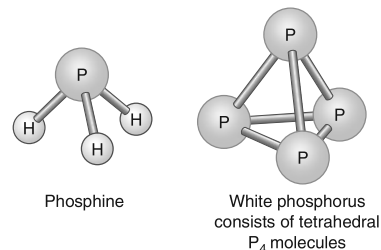
EXAMPLE **Multiplying a Half-Reaction Does Not Change $E°$**

If we multiply a half-reaction by any factor, $E°$ does not change. However, the factor n before the log term and the form of the reaction quotient, Q, do change. Let's write the Nernst equation for the reaction in the preceding example, multiplied by 2:

$$\frac{1}{2}P_4(s, \text{white}) + 6H^+ + 6e^- \rightleftharpoons 2PH_3(g) \qquad E° = -0.046 \text{ V}$$

Solution

$$E = -0.046 - \frac{0.059\ 16}{6}\log\frac{P_{PH_3}^2}{[H^+]^6}$$

Even though this Nernst equation does not look like the one in the preceding example, Box 14-4 shows that the numerical value of E is unchanged. The squared reaction quotient cancels the doubled value of n in front of the log term.

TEST YOURSELF Write the Nernst equation for $P_4 + 12H^+ + 12e^- \rightleftharpoons 4PH_3$. From Box 14-4, show that E is the same as if the reaction were written with $\frac{1}{2}P_4$ or $\frac{1}{4}P_4$.

Nernst Equation for a Complete Reaction

In Figure 14-6, the measured voltage is the difference between the potentials of the two electrodes:

Nernst equation for a complete cell: $\qquad E = E_+ - E_- \qquad$ (14-17)

where E_+ is the potential of the electrode attached to the positive terminal of the potentiometer and E_- is the potential of the electrode attached to the negative terminal. The potential of each half-reaction (*written as a reduction*) is governed by a Nernst equation, and the voltage for the complete reaction is the difference between the two half-cell potentials.
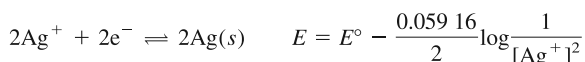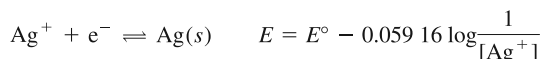
Here is a procedure for writing a net cell reaction and finding its voltage:

Step 1 Write *reduction* half-reactions for both half-cells and find $E°$ for each in Appendix H. Multiply the half-reactions as necessary so that they both contain the same number of electrons. When you multiply a reaction, you *do not* multiply $E°$.

Step 2 Write a Nernst equation for the right half-cell, which is attached to the positive terminal of the potentiometer. This is E_+.

Step 3 Write a Nernst equation for the left half-cell, which is attached to the negative terminal of the potentiometer. This is E_-.

Step 4 Find the net cell voltage by subtraction: $E = E_+ - E_-$.

Step 5 Write the net cell reaction by subtracting the left half-reaction from the right half-reaction. (Subtraction is equivalent to reversing the left half-reaction and adding.)

Electrons flow through the circuit from the more negative to the more positive electrode.

Electrons flow spontaneously through the circuit from the more negative electrode to the more positive electrode. If the net cell voltage that you calculated, E ($= E_+ - E_-$), is positive, then electrons flow through the wire from the left-hand electrode to the right-hand electrode. If the net cell voltage is negative, then electrons flow in the opposite direction.

EXAMPLE **Nernst Equation for a Complete Reaction**

Find the voltage of the cell in Figure 14-6 if the right half-cell contains 0.50 M $AgNO_3(aq)$ and the left half-cell contains 0.010 M $Cd(NO_3)_2(aq)$. Write the net cell reaction and state in which direction electrons flow.

Solution

Step 1 Right electrode: $\qquad\qquad 2Ag^+ + 2e^- \rightleftharpoons 2Ag(s) \qquad E_+° = 0.799$ V

Left electrode: $\qquad\qquad Cd^{2+} + 2e^- \rightleftharpoons Cd(s) \qquad E_-° = -0.402$ V
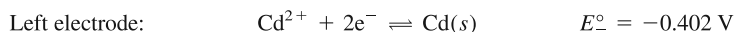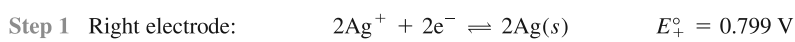
Step 2 Nernst equation for right electrode:
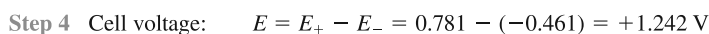
Pure solids, pure liquids, and solvents are omitted from Q.

$$E_+ = E_+° - \frac{0.059\ 16}{2}\log\frac{1}{[Ag^+]^2} = 0.799 - \frac{0.059\ 16}{2}\log\frac{1}{[0.50]^2} = 0.781\text{ V}$$
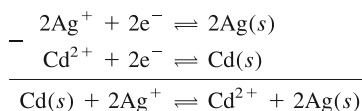
Step 3 Nernst equation for left electrode:

$$E_- = E_-° - \frac{0.059\ 16}{2}\log\frac{1}{[Cd^{2+}]} = -0.402 - \frac{0.059\ 16}{2}\log\frac{1}{[0.010]} = -0.461\text{ V}$$

The silver electrode potential is most positive, so *electrons flow from Cd to Ag through the circuit* (Figure 14-9).

Step 4 Cell voltage: $\qquad E = E_+ - E_- = 0.781 - (-0.461) = +1.242$ V

Step 5 Net cell reaction:

Subtracting a reaction is the same as reversing the reaction and adding.

$$\begin{array}{r} 2Ag^+ + 2e^- \rightleftharpoons 2Ag(s) \\ - \quad Cd^{2+} + 2e^- \rightleftharpoons Cd(s) \\ \hline Cd(s) + 2Ag^+ \rightleftharpoons Cd^{2+} + 2Ag(s) \end{array}$$

TEST YOURSELF Does the reaction go in the same direction if the cells contain 5.0 μM $AgNO_3$ and 1.0 M $Cd(NO_3)_2$? (***Answer:*** Yes: $E_+ = 0.485$ V, $E_- = -0.402$ V, $E = +0.887$ V)

What if you had written the Nernst equation for the right half-cell with just one electron instead of two?

$$Ag^+ + e^- \rightleftharpoons Ag(s)$$
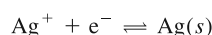
Would the net cell voltage be different from what we calculated? It better not be, because the chemistry is still the same. Box 14-4 shows that *neither $E°$ nor E depend on how we write the*

Electrons flow from Cd to Ag

Cd^{2+} | Cd
$E = -0.461$ V

Ag$^+$ | Ag
$E = 0.781$ V

−1.0   −0.5   0   0.5   1.0

E(cell) = 0.781 − (−0.461)
= 1.242 V

FIGURE 14-9 Electrons always flow from the more negative to the more positive electrode. That is, they always flow to the right in this diagram.[16]

reaction. Box 14-5 shows how to derive standard reduction potentials for half-reactions that are the sum of other half-reactions.

Different Descriptions of the Same Reaction

In Figure 14-4, the right half-reaction can be written

$$\text{AgCl}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{Cl}^- \qquad E_+^\circ = 0.222 \text{ V} \qquad (14\text{-}18)$$

$$E_+ = E_+^\circ - 0.059\,16 \log[\text{Cl}^-] = 0.222 - 0.059\,16 \log(0.033\,4) = 0.309_3 \text{ V} \quad (14\text{-}19)$$

The Cl$^-$ in the silver half-reaction was derived from 0.016 7 M CdCl$_2$(aq).

Suppose that a different, less handsome, author had written this book and had chosen to describe the half-reaction differently:

$$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}(s) \qquad E_+^\circ = 0.799 \text{ V} \qquad (14\text{-}20)$$
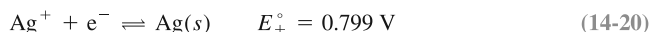
This description is just as valid as the previous one. In both cases, Ag(I) is reduced to Ag(0).

If the two descriptions are equally valid, then they should predict the same voltage. The Nernst equation for Reaction 14-20 is

$$E_+ = 0.799 - 0.059\,16 \log\frac{1}{[\text{Ag}^+]}$$

**BOX 14-5**   **Latimer Diagrams: How to Find E° for a New Half-Reaction**

A **Latimer diagram** displays standard reduction potentials, E°, connecting various oxidation states of an element.[17] For example, in acid solution, the following standard reduction potentials are observed:
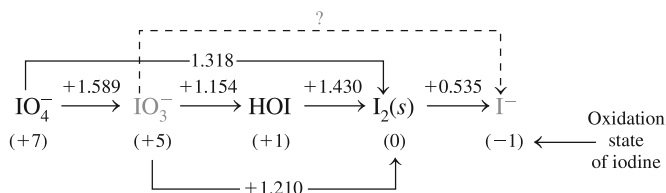
The notation IO$_3^-$ $\xrightarrow{+1.154}$ HOI stands for the balanced equation

$$\text{IO}_3^- + 5\text{H}^+ + 4e^- \rightleftharpoons \text{HOI} + 2\text{H}_2\text{O} \qquad E^\circ = +1.154 \text{ V}$$
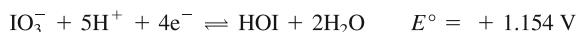
We can derive reduction potentials for arrows that are not shown in the diagram by using ΔG°. For example, the reaction shown by the dashed line in the Latimer diagram is

$$\text{IO}_3^- + 6\text{H}^+ + 6e^- \rightleftharpoons \text{I}^- + 3\text{H}_2\text{O}$$
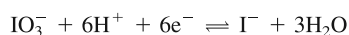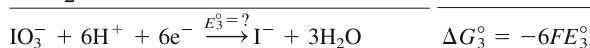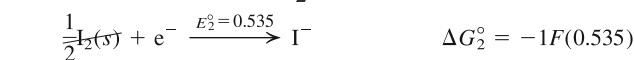
To find E° for this reaction, express the reaction as a sum of reactions whose potentials are known.

The standard free energy change, ΔG°, for a reaction is given by Equation 14-5:

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

In this equation, $n = 1$ unit charge per electron (a dimensionless number) and N is the number of moles of electrons in the half-reaction. The product nN is numerically the same as the number of electrons in the half-reaction and has the dimensions of mol.

When two reactions are added, ΔG° is the sum of ΔG° values for each reaction. To apply free energy to our problem, we write reactions whose sum is the desired reaction:

$$\text{IO}_3^- + 6\text{H}^+ + 5e^- \xrightarrow{E_1^\circ = 1.210} \tfrac{1}{2}\text{I}_2(s) + 3\text{H}_2\text{O} \quad \Delta G_1^\circ = -5F(1.210)$$

$$\tfrac{1}{2}\text{I}_2(s) + e^- \xrightarrow{E_2^\circ = 0.535} \text{I}^- \qquad \Delta G_2^\circ = -1F(0.535)$$

$$\overline{\text{IO}_3^- + 6\text{H}^+ + 6e^- \xrightarrow{E_3^\circ = ?} \text{I}^- + 3\text{H}_2\text{O} \qquad \Delta G_3^\circ = -6FE_3^\circ}$$
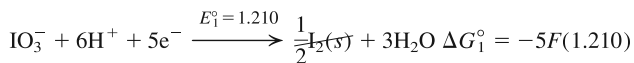
But, because $\Delta G_1^\circ + \Delta G_2^\circ = \Delta G_3^\circ$, we can solve for E_3°:

$$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

$$-6FE_3^\circ = -5F(1.210) - 1F(0.535)$$

$$E_3^\circ = \frac{5(1.210) + 1(0.535)}{6} = 1.098 \text{ V}$$

To find the concentration of Ag^+, we use the solubility product for AgCl. The cell contains 0.033 4 M Cl^- and solid AgCl, so we can say

$$[Ag^+] = \frac{K_{sp} \text{ (for AgCl)}}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{0.033\ 4} = 5.4 \times 10^{-9} \text{ M}$$

Putting this value of $[Ag^+]$ into the Nernst equation gives

$$E_+ = 0.799 - 0.05916 \log\frac{1}{5.4 \times 10^{-9}} = 0.309_9 \text{ V}$$

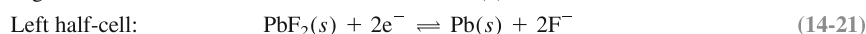which differs slightly from the value in Equation 14-19 because of the accuracy of K_{sp} and the neglect of activity coefficients. Reactions 14-18 and 14-20 give the same voltage in the Nernst equation because they describe the same cell.

The cell voltage cannot depend on how we write the reaction!

Advice for Finding Relevant Half-Reactions

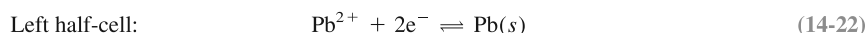**How to figure out the half-cell reactions**

When faced with a cell drawing or a line diagram, first write reduction reactions for each half-cell. To do this, *look in the cell for an element in two oxidation states*. For the cell

$$Pb(s)|PbF_2(s)|F^-(aq)\|Cu^{2+}(aq)|Cu(s)$$
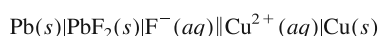
we see Pb in two oxidation states, as $Pb(s)$ and $PbF_2(s)$, and Cu in two oxidation states, as Cu^{2+} and $Cu(s)$. Thus, the half-reactions are

Right half-cell: $\qquad\qquad Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$

Left half-cell: $\qquad\qquad PbF_2(s) + 2e^- \rightleftharpoons Pb(s) + 2F^- \qquad\qquad$ (14-21)

You might have chosen to write the Pb half-reaction as

Left half-cell: $\qquad\qquad Pb^{2+} + 2e^- \rightleftharpoons Pb(s) \qquad\qquad$ (14-22)

because you know that if $PbF_2(s)$ is present, there must be some Pb^{2+} in the solution. Reactions 14-21 and 14-22 are equally valid and must predict the same cell voltage. Your choice of reactions depends on whether the F^- or Pb^{2+} concentration is easier to figure out.

Don't invent species not shown in the cell. Use what is shown in the line diagram to select the half-reactions.

We described the left half-cell in terms of a redox reaction involving Pb because Pb is the element that appears in two oxidation states. We would not write a reaction such as $F_2(g) + 2e^- \rightleftharpoons 2F^-$ because $F_2(g)$ is not shown in the line diagram of the cell.

The Nernst Equation Is Used in Measuring Standard Reduction Potentials

Problem 14-22 gives an example of the use of the Nernst equation to find $E°$.

The standard reduction potential would be observed if the half-cell of interest (with unit activities) were connected to a standard hydrogen electrode, as it is in Figure 14-8. It is nearly impossible to construct such a cell, because we have no way to adjust concentrations and ionic strength to give unit activities. In reality, activities less than unity are used in each half-cell, and the Nernst equation is employed to extract the value of $E°$ from the cell voltage.[18] In the hydrogen electrode, standard buffers with known pH (Table 15-3) are used to obtain known activities of H^+.

14-5 $E°$ and the Equilibrium Constant

A galvanic cell produces electricity because the cell reaction is not at equilibrium. The potentiometer allows negligible current to flow through it (Box 14-6), so concentrations in the cell remain unchanged. If we replaced the potentiometer with a wire, there would be much more current and concentrations would change until the cell reached equilibrium. At that point, nothing would drive the reaction, and E would be 0. When a battery (which is a galvanic cell) runs down to 0 V, the chemicals inside have reached equilibrium and the battery is "dead."

At equilibrium, E (not $E°$) = 0.

Now let's relate E for a whole cell to the reaction quotient, Q, for the net cell reaction. For the two half-reactions

Net cell reaction:
 $aA + bB \rightleftharpoons cC + dD$

Right electrode:	$aA + ne^- \rightleftharpoons cC$	$E_+°$
Left electrode:	$dD + ne^- \rightleftharpoons bB$	$E_-°$
Net reaction:	$aA + bB \rightleftharpoons cC + dD$	$E°$

CHAPTER 14 Fundamentals of Electrochemistry

Why doesn't operation of a cell change the concentrations in the cell? Cell voltage is measured under conditions of *negligible current flow*. The resistance of a high-quality pH meter is 10^{13} Ω. If a cell produces 1 V, the current through the circuit is

$$I = \frac{E}{R} = \frac{1 \text{ V}}{10^{13} \text{ }\Omega} = 10^{-13} \text{ A}$$

The electron flow is

$$\frac{10^{-13} \text{ C/s}}{9.649 \times 10^4 \text{ C/mol}} = 10^{-18} \text{ mol e}^-/\text{s}$$

which produces negligible oxidation and reduction of reagents in the cell. *The meter measures the voltage of the cell without affecting concentrations in the cell.*

If a salt bridge were left in a real cell for very long, concentrations and ionic strength would change because of diffusion between each compartment and the salt bridge. Cells should be set up for such a short time that mixing is insignificant.

the Nernst equation looks like this:

$$E = E_+ - E_- = E_+^\circ - \frac{0.059\ 16}{n}\log\frac{\mathcal{A}_C^c}{\mathcal{A}_A^a} - \left(E_-^\circ - \frac{0.059\ 16}{n}\log\frac{\mathcal{A}_B^b}{\mathcal{A}_D^d}\right)$$

$$E = \underbrace{(E_+^\circ - E_-^\circ)}_{E^\circ} - \frac{0.059\ 16}{n}\log\underbrace{\frac{\mathcal{A}_C^c\mathcal{A}_D^d}{\mathcal{A}_A^a\mathcal{A}_B^b}}_{Q} = E^\circ - \frac{0.059\ 16}{n}\log Q \qquad \text{(14-23)} \qquad \log a + \log b = \log ab$$

Equation 14-23 is true at any time. In the special case when the cell is at equilibrium, $E = 0$ and $Q = K$, the equilibrium constant. Therefore, Equation 14-23 is transformed into these most important forms at equilibrium:

Finding E° from K: $\qquad E^\circ = \frac{0.059\ 16}{n}\log K \qquad$ (at 25°C) $\qquad$ (14-24)

To go from Equation 14-24 to 14-25:

$$\frac{0.059\ 16}{n}\log K = E^\circ$$

$$\log K = \frac{nE^\circ}{0.059\ 16}$$

$$10^{\log K} = 10^{nE^\circ/0.059\ 16}$$

$$K = 10^{nE^\circ/0.059\ 16}$$

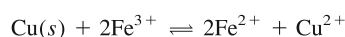*Finding K from E°:* $\qquad K = 10^{nE^\circ/0.059\ 16} \qquad$ (at 25°C) $\qquad$ (14-25)

Equation 14-25 allows us to deduce the equilibrium constant from E°. Alternatively, we can find E° from K with Equation 14-24.
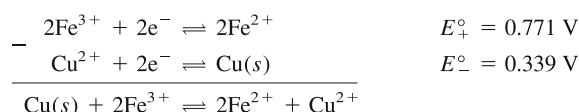
EXAMPLE **Using E° to Find the Equilibrium Constant**

Find the equilibrium constant for the reaction

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

Solution Divide the reaction into two half-reactions found in Appendix H:

$$2\text{Fe}^{3+} + 2e^- \rightleftharpoons 2\text{Fe}^{2+} \qquad\qquad E_+^\circ = 0.771 \text{ V}$$
$$-\ \underline{\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}(s) \qquad\qquad E_-^\circ = 0.339 \text{ V}}$$
$$\text{Cu}(s) + 2\text{Fe}^{3+} \rightleftharpoons 2\text{Fe}^{2+} + \text{Cu}^{2+}$$

We associate E_-° with the half-reaction that must be *reversed* to get the desired net reaction.

Then find E° for the net reaction

$$E^\circ = E_+^\circ - E_-^\circ = 0.771 - 0.339 = 0.432 \text{ V}$$

and compute the equilibrium constant with Equation 14-25:

$$K = 10^{(2)(0.432)/(0.059\ 16)} = 4 \times 10^{14}$$

A modest value of E° produces a large equilibrium constant. The value of K is correctly expressed with one significant figure because E° has three digits. Two are used for the exponent (14), and one is left for the multiplier (4).

Significant figures for logs and exponents were discussed in Section 3-2.

TEST YOURSELF Find K for the reaction $\text{Cu}(s) + 2\text{Ag}^+ \rightleftharpoons 2\text{Ag}(s) + \text{Cu}^{2+}$. (*Answer: $E^\circ = 0.460$ V, $K = 4 \times 10^{15}$*)

Finding K for Net Reactions That Are Not Redox Reactions

Consider the following half-reactions whose difference is the solubility reaction for iron(II) carbonate (which is not a redox reaction):
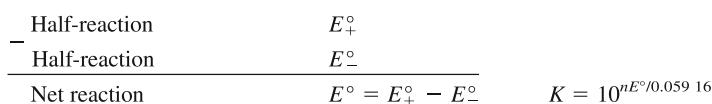
$$\begin{array}{ll} FeCO_3(s) + 2e^- \rightleftharpoons Fe(s) + CO_3^{2-} & E_+^\circ = -0.756 \text{ V} \\ \underline{- \quad Fe^{2+} + 2e^- \rightleftharpoons Fe(s)} & \underline{E_-^\circ = -0.44 \text{ V}} \\ \quad\quad FeCO_3(s) \rightleftharpoons Fe^{2+} + CO_3^{2-} & E^\circ = -0.756 - (-0.44) = -0.31_6 \text{ V} \\ \quad\quad\quad\;\; \text{Iron(II)} & \\ \quad\quad\quad\;\; \text{carbonate} & \end{array}$$
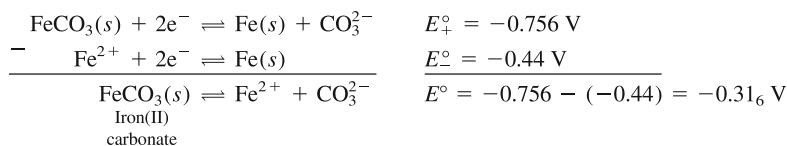
$$K = K_{sp} = 10^{(2)(-0.31_6)/(0.059\ 16)} = 10^{-11}$$
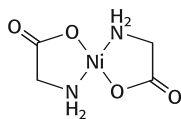
From E° for the net reaction, we can compute K_{sp} for iron(II) carbonate. Potentiometric measurements allow us to find equilibrium constants that are too small or too large to measure by determining concentrations of reactants and products directly.

"Wait!" you protest. "How can there be a redox potential for a reaction that is not a redox reaction?" Box 14-5 shows that the redox potential is just another way of expressing the free energy change of the reaction. The more energetically favorable the reaction (the more negative ΔG°), the more positive is E°.

The general form of a problem involving the relation between E° values for half-reactions and K for a net reaction is
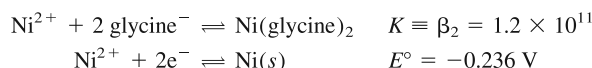
$$\begin{array}{ll} \text{Half-reaction} & E_+^\circ \\ \underline{- \quad \text{Half-reaction}} & \underline{E_-^\circ} \\ \quad\;\; \text{Net reaction} & E^\circ = E_+^\circ - E_-^\circ \quad\quad K = 10^{nE^\circ/0.059\ 16} \end{array}$$

If you know E_-° and E_+°, you can find E° and K for the net cell reaction. Alternatively, if you know E° and either E_-° or E_+°, you can find the missing standard potential. If you know K, you can calculate E° and use it to find either E_-° or E_+°, provided you know one of them.

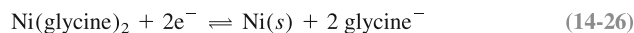---

EXAMPLE Relating E° and K

From the formation constant of $Ni(glycine)_2$ plus E° for the $Ni^{2+} \mid Ni(s)$ couple,

$$Ni^{2+} + 2\ glycine^- \rightleftharpoons Ni(glycine)_2 \quad K \equiv \beta_2 = 1.2 \times 10^{11}$$
$$Ni^{2+} + 2e^- \rightleftharpoons Ni(s) \quad\quad E^\circ = -0.236 \text{ V}$$

deduce the value of E° for the reaction

$$Ni(glycine)_2 + 2e^- \rightleftharpoons Ni(s) + 2\ glycine^- \quad\quad\quad (14\text{-}26)$$

Solution We need to see the relations among the three reactions:

$$\begin{array}{ll} \quad\quad Ni^{2+} + 2e^- \rightleftharpoons Ni(s) & E_+^\circ = -0.236 \text{ V} \\ \underline{- \quad Ni(glycine)_2 + 2e^- \rightleftharpoons Ni(s) + 2\ glycine^-} & \underline{E_-^\circ = ?} \\ \quad\quad Ni^{2+} + 2\ glycine^- \rightleftharpoons Ni(glycine)_2 & E^\circ = ?\ K = 1.2 \times 10^{11} \end{array}$$
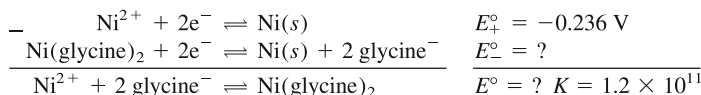
We know that $E_+^\circ - E_-^\circ$ must equal E°, so we can deduce the value of E_-° if we can find E°. But E° can be determined from the equilibrium constant for the net reaction:

$$E^\circ = \frac{0.059\ 16}{n}\log K = \frac{0.059\ 16}{2}\log(1.2 \times 10^{11}) = 0.328 \text{ V}$$

Hence, the standard reduction potential for half-reaction 14-26 is

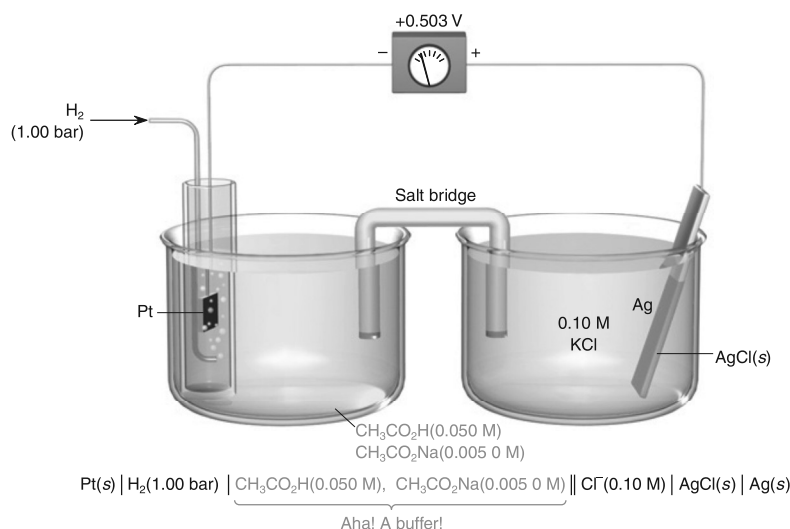$$E_-^\circ = E_+^\circ - E^\circ = -0.236 - 0.328 = -0.564 \text{ V}$$

TEST YOURSELF Select half-reactions in Appendix H to find the formation constant β_2 for $Cu^+ + 2\ ethylenediamine \rightleftharpoons Cu(ethylenediamine)_2^+$. (*Answer:* $E^\circ = 0.637$ V, $\beta_2 = 6 \times 10^{10}$)

14-6 Cells as Chemical Probes[19]

It is essential to distinguish two classes of equilibria associated with galvanic cells:

1. Equilibrium *between* the two half-cells
2. Equilibrium *within* each half-cell

Margin notes:

E° for dissolution of iron(II) carbonate is negative, which means that the reaction is "not spontaneous." "Not spontaneous" simply means $K < 1$.

Possible structure of $Ni(glycine)_2$

The more negative potential of -0.564 V for reducing $Ni(glycine)_2$ compared to -0.236 V for reducing Ni^{2+} tells us that it is harder to reduce $Ni(glycine)_2$ than Ni^{2+}. Complexation with glycine makes it harder to reduce Ni^{2+}.

$$Pt(s) \,|\, H_2(1.00 \text{ bar}) \,|\, CH_3CO_2H(0.050 \text{ M}), \ CH_3CO_2Na(0.005 \text{ 0 M}) \,\|\, Cl^-(0.10 \text{ M}) \,|\, AgCl(s) \,|\, Ag(s)$$

Aha! A buffer!

If a galvanic cell has a nonzero voltage, then the net cell reaction is not at equilibrium. We say that equilibrium *between* the two half-cells has not been established.

*We allow half-cells to stand long enough to come to chemical equilibrium **within** each half-cell.* For example, in the right-hand half-cell in Figure 14-10, the reaction
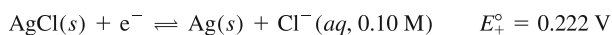
$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
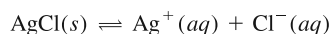
is at equilibrium. It is not part of the net cell reaction. It simply occurs when AgCl(s) is in contact with water. In the left half-cell, the reaction

$$CH_3CO_2H \rightleftharpoons CH_3CO_2^- + H^+$$
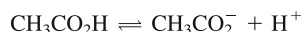
has also come to equilibrium. Neither reaction is part of the net cell redox reaction.

The redox reaction for the right half-cell of Figure 14-10 is

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq, 0.10 \text{ M}) \qquad E_+^\circ = 0.222 \text{ V}$$

But what is the reaction in the left half-cell? The only element we find in two oxidation states is hydrogen. We see that $H_2(g)$ bubbles into the cell, and we also realize that every aqueous solution contains H^+. Therefore, hydrogen is present in two oxidation states, and the half-reaction that takes place on the catalytic Pt surface can be written as

$$2H^+(aq, ? \text{ M}) + 2e^- \rightleftharpoons H_2(g, 1.00 \text{ bar}) \qquad E_-^\circ = 0$$
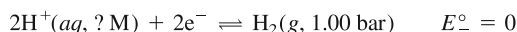
The net cell reaction is not at equilibrium, because the measured voltage is 0.503 V, not 0 V.

The Nernst equation for the net cell reaction is

$$E = E_+ - E_- = (0.222 - 0.059 \ 16 \log[Cl^-]) - \left(0 - \frac{0.059 \ 16}{2} \log \frac{P_{H_2}}{[H^+]^2}\right)$$

After inserting the known quantities, we discover that the only unknown is $[H^+]$. *The measured voltage therefore allows us to find $[H^+]$ in the left half-cell:*

$$0.503 = (0.222 - 0.059 \ 16 \log[0.10]) - \left(0 - \frac{0.059 \ 16}{2} \log \frac{1.00}{[H^+]^2}\right)$$

$$\Rightarrow [H^+] = 1.8 \times 10^{-4} \text{ M}$$

This, in turn, allows us to evaluate the equilibrium constant for the acid-base reaction that has come to equilibrium in the left half-cell:

$$K_a = \frac{[CH_3CO_2^-][H^+]}{[CH_3CO_2H]} = \frac{(0.005 \ 0)(1.8 \times 10^{-4})}{0.050} = 1.8 \times 10^{-5}$$

The cell in Figure 14-10 acts as a *probe* to measure $[H^+]$ in the left half-cell. Using this type of cell, we could determine the equilibrium constant for acid dissociation or base hydrolysis in the left half-cell.

A chemical reaction that occurs *within one half-cell* will reach equilibrium and is assumed to remain at equilibrium. Such a reaction is not the net cell reaction.

Question Why can we assume that the concentrations of acetic acid and acetate ion are equal to their initial (formal) concentrations?

Survival Tips

Problems in this chapter include some brainbusters designed to bring together your knowledge of electrochemistry, chemical equilibrium, solubility, complex formation, and acid-base chemistry. They require you to find the equilibrium constant for a reaction that occurs in only one half-cell. The reaction of interest is not the net cell reaction and is not a redox reaction. Here is a good approach:
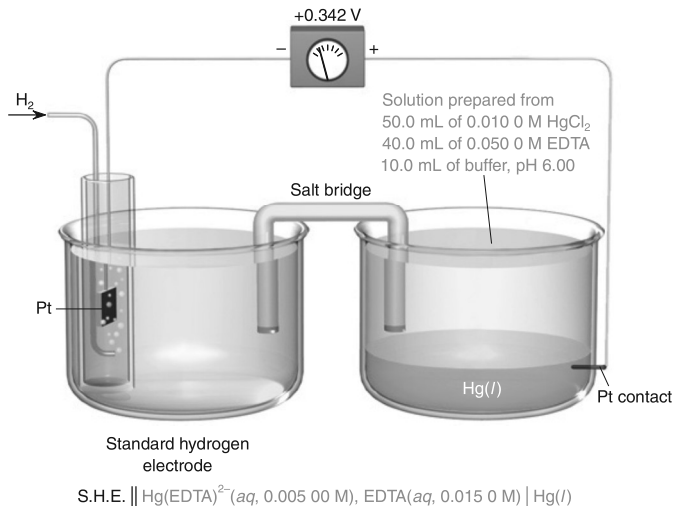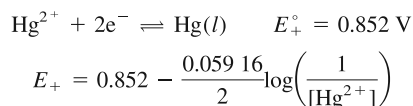
Step 1 Write the two half-reactions and their standard potentials. If you choose a half-reaction for which you cannot find $E°$, then find another way to write the reaction.

Step 2 Write a Nernst equation for the net reaction and put in all the known quantities. If all is well, there will be only one unknown in the equation.

Step 3 Solve for the unknown concentration and use that concentration to solve the chemical equilibrium problem that was originally posed.

> Half-reactions that you write *must* involve species that appear in two oxidation states in the cell.
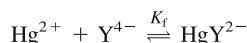

EXAMPLE Analyzing a Very Complicated Cell

The cell in Figure 14-11 measures the formation constant (K_f) of $Hg(EDTA)^{2-}$. The right-hand compartment contains 0.500 mmol of Hg^{2+} and 2.00 mmol of EDTA in 0.100 L buffered to pH 6.00. The voltage is $+0.342$ V. Find the value of K_f for $Hg(EDTA)^{2-}$.

Solution

Step 1 The left half-cell is a standard hydrogen electrode for which we can say $E_- = 0$. In the right half-cell, mercury is in two oxidation states. So let's write the half-reaction

$$Hg^{2+} + 2e^- \rightleftharpoons Hg(l) \qquad E_+° = 0.852 \text{ V}$$

$$E_+ = 0.852 - \frac{0.059\ 16}{2}\log\left(\frac{1}{[Hg^{2+}]}\right)$$

FIGURE 14-11 A galvanic cell that can be used to measure the formation constant for $Hg(EDTA)^{2-}$.

+0.342 V

H₂

Solution prepared from
50.0 mL of 0.010 0 M HgCl₂
40.0 mL of 0.050 0 M EDTA
10.0 mL of buffer, pH 6.00

Salt bridge

Pt

Hg(*l*)

Pt contact

Standard hydrogen
electrode

S.H.E. ‖ Hg(EDTA)²⁻(*aq*, 0.005 00 M), EDTA(*aq*, 0.015 0 M) │ Hg(*l*)

In the right half-cell, the reaction between Hg^{2+} and EDTA is

$$Hg^{2+} + Y^{4-} \overset{K_f}{\rightleftharpoons} HgY^{2-}$$

Because we expect K_f to be large, we assume that virtually all the Hg^{2+} has reacted to make HgY^{2-}. Therefore, the concentration of HgY^{2-} is 0.500 mmol/100 mL = 0.005 00 M. The remaining EDTA has a total concentration of $(2.00 - 0.50)$ mmol/100 mL = 0.015 0 M. The right-hand compartment therefore contains 0.005 00 M HgY^{2-}, 0.015 0 M EDTA, and a small, unknown concentration of Hg^{2+}.

The formation constant for HgY^{2-} can be written

$$K_f = \frac{[HgY^{2-}]}{[Hg^{2+}][Y^{4-}]} = \frac{[HgY^{2-}]}{[Hg^{2+}]\alpha_{Y^{4-}}[EDTA]}$$

where [EDTA] is the formal concentration of EDTA not bound to metal. In this cell, [EDTA] = 0.015 0 M. The fraction of EDTA in the form Y^{4-} is $\alpha_{Y^{4-}}$ (Section 12-2). Because we know that $[HgY^{2-}]$ = 0.005 00 M, all we need to find is $[Hg^{2+}]$ in order to evaluate K_f.

Step 2   The Nernst equation for the net cell reaction is

$$E = 0.342 = E_+ - E_- = \left[0.852 - \frac{0.059\ 16}{2}\log\left(\frac{1}{[Hg^{2+}]}\right) \right] - (0)$$

in which the only unknown is $[Hg^{2+}]$.

Step 3   Now we solve the Nernst equation to find $[Hg^{2+}] = 5._7 \times 10^{-18}$ M, and this value of $[Hg^{2+}]$ allows us to evaluate the formation constant for HgY^{2-}:

$$K_f = \frac{[HgY^{2-}]}{[Hg^{2+}]\alpha_{Y^{4-}}[EDTA]} = \frac{(0.005\ 00)}{(5._7 \times 10^{-18})(1.8 \times 10^{-5})(0.015\ 0)}$$

$$= 3 \times 10^{21}$$

The mixture of EDTA plus $Hg(EDTA)^{2-}$ in the cathode serves as a mercuric ion "buffer" that fixes the concentration of Hg^{2+}. This concentration, in turn, determines the cell voltage.

TEST YOURSELF   Find K_f if the cell voltage had been 0.300 V. (*Answer: 8×10^{22}*)

14-7   Biochemists Use $E^{\circ\prime}$

In respiration, O_2 oxidizes molecules from food to yield energy or metabolic intermediates. The standard reduction potentials that we have been using so far apply to systems in which all activities of reactants and products are unity. If H^+ is involved in the reaction, E° applies when pH = 0 ($\mathcal{A}_{H^+} = 1$). *Whenever H^+ appears in a redox reaction, or whenever reactants or products are acids or bases, reduction potentials are pH dependent.*

Because the pH inside a plant or animal cell is about 7, reduction potentials that apply at pH 0 are not particularly appropriate. For example, at pH 0, ascorbic acid (vitamin C) is a more powerful reducing agent than succinic acid. However, at pH 7, this order is reversed. It is the reducing strength at pH 7, not at pH 0, that is relevant to a living cell.

The *standard potential* for a redox reaction is defined for a galvanic cell in which all activities are unity. The **formal potential** is the reduction potential that applies under a *specified* set of conditions (including pH, ionic strength, and concentration of complexing agents). Biochemists call the formal potential at pH 7 $E^{\circ\prime}$ (read "E zero prime"). Table 14-2 lists $E^{\circ\prime}$ values for some biological redox couples.

Relation Between E° and $E^{\circ\prime}$

Consider the half-reaction

$$aA + ne^- \rightleftharpoons bB + mH^+ \qquad E^\circ$$
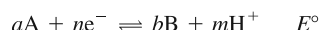
in which A is an oxidized species and B is a reduced species. Both A and B might be acids or bases, as well. The Nernst equation for this half-reaction is

$$E = E^\circ - \frac{0.059\ 16}{n}\log\frac{[B]^b[H^+]^m}{[A]^a}$$

To find $E^{\circ\prime}$, we rearrange the Nernst equation to a form in which the log term contains only the *formal concentrations* of A and B raised to the powers a and b, respectively.

Recipe for $E^{\circ\prime}$: $$E = \underbrace{E^\circ + \text{other terms}}_{\substack{\text{All of this is called } E^{\circ\prime} \\ \text{when pH} = 7}} - \frac{0.059\ 16}{n}\log\frac{F_B^b}{F_A^a} \qquad \text{(14-27)}$$

The entire collection of terms over the brace, evaluated at pH = 7, is called $E^{\circ\prime}$.

TABLE 14-2 Reduction potentials of biological interest

Reaction	$E°$ (V)	$E°'$ (V)
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229	+0.815
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.771	+0.771
$I_2 + 2e^- = 2I^-$	+0.535	+0.535
Cytochrome a (Fe^{3+}) + $e^- \rightleftharpoons$ cytochrome a (Fe^{2+})	+0.290	+0.290
$O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.695	+0.281
Cytochrome c (Fe^{3+}) + $e^- \rightleftharpoons$ cytochrome c (Fe^{2+})	—	+0.254
2, 6-Dichlorophenolindophenol + $2H^+ + 2e^- \rightleftharpoons$ reduced 2,6-dichlorophenolindophenol	—	+0.22
Dehydroascorbate + $2H^+ + 2e^- \rightleftharpoons$ ascorbate + H_2O	+0.390	+0.058
Fumarate + $2H^+ + 2e^- \rightleftharpoons$ succinate	+0.433	+0.031
Methylene blue + $2H^+ + 2e^- \rightleftharpoons$ reduced product	+0.532	+0.011
Glyoxylate + $2H^+ + 2e^- \rightleftharpoons$ glycolate	—	−0.090
Oxaloacetate + $2H^+ + 2e^- \rightleftharpoons$ malate	+0.330	−0.102
Pyruvate + $2H^+ + 2e^- \rightleftharpoons$ lactate	+0.224	−0.190
Riboflavin + $2H^+ + 2e^- \rightleftharpoons$ reduced riboflavin	—	−0.208
FAD + $2H^+ + 2e^- \rightleftharpoons FADH_2$	—	−0.219
(Glutathione-S)$_2$ + $2H^+ + 2e^- \rightleftharpoons$ 2 glutathione-SH	—	−0.23
Safranine T + $2e^- \rightleftharpoons$ leucosafranine T	−0.235	−0.289
$(C_6H_5S)_2 + 2H^+ + 2e^- \rightleftharpoons 2C_6H_5SH$	—	−0.30
$NAD^+ + H^+ + 2e^- \rightleftharpoons NADH$	−0.105	−0.320
$NADP^+ + H^+ + 2e^- \rightleftharpoons NADPH$	—	−0.324
Cystine + $2H^+ + 2e^- \rightleftharpoons$ 2 cysteine	—	−0.340
Acetoacetate + $2H^+ + 2e^- \rightleftharpoons$ L-β-hydroxybutyrate	—	−0.346
Xanthine + $2H^+ + 2e^- \rightleftharpoons$ hypoxanthine + H_2O	—	−0.371
$2H^+ + 2e^- \rightleftharpoons H_2$	0.000	−0.414
Gluconate + $2H^+ + 2e^- \rightleftharpoons$ glucose + H_2O	—	−0.44
$SO_4^{2-} + 2e^- + 2H^+ \rightleftharpoons SO_3^{2-} + H_2O$	—	−0.454
$2SO_3^{2-} + 2e^- + 4H^+ \rightleftharpoons S_2O_4^{2-} + 2H_2O$	—	−0.527

To convert [A] or [B] into F_A or F_B, we use fractional composition equations (Section 10-5), which relate the formal (that is, total) concentration of *all* forms of an acid or a base to its concentration in a *particular* form:

For a monoprotic acid:

$$F = [HA] + [A^-]$$

For a diprotic acid:

$$F = [H_2A] + [HA^-] + [A^{2-}]$$

Monoprotic system:

$$[HA] = \alpha_{HA}F = \frac{[H^+]F}{[H^+] + K_a} \tag{14-28}$$

$$[A^-] = \alpha_{A^-}F = \frac{K_aF}{[H^+] + K_a} \tag{14-29}$$

Diprotic system:

$$[H_2A] = \alpha_{H_2A}F = \frac{[H^+]^2F}{[H^+]^2 + [H^+]K_1 + K_1K_2} \tag{14-30}$$

$$[HA^-] = \alpha_{HA^-}F = \frac{K_1[H^+]F}{[H^+]^2 + [H^+]K_1 + K_1K_2} \tag{14-31}$$

$$[A^{2-}] = \alpha_{A^{2-}}F = \frac{K_1K_2F}{[H^+]^2 + [H^+]K_1 + K_1K_2} \tag{14-32}$$

where F is the formal concentration of HA or H_2A, K_a is the acid dissociation constant for HA, and K_1 and K_2 are the acid dissociation constants for H_2A.

One way to *measure* $E°'$ is to establish a half-cell in which the formal concentrations of the oxidized and reduced species are equal and the pH is adjusted to 7. Then the log term in Equation 14-27 is zero and the measured potential (versus S.H.E.) is $E°'$.

EXAMPLE **Calculating the Formal Potential**

Find $E^{\circ\prime}$ for the reaction

$$\text{Dehydroascorbic acid}^{20} \text{ (oxidized)} + 2H^+ + 2e^- \rightleftharpoons \text{Ascorbic acid (vitamin C) (reduced)} + H_2O \qquad E^\circ = 0.390 \text{ V} \quad (14\text{-}33)$$

Dehydroascorbic acid (oxidized)

Ascorbic acid (vitamin C) (reduced)
$pK_1 = 4.10 \qquad pK_2 = 11.79$

Acidic protons
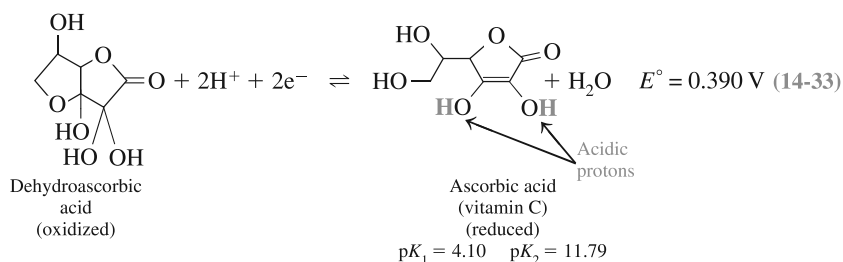
Solution Abbreviating dehydroascorbic acid[20] as D, and ascorbic acid as H_2A, we rewrite the reduction as

$$D + 2H^+ + 2e^- \rightleftharpoons H_2A + H_2O$$
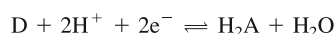
for which the Nernst equation is

$$E = E^\circ - \frac{0.059\ 16}{2}\log\frac{[H_2A]}{[D][H^+]^2} \qquad (14\text{-}34)$$

D is not an acid or a base, so its formal concentration equals its molar concentration: $F_D = [D]$. For the diprotic acid H_2A, we use Equation 14-30 to express $[H_2A]$ in terms of F_{H_2A}:

$$[H_2A] = \frac{[H^+]^2 F_{H_2A}}{[H^+]^2 + [H^+]K_1 + K_1K_2}$$

Putting these values into Equation 14-34 gives

$$E = E^\circ - \frac{0.059\ 16}{2}\log\left(\frac{\dfrac{[H^+]^2 F_{H_2A}}{[H^+]^2 + [H^+]K_1 + K_1K_2}}{F_D[H^+]^2}\right)$$

which can be rearranged to the form

$$E = E^\circ - \underbrace{\frac{0.059\ 16}{2}\log\left(\frac{1}{[H^+]^2 + [H^+]K_1 + K_1K_2}\right)}_{\substack{\text{Formal potential } (= E^{\circ\prime} \text{ if pH} = 7) \\ = +0.062 \text{ V}}} - \frac{0.059\ 16}{2}\log\frac{F_{H_2A}}{F_D} \qquad (14\text{-}35)$$

Putting the values of E°, K_1, and K_2 into Equation 14-35 and setting $[H^+] = 10^{-7.00}$, we find $E^{\circ\prime} = +0.062$ V.

TEST YOURSELF Compute $E^{\circ\prime}$ for the reaction $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$. (***Answer:*** 0.815 V)

Curve *a* in Figure 14-12 shows how the calculated formal potential for Reaction 14-33 depends on pH. The potential decreases as the pH increases, until pH $\approx pK_2 = 11.79$. Above pK_2, A^{2-} is the dominant form of ascorbic acid, and no protons are involved in the net redox reaction. Therefore, the potential becomes independent of pH.

A biological example of $E^{\circ\prime}$ is the reduction of Fe(III) in the protein transferrin. This protein has two Fe(III)-binding sites, one in each half of the molecule designated C and N for the carboxyl and amino terminals of the peptide chain. Transferrin carries Fe(III) through the blood to cells that require iron. Membranes of these cells have a receptor that binds Fe(III)-transferrin and takes it into a compartment called an endosome into which H^+ is pumped to lower the pH to ~5.8. Iron is released from transferrin in the endosome and continues into the cell as Fe(II) attached to an intracellular metal-transport protein. The entire cycle of transferrin uptake, metal removal, and transferrin release back to the bloodstream takes 1−2 min. The time required for Fe(III) to dissociate from transferrin at pH 5.8 is ~6 min, which is too long to account for release in the endosome. The reduction potential of Fe(III)-transferrin at pH 5.8 is $E^{\circ\prime} = -0.52$ V, which is too low for physiologic reductants.
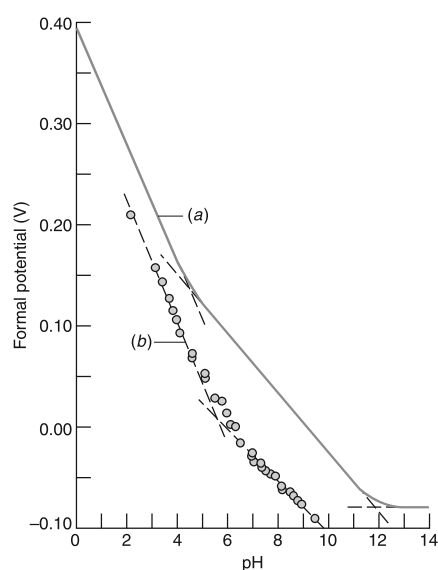
FIGURE 14-12 Reduction potential of ascorbic acid, showing its dependence on pH. (a) Graph of the function labeled formal potential in Equation 14-35. (b) Experimental polarographic half-wave reduction potential of ascorbic acid in a medium of ionic strength = 0.2 M. The half-wave potential (Chapter 17) is nearly the same as the formal potential. At high pH (>12), the half-wave potential does not level off to a slope of 0, as Equation 14-35 predicts. Instead, hydrolysis of ascorbic acid occurs and the chemistry is more complex than Reaction 14-33. [Data from J. J. Ruiz, A. Aldaz, and M. Dominguez, *Can. J. Chem.* **1977**, *55*, 2799; ibid., **1978**, *56*, 1533.]
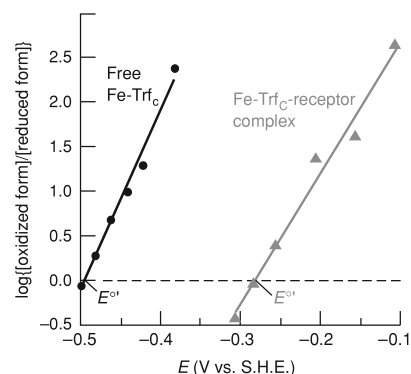
FIGURE 14-13 Spectroscopic measurement of log{[Fe(III)Trf$_C$]/[Fe(II)Trf$_C$]} versus potential at pH 5.8. [Data from S. Dhungana, C. H. Taboy, O. Zak, M. Larvie, A. L. Crumbliss, and P. Aisen, "Redox Properties of Human Transferrin Bound to Its Receptor," *Biochemistry* **2004**, *43*, 205.]

The mystery of how Fe(III) is released from transferrin in the endosome was solved by measuring $E^{\circ\prime}$ for the Fe(III)-transferrin-receptor complex at pH 5.8. To simplify the chemistry, transferrin was cleaved and only the C-terminal half of the protein (designated Trf$_C$) was used. Figure 14-13 shows measurements of log{[Fe(III)Trf$_C$]/[Fe(II)Trf$_C$]} for free protein and for the protein-receptor complex. In Equation 14-27, $E = E^{\circ\prime}$ when the log term is zero (that is, when [Fe(III)Trf$_C$] = [Fe(II)Trf$_C$]). Figure 14-13 shows that $E^{\circ\prime}$ for Fe(III)Trf$_C$ is near −0.50 V, but $E^{\circ\prime}$ for the Fe(III)Trf$_C$-receptor complex is −0.29 V. The reducing agents NADH and NADPH in Table 14-2 are strong enough to reduce Fe(III)Trf$_C$ bound to its receptor at pH 5.8, but not strong enough to reduce free Fe(III)-transferrin.

Terms to Understand

ampere	Faraday constant	oxidant	reduction
anode	formal potential	oxidation	resistance
cathode	galvanic cell	oxidizing agent	salt bridge
coulomb	half-reaction	potentiometer	standard hydrogen electrode
current	joule	power	standard reduction potential
$E^{\circ\prime}$	Latimer diagram	reaction quotient	volt
electric potential	Nernst equation	redox reaction	watt
electrochemistry	ohm	reducing agent	
electrode	Ohm's law	reductant	

Summary

Electric current is the number of coulombs of charge per second passing a point. The electric potential difference, E (volts), between two points is the work (joules) per unit charge that is needed or can be done when charge moves from one point to the other. For N moles of a species with n charges per molecule, the electric charge in coulombs is $q = nNF$, where F is the Faraday constant (C/mol). Work done when a charge of q coulombs passes through a potential difference of E volts is work = $E \cdot q$. The maximum work that can be done on the surroundings by a spontaneous chemical reaction is related to the free energy change for the reaction: work = $-\Delta G$. If