ELECTROCHEMISTRY

Chapter 12

What Are the Key Ideas? The tendency of electrons to be transferred in a chemical reaction depends on the species involved and their concentrations. When the process is spontaneous and reduction and oxidation occur at different locations, the reaction can do work and drive electrons through an external circuit.

Why Do We Need to Know This Material? The topics described in this chapter may one day unlock a virtually inexhaustible supply of clean energy supplied daily by the Sun. The key is electrochemistry, the study of the interaction of electricity and chemical reactions. The transfer of electrons from one species to another is one of the fundamental processes underlying life, photosynthesis, fuel cells, and the refining of metals. An understanding of how electrons are transferred helps us to design ways to use chemical reactions to generate electricity and to use electricity to bring about chemical reactions. Electrochemical measurements also allow us to determine the values of thermodynamic quantities.

What Do We Need to Know Already? This chapter extends the thermodynamic discussion presented in Chapter 7. In particular, it builds on the concept of Gibbs free energy (Section 7.12), its relation to maximum nonexpansion work (Section 7.14), and the dependence of the reaction Gibbs free energy on the reaction quotient (Section 9.3). For a review of redox reactions, see Section K. To prepare for the quantitative treatment of electrolysis, review stoichiometry in Section L.

Electricity has been observed since ancient times in the form of lightning, as sparks given off when metals strike one another, and as shocks from static electricity. However, its nature and its usefulness were unknown until the late eighteenth century, when the Italian scientist Luigi Galvani discovered that by touching the muscles of dead animals, mainly frogs, with a rod bearing static electricity, he could make their muscles twitch. He believed that electricity came from the muscles themselves. However, at the end of that century another Italian, Alessandro Volta, suggested that the electricity came from the fact that the muscles were between two different metals when touched by the rod. He proved that the electricity came from metals by constructing a tower of alternating discs of different metals in layers separated by paper strips soaked in a solution of table salt (Fig. 12.1). This apparatus, a "voltaic pile," was the first electrical storage device, a simple battery, but because it opened a door to a new understanding of the structure of matter, it amazed the scientists and even the rulers of the day. Eventually scientists realized that the electricity arose from electrons passing from one metal to another in redox reactions.

These early observations have evolved into the branch of chemistry called **electrochemistry**. This subject deals not only with the use of spontaneous chemical reactions to produce electricity but also with the use of electricity to drive nonspontaneous reactions forward. Electrochemistry also provides techniques for monitoring chemical reactions and measuring properties of solutions such as the pK_a of an acid. Electrochemistry even allows us to monitor the activity of our brain and heart (perhaps while we are trying to master chemistry), the pH of our blood, and the presence of pollutants in our water supply.

REPRESENTING REDOX REACTIONS

We begin with a review of redox reactions, which were introduced in Section K. In this chapter we take a closer look at them and see how they can be used to generate electricity, particularly in aqueous solution.

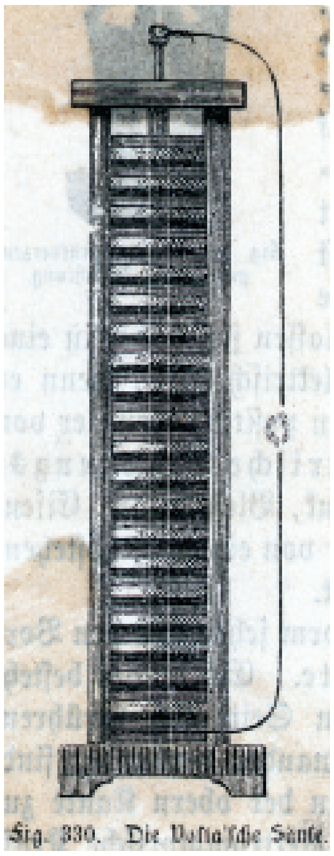


FIGURE 12.1 Volta used this stack of alternating disks of two different metals separated by paper soaked in salt water to produce the first sustainable electric current.

We need to be able to write balanced chemical equations to describe redox reactions. It might seem that this task ought to be simple. However, some redox reactions can be tricky to balance, and special techniques, which we describe in Sections 12.1 and 12.2, have been developed to simplify the procedure.

12.1 Half-Reactions

The key to writing and balancing equations for redox reactions is to think of the reduction and oxidation processes individually. We saw in Section K that oxidation is the loss of electrons and reduction the gain of electrons.

We consider oxidation first. To show the removal of electrons from a species that is being oxidized in a redox reaction, we write the chemical equation for an oxidation half-reaction. A **half-reaction** is the oxidation or reduction part of the reaction considered alone. For example, one battery that Volta built used silver and zinc plates to carry out the reaction

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

To show the oxidation of zinc we write

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

An oxidation half-reaction is a *conceptual* way of reporting an oxidation: the electrons are never actually free. In an equation for an oxidation half-reaction, the electrons released always appear on the right of the arrow. Their state is not given, because they are in transit and do not have a definite physical state. The reduced and oxidized species in a half-reaction jointly form a **redox couple**. In this example, the redox couple consists of Zn^{2+} and Zn, and is denoted Zn^{2+}/Zn. A redox couple has the form Ox/Red, where Ox is the oxidized form of the species and Red is the reduced form.

A note on good practice: Distinguish a conceptual half-reaction from an actual ionization, where the electron is removed and which we would write, for example, as $\mathrm{Na(g)} \rightarrow \mathrm{Na^{+}(g)} + \mathrm{e^{-}(g)}$, with the state of the electron specified.

Now consider reduction. To show the addition of electrons to a species we write the corresponding half-reaction for electron gain. For example, to show the reduction of Ag^{+} ions to Ag metal we write

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

This half-reaction, too, is conceptual: the electrons are not actually free. In the equation for a reduction half-reaction, the electrons gained always appear on the left of the arrow. In this example, the redox couple is Ag^{+}/Ag.

Half-reactions express the two contributions (oxidation and reduction) to an overall redox reaction.

12.2 Balancing Redox Equations

Balancing the chemical equation for a redox reaction by inspection can be a real challenge, especially for one taking place in aqueous solution, when water may participate and we must include H_2O and either H^{+} or OH^{-}. In such cases, it is easier to simplify the equation by separating it into its reduction and oxidation half-reactions, balance the half-reactions separately, and then add them together to obtain the balanced equation for the overall reaction. When adding the equations for half-reactions, we match the number of electrons released by oxidation with the number used in reduction, because electrons are neither created nor destroyed in chemical reactions. The procedure is outlined in Toolbox 12.1 and illustrated in Examples 12.1 and 12.2.

In redox reactions, it is conventional to write H^{+} rather than H_3O^{+}.

TOOLBOX 12.1 HOW TO BALANCE COMPLICATED REDOX EQUATIONS

CONCEPTUAL BASIS

When balancing redox equations, we consider the gain of electrons (reduction) separately from the loss of electrons (oxidation), express each of these processes as a half-reaction, and then balance both atoms and charge in each of the two half-reactions. When we combine the half-reactions, the number of electrons released in the oxidation must equal the number used in the reduction.

PROCEDURE

The general procedure for balancing the chemical equation for a redox reaction is first to balance the half-reactions separately.

Step 1 Identify the species being oxidized and the species being reduced from the changes in their oxidation numbers.

Step 2 Write the two skeletal (unbalanced) equations for the oxidation and reduction half-reactions.

Step 3 Balance all elements in the half-reactions except O and H.

Step 4 In acidic solution, balance O by using H_2O and then balance H by using H^+. In basic solution, balance O by using H_2O; then balance H by adding H_2O to the side of each half-reaction that needs H and adding OH^- to the other side.

When we add . . . OH^- . . . → . . . H_2O . . . to a half-reaction, we are effectively adding one H atom to the right. When we add . . . H_2O . . . → . . . OH^- . . ., we are effectively adding one H atom to the left. Note that one H_2O molecule is added for each H atom needed.

Step 5 Balance the electric charges by adding electrons to the left for reductions and to the right for oxidations until the charges on the two sides of the arrow are the same.

Step 6 Multiply all species in either one or both half-reactions by factors that result in equal numbers of electrons in the two half-reactions, and then add the two equations and include physical states.

Finally, simplify the appearance of the equation by canceling species that appear on both sides of the arrow and check to make sure that charges as well as numbers of atoms balance. In some cases it is possible to simplify the half-reactions before they are combined.

Examples 12.1 and 12.2 illustrate this procedure.

EXAMPLE 12.1 Sample exercise: Balancing a redox equation in acidic solution

Permanganate ions, MnO_4^-, react with oxalic acid, $H_2C_2O_4$, in acidic aqueous solution, producing manganese(II) ions and carbon dioxide. The skeletal equation is

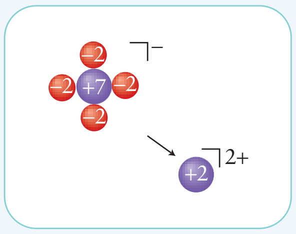
$$MnO_4^-(aq) + H_2C_2O_4(aq) \longrightarrow Mn^{2+}(aq) + CO_2(g)$$ ⚠

SOLUTION To balance this equation, work through the procedure for an acidic solution set out in Toolbox 12.1.

Reduction half-reaction:

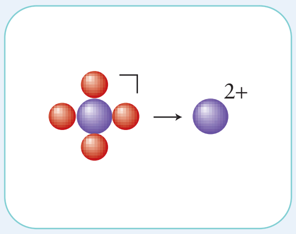
Step 1 Identify the species being reduced.

The oxidation number of Mn decreases from +7 to +2, so the Mn in the MnO_4^- ion is reduced.



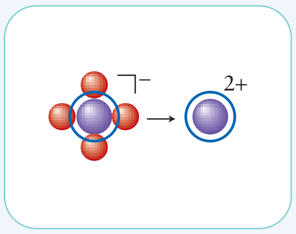
Step 2 Write the skeletal equation for reduction.

$MnO_4^- \longrightarrow Mn^{2+}$



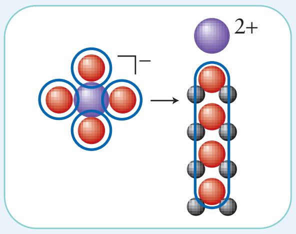
Step 3 Balance all elements except H and O.

$MnO_4^- \longrightarrow Mn^{2+}$



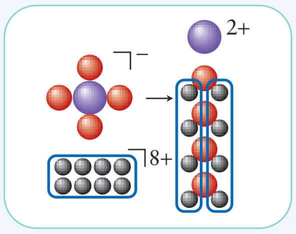
Step 4 Balance the O atoms by adding H_2O.

$MnO_4^- \longrightarrow Mn^{2+} + 4\,H_2O$



Balance the H atoms by adding H^+.

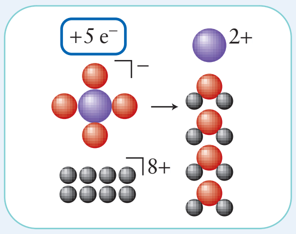
$MnO_4^- + 8\,H^+ \longrightarrow Mn^{2+} + 4\,H_2O$



Step 5 Balance the net charges by adding electrons.

Net charge on the left is +7 and on the right it is +2; we need 5 electrons on the left to bring it to +2.

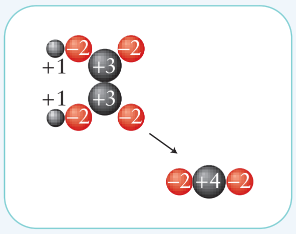
$MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O$



Oxidation half-reaction:

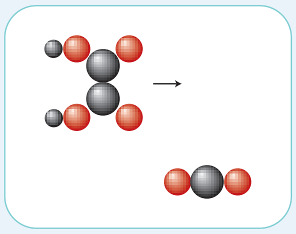
Step 1 Identify the species being oxidized.

The oxidation number of carbon increases from +3 to +4, so the C atoms in the oxalic acid are oxidized.



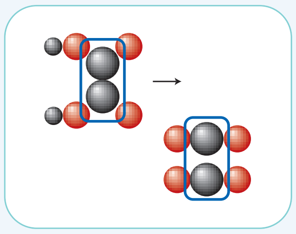
Step 2 Write the skeletal equation for oxidation.

$H_2C_2O_4 \longrightarrow CO_2$



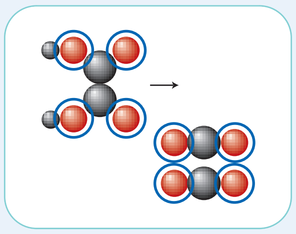
Step 3 Balance all elements except H and O.

$H_2C_2O_4 \longrightarrow 2\,CO_2$



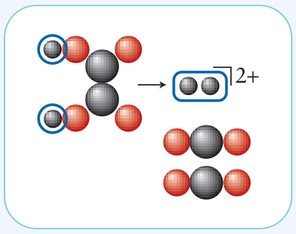
Step 4 Balance the O atoms by adding H_2O (none required).

$$H_2C_2O_4 \longrightarrow 2\ CO_2$$



Balance the H atoms by adding H^+.

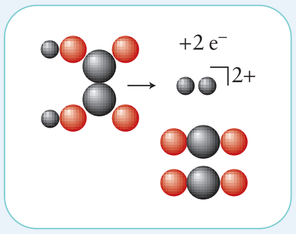
$$H_2C_2O_4 \longrightarrow 2\ CO_2 + 2\ H^+$$



Step 5 Balance charge by adding electrons.

Net charge on the left is 0 and on the right it is +2; we need 2 electrons on the right to bring it to 0.

$$H_2C_2O_4 \longrightarrow 2\ CO_2 + 2\ H^+ + 2\ e^-$$



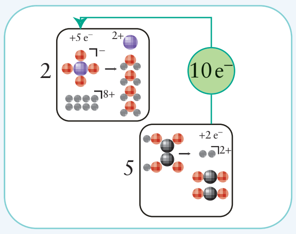
A note on good practice: At this point, check that the number of electrons lost or gained in each half-reaction is the same as the change in oxidation number of the element oxidized or reduced.

Step 6 Write the overall equation. In the half-reactions, 2 electrons are lost, but 5 are gained, so we need 10 in each half-reaction.

Multiply the reduction half-reaction by 2 and multiply the oxidation half-reaction by 5.

$$2\ MnO_4^- + 16\ H^+ + 10\ e^- \longrightarrow 2\ Mn^{2+} + 8\ H_2O$$

$$5\ H_2C_2O_4 \longrightarrow 10\ CO_2 + 10\ H^+ + 10\ e^-$$



Add the equations and cancel electrons.

$$2\ MnO_4^- + 5\ H_2C_2O_4 + 16\ H^+ \longrightarrow 2\ Mn^{2+} + 8\ H_2O + 10\ CO_2 + 10\ H^+$$

Cancel 10 H^+ ions on each side and include physical states.

$$2\ MnO_4^-(aq) + 5\ H_2C_2O_4(aq) + 6\ H^+(aq) \longrightarrow 2\ Mn^{2+}(aq) + 8\ H_2O(l) + 10\ CO_2(g)$$

Elements and charge are both balanced; so this is the fully balanced net ionic equation.

SELF-TEST 12.1A Copper reacts with dilute nitric acid to form copper(II) nitrate and the gas nitric oxide, NO. Write the net ionic equation for the reaction.
[***Answer:*** $3\ Cu(s) + 2\ NO_3^-(aq) + 8\ H^+(aq) \rightarrow 3\ Cu^{2+}(aq) + 2\ NO(g) + 4\ H_2O(l)$]

SELF-TEST 12.1B Acidified potassium permanganate solution reacts with sulfurous acid, $H_2SO_3(aq)$, to form sulfuric acid and manganese(II) ions. Write the net ionic equation for the reaction. In acidic aqueous solution, H_2SO_3 is present as electrically neutral molecules and sulfuric acid is present as HSO_4^- ions.

EXAMPLE 12.2 Sample exercise: Balancing a redox equation in basic solution

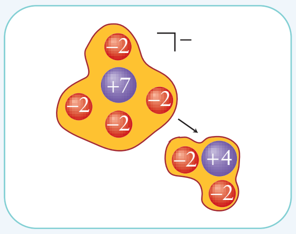
The products of the reaction between bromide ions and permanganate ions, MnO_4^-, in basic aqueous solution are solid manganese(IV) oxide, MnO_2, and bromate ions. Balance the net ionic equation for the reaction.

SOLUTION Work through the procedure for a basic solution set out in Toolbox 12.1.

Reduction half-reaction:

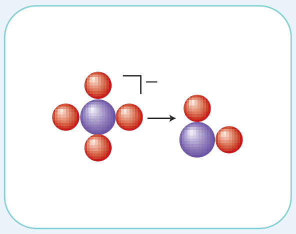
Step 1 Identify the species being reduced.

The oxidation number of Mn changes from +7 in MnO_4^- to +4 in MnO_2, so the Mn in MnO_4^- is reduced ("permanganate is reduced").

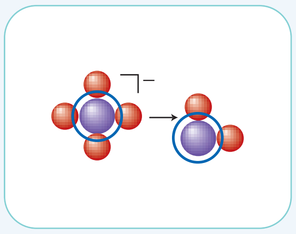


Step 2 Write the skeletal equation for reduction.

$MnO_4^- \longrightarrow MnO_2$

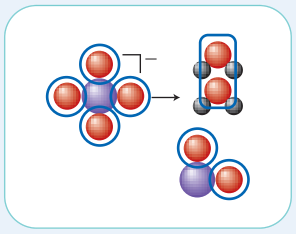


Step 3 Mn atoms are balanced.



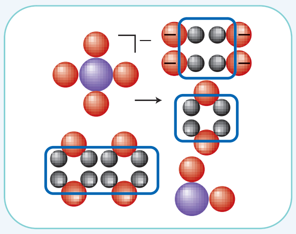
Step 4 Balance the O atoms by adding H_2O.

$MnO_4^- \longrightarrow MnO_2 + 2\ H_2O$



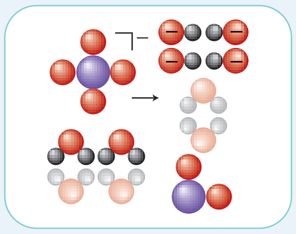
Balance the H atoms by adding (for each H atom needed) one H_2O molecule to the side of each equation that needs hydrogen and one OH^- ion to the opposite side.

$MnO_4^- + 4\ H_2O \longrightarrow MnO_2 + 2\ H_2O + 4\ OH^-$



Cancel like species on opposite sides of the arrow (in this case, 2 H_2O).

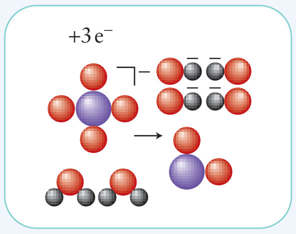
$MnO_4^- + 2\ H_2O \longrightarrow MnO_2 + 4\ OH^-$



Step 5 Balance charge by adding electrons.

Net charge on the left is −1 and on the right it is −4; we need 3 electrons on the left to bring it to −4.

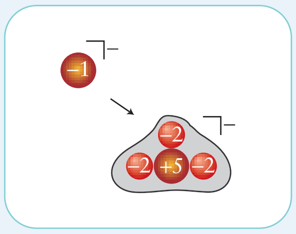
$MnO_4^- + 2\,H_2O + 3\,e^- \longrightarrow MnO_2 + 4\,OH^-$



Oxidation half-reaction:

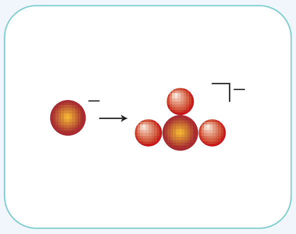
Step 1 Identify the species being oxidized.

The oxidation number of Br increases from −1 in Br^- to +5 in BrO_3^-, and so Br^- is oxidized.

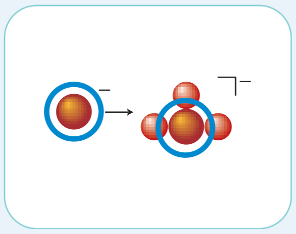


Step 2 Write the skeletal equation for oxidation.

$Br^- \longrightarrow BrO_3^-$

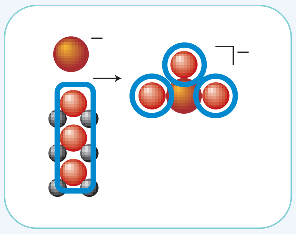


Step 3 The Br atoms are balanced.



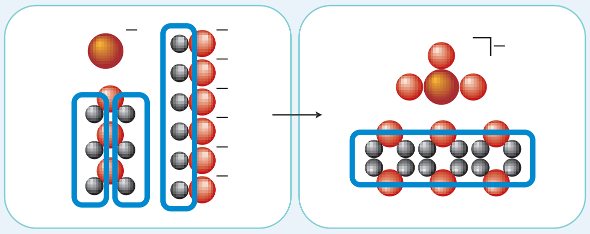
Step 4 Balance the O atoms by adding H_2O.

$Br^- + 3\,H_2O \longrightarrow BrO_3^-$



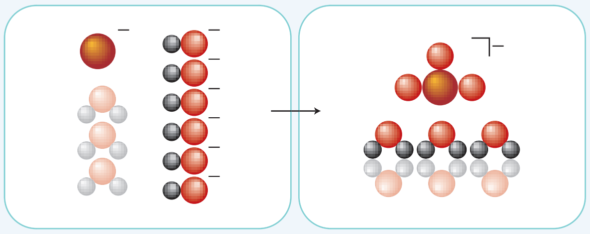
Balance the H atoms by adding (for each H atom needed) one H_2O molecule to the side of each equation that needs hydrogen and one OH^- ion to the opposite side.

$Br^- + 3\,H_2O + 6\,OH^- \longrightarrow BrO_3^- + 6\,H_2O$



Cancel like species on opposite sides of the arrow (in this case, 3 H_2O).

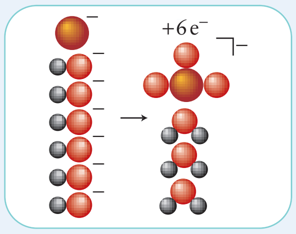
$Br^- + 6\,OH^- \longrightarrow BrO_3^- + 3\,H_2O$



Step 5 Balance charge by adding electrons.

Net charge on the left is −7 and on the right it is −1; we need 6 electrons on the right to bring it to −7.

$$\mathrm{Br^- + 6\,OH^- \longrightarrow BrO_3^- + 3\,H_2O + 6\,e^-}$$



A note on good practice: As before, at this point check that the number of electrons lost or gained in each half-reaction is the same as the change in oxidation number of the element oxidized or reduced.

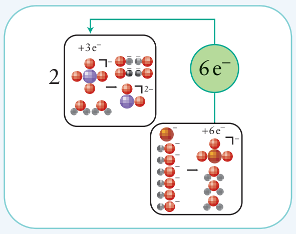
Step 6 Write the overall equation. Because 6 electrons are lost and 3 gained, we need 6 in each half-reaction.

Multiply the reduction half-reaction by 2.

$$\mathrm{2\,MnO_4^- + 4\,H_2O + 6\,e^- \longrightarrow 2\,MnO_2 + 8\,OH^-}$$

The oxidation half-reaction remains unchanged.

$$\mathrm{Br^- + 6\,OH^- \longrightarrow BrO_3^- + 3\,H_2O + 6\,e^-}$$



Add the two equations and cancel the electrons.

$$\mathrm{2\,MnO_4^- + Br^- + 6\,OH^- + 4\,H_2O \longrightarrow 2\,MnO_2 + BrO_3^- + 8\,OH^- + 3\,H_2O}$$

Cancel 3 H_2O and 6 OH^-, then include the physical states.

$$\mathrm{2\,MnO_4^-(aq) + Br^-(aq) + H_2O(l) \longrightarrow 2\,MnO_2(s) + BrO_3^-(aq) + 2\,OH^-(aq)}$$

SELF-TEST 12.2A An alkaline (basic) solution of hypochlorite ions reacts with solid chromium(III) hydroxide to produce aqueous chromate ions and chloride ions. Write the net ionic equation for the reaction.

[*Answer:* $\mathrm{2\,Cr(OH)_3(s) + 4\,OH^-(aq) + 3\,ClO^-(aq) \rightarrow 2\,CrO_4^{2-}(aq) + 5\,H_2O(l) + 3\,Cl^-(aq)}$]

SELF-TEST 12.2B When iodide ions react with iodate ions in basic aqueous solution, triiodide ions, I_3^-, are formed. Write the net ionic equation for the reaction. (Note that the same product is obtained in each half-reaction.)

The chemical equation for a reduction half-reaction is added to the equation for an oxidation half-reaction to form the balanced chemical equation for the overall redox reaction.

GALVANIC CELLS

Whenever we turn on a portable CD player or a laptop computer, we are completing a circuit that allows a chemical reaction to take place in a battery, a direct descendant of Volta's pile of metals and paper. A battery is an example of an electrochemical cell. In general, an **electrochemical cell** is a device in which an electric current—a flow of electrons through a circuit—is either produced by a spontaneous chemical reaction or used to bring about a nonspontaneous reaction. A **galvanic cell** is an electrochemical cell in which a spontaneous chemical reaction is used to generate an electric current. Technically, a **battery** is a collection of galvanic cells joined in series; so the voltage that it produces—its ability to push an electric current through a circuit—is the sum of the voltages of each cell.

Galvanic cells are also known as *voltaic cells.*

The formal term for "voltage" is potential difference, measured in volts: 1 V = 1 J·C^{-1} (see Section 12.4).

12.3 The Structure of Galvanic Cells

How can a spontaneous reaction be used to generate an electric current? To find the answer, consider the redox reaction between zinc metal and copper(II) ions:

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

If we were to place a piece of zinc metal into an aqueous copper(II) sulfate solution, we would see a layer of metallic copper begin to deposit on the surface of the zinc (see Fig. K.5). If we could watch the reaction at the atomic level, we would see that, as the reaction takes place, electrons are transferred from the Zn atoms to adjacent Cu^{2+} ions in the solution. These electrons reduce the Cu^{2+} ions to Cu atoms, which stick to the surface of the zinc or form a finely divided solid deposit in the beaker. The piece of zinc slowly disappears as its atoms give up electrons and form colorless Zn^{2+} ions that drift off into the solution. The Gibbs free energy of the system decreases as electrons are transferred and the reaction approaches equilibrium. However, although energy is released as heat, no electrical work is done.

Now suppose we separate the reactants but provide a pathway for the electrons to travel from the zinc metal to the copper(II) ions. The electrons can then do work—for example, drive an electric motor—as they pass from the species being oxidized to that being reduced. This is what happens when the reaction takes place in a galvanic cell. A galvanic cell consists of two **electrodes**, or metallic conductors, which make electrical contact with the contents of the cell but not with each other, and an **electrolyte**, an ionically conducting medium, inside the cell. In an *ionic conductor* an electric current is carried by the movement of ions. The electrolyte is typically an aqueous solution of an ionic compound. Oxidation takes place at one electrode as the species being oxidized releases electrons into the metallic conductor. Reduction takes place at the other electrode, where the species that is undergoing reduction collects electrons from the metallic conductor (Fig. 12.2). We can think of the overall chemical reaction as pushing electrons onto one electrode and pulling them off the other electrode. This push–pull process sets up a flow of electrons in the external circuit joining the two electrodes, and that current can be used to do electrical work.

The electrode at which oxidation takes place is called the **anode**. The electrode at which reduction takes place is called the **cathode**. Electrons are released by the oxidation half-reaction at the anode, travel through the external circuit, and reenter the cell at the cathode, where they are used in the reduction half-reaction. A commercial galvanic cell has its cathode marked with a + sign and its anode with a − sign.

The *Daniell cell* is an early example of a galvanic cell that makes use of the oxidation of copper by zinc ions, as in reaction A. The British chemist John Daniell invented it in 1836, when the growth of telegraphy created an urgent need for a reliable, steady source of electric current. Daniell set up the arrangement shown in Fig. 12.3, in which the two reactants are separated: the zinc metal is immersed in a solution of zinc sulfate and the copper electrode is immersed in a solution of copper(II) sulfate. For the electrons to travel from Zn atoms to Cu^{2+} ions and bring about the spontaneous reaction, they must pass from the zinc metal through the wire that serves as the external circuit, then through the copper electrode, then to the copper(II) solution. The Cu^{2+} ions are converted into Cu atoms at the cathode by the reduction half-reaction

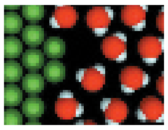
$$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$$

At the same time zinc atoms are converted into Zn^{2+} ions at the anode by the oxidation half-reaction

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

As Cu^{2+} ions are reduced, the solution at the cathode becomes negatively charged and the solution at the anode begins to develop a positive charge as the additional Zn^{2+} ions enter the solution. To prevent this charge buildup, which would quickly stop the flow of electrons, the two solutions are in contact through a porous wall: ions provided by the electrolyte solutions move between the two compartments and complete the electrical circuit.

The electrodes in the Daniell cell are made of the metals involved in the reaction. However, not all electrode reactions include a conducting solid directly. For example, to use the reduction $2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$ at an electrode, a



Animation: Figure 12.2 Flow of current through an electrochemical cell

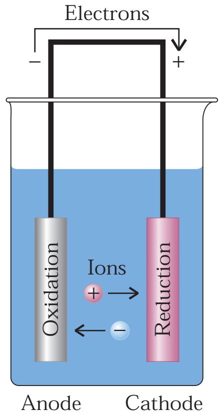


FIGURE 12.2 In an electrochemical cell, a reaction takes place in two separate regions. Oxidation takes place at one electrode (the anode), and the electrons released travel through the external circuit to the other electrode, the cathode, where they cause reduction. The circuit is completed by ions, which carry the electric charge through the solution.

The term "electrolyte" was first introduced in Section I to refer to the solute. In the discussion of electrochemical cells, the term is commonly used to refer to the ionically conducting medium.

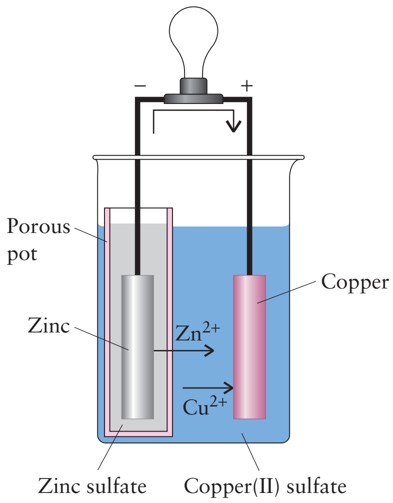


FIGURE 12.3 The Daniell cell consists of copper and zinc electrodes dipping into solutions of copper(II) sulfate and zinc sulfate, respectively. The two solutions make contact through the porous barrier, which allows ions to pass through and complete the electric circuit.

chemically inert metallic conductor, such as an unreactive metal or graphite, must carry the electrons into or out of the electrode compartment. Platinum is customarily used as the electrode for hydrogen: the gas is bubbled over the metal immersed in a solution that contains hydrogen ions. This arrangement is called a *hydrogen electrode*. The entire compartment with metal conductor and electrolyte solution is commonly referred to as "the electrode" or as a **half-cell.**

> ***In a galvanic cell, a spontaneous chemical reaction draws electrons into the cell through the cathode, the site of reduction, and releases them at the anode, the site of oxidation.***

12.4 Cell Potential and Reaction Gibbs Free Energy

The **cell potential**, E, is a measure of the ability of a cell reaction to force electrons through a circuit. A reaction with a lot of pushing-and-pulling power generates a high cell potential (colloquially, a high voltage). A reaction with little pushing-and-pulling power generates only a small potential (a low voltage). An exhausted battery is a cell in which the reaction is at equilibrium; it has lost its power to move electrons and has a potential of zero. The SI unit of potential is the **volt** (V). A volt is defined so that a charge of one coulomb (1 C) falling through a potential difference of one volt (1 V) releases one joule (1 J) of energy:

One coulomb is the magnitude of the charge delivered by a current of one ampere flowing for one second: $1\ \text{C} = 1\ \text{A·s}$.

$$1\ \text{V·C} = 1\ \text{J}$$

Cell potential is analogous to gravitational potential. The maximum work that a falling weight can do is equal to its mass times the difference in gravitational potential. Similarly, the maximum work that an electron can do is equal to its charge times the difference in electrical potential through which it falls. To interpret this idea in terms of thermodynamics, recall from Section 7.14 that the value of ΔG gives the maximum nonexpansion work that can be obtained from a process at constant temperature and pressure. As explained there, *nonexpansion work* is any work other than that resulting from a change in volume. For example, electrical work and mechanical work, such as muscle contraction (which changes the shape of the muscle, but not its volume), are types of nonexpansion work. Our immediate task, therefore, is to find a relation between the thermodynamic property (the Gibbs free energy of a reaction) and the electrochemical property (the cell potential produced by that reaction).

HOW DO WE DO THAT?

To find the connection between cell potential and Gibbs free energy, recall that in Section 7.14 (Eq. 21) we saw that the change in Gibbs free energy is the maximum nonexpansion work that a reaction can do at constant pressure and temperature:

$$\Delta G = w_e$$

The work done when an amount n of electrons (in moles) travels through a potential difference E is their total charge times the potential difference. The charge of one electron is $-e$; the charge per mole of electrons is $-eN_A$, where N_A is Avogadro's constant. Therefore, the total charge is $-neN_A$ and the work done is

$$w_e = -neN_AE$$

Faraday's constant, F, is the magnitude of the charge per mole of electrons (the product of the elementary charge e and Avogadro's constant N_A):

$$\begin{aligned} F = eN_A &= (1.602\,177 \times 10^{-19}\ \text{C}) \times \{6.0223 \times 10^{23}\ (\text{mol e}^-)^{-1}\} \\ &= 9.6485 \times 10^4\ \text{C·(mol e}^-)^{-1} \end{aligned}$$

Faraday's constant is normally abbreviated to $F = 9.6485 \times 10^4\ \text{C·mol}^{-1}$ (or 96.485 kC·mol^{-1}). We can now write the preceding expression for work as

$$w_e = -nFE$$

When this equation is combined with the thermodynamic equation, we obtain

$$\Delta G = -nFE$$

The units of ΔG are joules (or kilojoules), with a value that depends not only on E, but also on the amount n (in moles) of electrons transferred in the reaction. Thus, in reaction A, $n = 2$ mol. As in the discussion of the relation between Gibbs free energy and equilibrium constants (Section 9.3), we shall sometimes need to use this relation in its "molar" form, with n interpreted as a pure number (its value with the unit "mol" struck out). Then we write

$$\Delta G_r = -nFE$$

The units of ΔG_r are joules (or kilojoules) per mole. The subscript r is always the signal that we are using this "molar" form.

The relation that we have derived,

$$\Delta G = -nFE \tag{1}^*$$

relates the thermodynamic information that we have been compiling since Chapter 6 to the electrochemical information in this chapter. We see from this equation that E provides an experimental criterion of spontaneity: if the cell potential is positive, then the reaction Gibbs free energy is negative, and the cell reaction has a spontaneous tendency to form products. If the cell potential is negative, then the *reverse* of the cell reaction is spontaneous, and the cell reaction has a spontaneous tendency to form reactants.

There is a hidden assumption in the derivation of Eq. 1. *Maximum* nonexpansion work is obtained when a cell is operating *reversibly*. Therefore, Eq. 1 applies only when the pushing power of the cell is balanced against an external matching source of potential. In practice, that means using a voltmeter with such a high resistance that the potential difference is measured without drawing any current. The cell potential under these conditions is the *maximum* potential that can be produced. It is called the **electromotive force**, emf, of the cell. From now on, E will always be taken to represent this emf. A *working cell*, one actually producing current, such as the cell in a CD player, will produce a potential that is smaller than that predicted by Eq. 1.

Remember the definition of reversibility in Section 6.3, which requires the pushing force of the system to be balanced against an equal and opposite force.

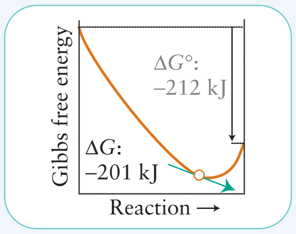
EXAMPLE 12.3 Sample exercise: Calculating the reaction Gibbs free energy

The emf of the Daniell cell for certain concentrations of copper and zinc ions is 1.04 V. What is the reaction Gibbs free energy under those conditions?

SOLUTION Use Eq. 1 to determine a reaction Gibbs free energy—a thermodynamic quantity—from a cell emf—an electrical quantity. From the chemical equation for the cell reaction (reaction A), we see that $n = 2$ mol.

From $\Delta G = -nFE$,

$$\begin{aligned}\Delta G &= -(2\text{ mol}) \times (9.6485 \times 10^4\ \text{C·mol}^{-1}) \times (1.04\text{ V})\\ &= -2.01 \times 10^5\ \text{C·V}\end{aligned}$$



Because 1 C·V = 1 J, we can conclude that the Gibbs free energy of reaction A under these conditions is −201 kJ; because this value is negative, the reaction is spontaneous in the forward direction for this composition of the cell.

A note on good practice: The value of n depends on the balanced equation. Check to ensure that n matches the number of moles of electrons transferred in the balanced equation.

SELF-TEST 12.3A The reaction taking place in a nicad cell is $Cd(s) + 2\,Ni(OH)_3(s) \rightarrow Cd(OH)_2(s) + 2\,Ni(OH)_2(s)$, and the emf of the cell when fully charged is 1.25 V. What is the reaction Gibbs free energy? (See Table 12.2.)

[*Answer:* −241 kJ]

SELF-TEST 12.3B The reaction taking place in the silver cell used in some cameras and wristwatches is $Ag_2O(s) + Zn(s) \rightarrow 2\,Ag(s) + ZnO(s)$, and the emf of the cell when new is 1.6 V. What is the reaction Gibbs free energy? (See Table 12.2.)

We shall often employ Eq. 1 for the *standard* reaction Gibbs free energy, ΔG°, when it becomes

$$\Delta G^\circ = -nFE^\circ \qquad \text{(2)*}$$

In this expression, E° is the **standard emf** of the cell, the emf measured when all the species taking part are in their standard states. In practice, this condition means that all gases are at 1 bar, all participating solutes are at 1 mol·L^{-1}, and all liquids and solids are pure. For example, to measure the standard emf of the Daniell cell, we use 1 M $CuSO_4(aq)$ and a pure copper electrode in one electrode compartment and 1 M $ZnSO_4(aq)$ and a pure zinc electrode in the other.

More precisely, all the solutes should be at unit activity, not unit molarity. Activities differ appreciably from molarities in electrolyte solution because ions interact over long distances. However, we ignore this complication here.

The value of E is the same, regardless of how we write the equation, but the value of ΔG° depends on the stoichiometric coefficients in the chemical equation. When we multiply all the coefficients by 2 the value of ΔG° doubles. However, multiplying all the coefficients by 2 also doubles the value of n, and so $E^\circ = -\Delta G^\circ/nF$ remains the same. That is, although the reaction Gibbs free energy changes when the chemical equation is multiplied by a factor, E° does not change:

	ΔG°	E°
$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$	−212 kJ	+1.10 eV
$2\,Zn(s) + 2\,Cu^{2+}(aq) \longrightarrow 2\,Zn^{2+}(aq) + 2\,Cu(s)$	−424 kJ	+1.10 eV

A practical implication of this conclusion is that the emf produced by a cell is independent of the size of the cell. To get a higher potential than predicted by Eq. 1, we have to construct a battery by joining cells in series: the potential is then the sum of the potentials of the individual cells (see Section 12.15 for some examples).

Cell emf and reaction Gibbs free energy are related by Eq. 1 ($\Delta G = -nFE$), and their standard values are related by Eq. 2 ($\Delta G^\circ = -nFE^\circ$). The magnitude of the emf is independent of how the chemical equation is written.

12.5 The Notation for Cells

Chemists use a special notation to specify the structure of electrode compartments in a galvanic cell. The two electrodes in the Daniell cell, for instance, are denoted $Zn(s)|Zn^{2+}(aq)$ and $Cu^{2+}(aq)|Cu(s)$. Each vertical line represents an interface between phases—in this case, between solid metal and ions in solution in the order reactant|product.

We report the structure of a cell in a symbolic **cell diagram**, by using the conventions specified by IUPAC and used by chemists throughout the world. The diagram for the Daniell cell, for instance, is

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

In the Daniell cell, zinc sulfate and copper(II) sulfate solutions meet inside the porous barrier to complete the circuit. However, when different ions mingle together, they can affect the cell voltage. To keep solutions from mixing, chemists use a **salt bridge** to join the two electrode compartments and complete the electrical circuit. A salt bridge typically consists of a gel containing a concentrated aqueous salt solution in an inverted U-tube (Fig. 12.4). The bridge allows a flow of ions, and so it completes the electrical circuit, but the ions are chosen so that they do not affect the cell reaction (often KCl is used). In a cell diagram, a salt bridge is shown by a double vertical line (‖), and so the arrangement in Fig. 12.4 is denoted

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

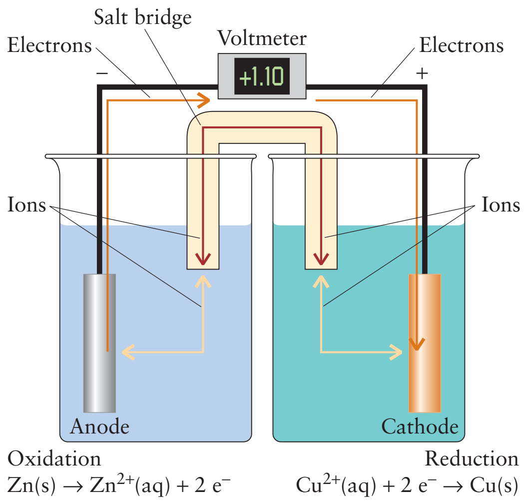


FIGURE 12.4 In a galvanic cell electrons produced by oxidation at the anode (−) travel through the external circuit and reenter the cell at the cathode (+), where they cause reduction. The circuit is completed inside the cell by migration of ions through the salt bridge. A salt bridge is not used in a working cell (one used to produce a current). When the emf of a cell is measured, no current actually flows: the voltmeter measures the tendency of the electrons to flow from one electrode to the other.

Any inert metallic component of an electrode is written as the outermost component of that electrode in the cell diagram. For example, a hydrogen electrode constructed with platinum is denoted $\mathrm{H^+(aq)|H_2(g)|Pt(s)}$ when it is the right-hand electrode in a cell diagram and $\mathrm{Pt(s)|H_2(g)|H^+(aq)}$ when it is the left-hand electrode. An electrode consisting of a platinum wire dipping into a solution of iron(II) and iron(III) ions is denoted either $\mathrm{Fe^{3+}(aq),Fe^{2+}(aq)|Pt(s)}$ or $\mathrm{Pt(s)|Fe^{3+}(aq),Fe^{2+}(aq)}$. In this case, the oxidized and reduced species are both in the same phase, and so a comma rather than a line is used to separate them. Pairs of ions in solution are normally written in the order Ox,Red.

When it is important to emphasize the spatial arrangement of an electrode, the order may reflect that arrangement, as in $\mathrm{Cl^-(aq)|Cl_2(g)|Pt(s)}$.

SELF-TEST 4A Write the diagram for a cell with a hydrogen electrode on the left and an iron(III)/iron(II) electrode on the right. The two electrode compartments are connected by a salt bridge and platinum is used as the conductor at each electrode.

[***Answer:*** $\mathrm{Pt(s)|H_2(g)|H^+(aq)\|Fe^{3+}(aq),Fe^{2+}(aq)|Pt(s)}$]

SELF-TEST 4B Write the diagram for a cell that has an electrode consisting of a manganese wire dipping into a solution of manganese(II) ions on the left, a salt bridge, and a copper(II)/copper(I) electrode on the right with a platinum wire.

The cell diagram is written to correspond to how the chemical equation for the reaction is written, not to the way that the cell is arranged in the laboratory. Thus, the Daniell cell can be described as either

$$\mathrm{Zn(s)|Zn^{2+}(aq)\|Cu^{2+}(aq)|Cu(s)} \quad \text{or} \quad \mathrm{Cu(s)|Cu^{2+}(aq)\|Zn^{2+}(aq)|Zn(s)}$$

However, as we shall shortly see, the two descriptions correspond to the direction in which we write the cell reaction and, therefore, to different signs used to report the cell emf.

As already remarked, the emf of a cell is measured with an electronic voltmeter (Fig. 12.5), and we identify the cathode by noting which terminal is positive. We can think of the + sign on the cathode as indicating where electrons tend to *enter* the cell from the external circuit and the − sign on the anode as showing where electrons tend to leave the cell. If the cathode is the electrode that we have placed on the right *of the cell diagram*, then by convention the emf of the cell described by the cell diagram is reported as positive, as in

Formerly, they were measured with a device called a *potentiometer*, but electronic devices are more reliable and easier to interpret.

$$\underset{\text{Anode }(-)}{\mathrm{Zn(s)|Zn^{2+}(aq)}}\|\underset{\text{Cathode }(+)}{\mathrm{Cu^{2+}(aq)|Cu(s)}} \qquad E = +1.10\ \mathrm{V}$$

(The emf depends on the concentrations of the ions, as we explore later; here we have reported the value observed when the two solutions have equal cation concentrations.) In this case, the electrons can be thought of as tending to travel

Lab Video: Figure 12.5 A galvanic cell

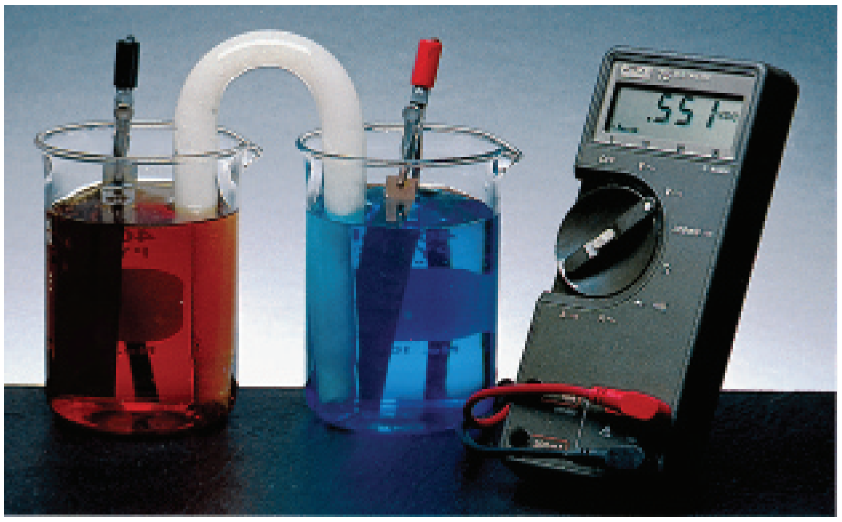


FIGURE 12.5 The cell potential is measured with an electronic voltmeter, a device designed to draw negligible current so that the composition of the cell does not change during the measurement. The display shows a positive value when the + terminal of the meter is connected to the cathode of the galvanic cell. The salt bridge completes the electric circuit within the cell.

through the external circuit from the left of the cell as written (the anode) to the right (the cathode). However, if the cathode is found to be the electrode that we have placed on the *left* of the cell diagram, then the emf of the cell is reported as negative, as in

$$\underset{\text{Cathode }(+)}{\mathrm{Cu(s)}|\mathrm{Cu^{2+}(aq)}}\|\underset{\text{Anode }(-)}{\mathrm{Zn^{2+}(aq)}|\mathrm{Zn(s)}} \qquad E = -1.10\ \mathrm{V}$$

In summary, the sign of the emf reported in conjunction with a cell diagram is the same as the sign of the right-hand electrode in the diagram.

A particular cell diagram corresponds to a specific direction of writing the corresponding cell reaction. *Solely for the purpose of writing the cell reaction corresponding to a given cell diagram*, we suppose that the right-hand electrode in the diagram is the site of reduction and that the left-hand electrode is the site of oxidation, and write the corresponding half-reactions. Thus, for the cell written as $\mathrm{Zn(s)}|\mathrm{Zn^{2+}(aq)}\|\mathrm{Cu^{2+}(aq)}|\mathrm{Cu(s)}$, we write

Left (L)	$\mathrm{Zn(s)}\vert\mathrm{Zn^{2+}(aq)}\Vert\mathrm{Cu^{2+}(aq)}\vert\mathrm{Cu(s)}$	Right (R)
$\mathrm{Zn(s)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{e^-}$		$\mathrm{Cu^{2+}(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cu(s)}$
(oxidation)		(reduction)
Overall (R + L): $\mathrm{Zn(s)} + \mathrm{Cu^{2+}(aq)} \longrightarrow \mathrm{Zn^{2+}(aq)} + \mathrm{Cu(s)}$		$E = +1.10$ V

Because $E > 0$, and therefore $\Delta G < 0$ for this reaction, the cell reaction as written is spontaneous for the concentrations of ions that we chose. For the alternative way of writing the cell diagram, $\mathrm{Cu(s)}|\mathrm{Cu^{2+}(aq)}\|\mathrm{Zn^{2+}(aq)}|\mathrm{Zn(s)}$, we would write

Left (L)	$\mathrm{Cu(s)}\vert\mathrm{Cu^{2+}(aq)}\Vert\mathrm{Zn^{2+}(aq)}\vert\mathrm{Zn(s)}$	Right (R)
$\mathrm{Cu(s)} \longrightarrow \mathrm{Cu^{2+}(aq)} + 2\,\mathrm{e^-}$		$\mathrm{Zn^{2+}(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Zn(s)}$
(oxidation)		(reduction)
Overall (L + R): $\mathrm{Zn^{2+}(aq)} + \mathrm{Cu(s)} \longrightarrow \mathrm{Zn(s)} + \mathrm{Cu^{2+}(aq)}$		$E = -1.10$ V

Because $E < 0$, and therefore $\Delta G > 0$, the *reverse* of the cell reaction as written is spontaneous for the chosen concentrations of ions.

The general procedure for writing the chemical equation for the reaction corresponding to a given cell diagram is set out in Toolbox 12.2.

TOOLBOX 12.2 HOW TO WRITE A CELL REACTION FOR A CELL DIAGRAM

CONCEPTUAL BASIS

A cell diagram corresponds to a specific cell reaction in which the right-hand electrode in the cell diagram is treated as the site of reduction and the left-hand electrode is treated as the site of oxidation. The sign of the emf then distinguishes whether the resulting reaction is spontaneous in the direction written ($E > 0$) or whether the reverse reaction is spontaneous ($E < 0$).

PROCEDURE

Step 1 Write the equation for the electrode on the right of the cell diagram as a reduction half-reaction (remember: **R**ight for **R**eduction).

Step 2 Write the equation for the electrode on the left of the cell diagram as an oxidation half-reaction.

Step 3 Multiply one or both equations by a factor if necessary to equalize the number of electrons, and then add the two equations.

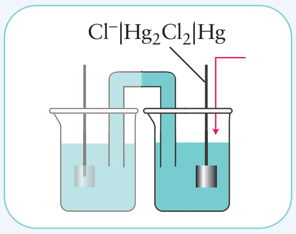
If the emf of the cell is positive, then the reaction is spontaneous as written. If the emf is negative, then the reverse reaction is spontaneous.

This procedure is illustrated in Example 12.4.

EXAMPLE 12.4 Sample exercise: Writing a cell reaction

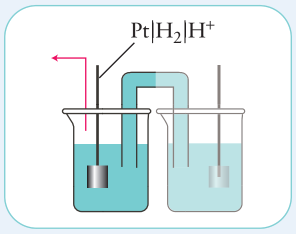
Write the cell reaction for the cell $Pt(s)|H_2(g)|HCl(aq)|Hg_2Cl_2(s)|Hg(l)$.

SOLUTION Follow the procedure set out in Toolbox 12.2:



Step 1 Write the equation for the reduction at the right-hand electrode.

$$Hg_2Cl_2(s) + 2\,e^- \longrightarrow 2\,Hg(l) + 2\,Cl^-(aq)$$

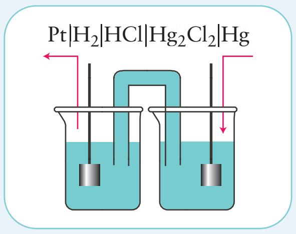


Step 2 Write the equation for the oxidation at the left-hand electrode.

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

Step 3 To balance electrons multiply the oxidation half-reaction by 2.

$$H_2(g) \longrightarrow 2\,H^+(aq) + 2\,e^-$$



Add the half-reactions together.

$$Hg_2Cl_2(s) + H_2(g) \longrightarrow 2\,Hg(l) + 2\,Cl^-(aq) + 2\,H^+(aq)$$

If the concentrations in the cell are such that it is reported as having a positive emf (that is, the mercury/mercury(I) chloride electrode is found to be positive), then the reaction as written is spontaneous. If the concentrations were such that the emf were reported as negative (that is, the hydrogen electrode were found to be positive), then the reverse of the reaction that we have derived would be spontaneous.

SELF-TEST 12.5A (a) Write the chemical equation for the reaction corresponding to the cell $Pt(s)|H_2(g)|H^+(aq)\|Co^{3+}(aq),Co^{2+}(aq)|Pt(s)$. (b) Given that the cell emf is reported as positive, is the cell reaction spontaneous as written?

[*Answer:* (a) $H_2(g) + 2\,Co^{3+}(aq) \rightarrow 2\,H^+(aq) + 2\,Co^{2+}(aq)$; (b) yes]

SELF-TEST 12.5B (a) Write the chemical equation for the reaction corresponding to the cell $Hg(l)|Hg_2Cl_2(s)|HCl(aq)\|Hg_2(NO_3)_2(aq)|Hg(l)$. (b) Given that the cell emf is reported as positive, is the cell reaction spontaneous as written?

> ***An electrode is designated by representing the interfaces between phases by a vertical line. A cell diagram depicts the physical arrangement of species and interfaces, with any salt bridge denoted by a double vertical line. The sign with which the emf is reported is the same as the measured sign of the right-hand electrode in the cell diagram. A positive emf indicates that the cell reaction is spontaneous as written.***

12.6 Standard Potentials

There are thousands of possible galvanic cells that can be studied. However, instead of having to learn about all these different cells, it is much simpler to learn about the smaller number of electrodes that are combined to form the cells. Under standard conditions (all solutes present at 1 $mol \cdot L^{-1}$; all gases at 1 bar), we can think of each electrode as making a characteristic contribution to the cell potential called its **standard potential**, $E°$. Each standard potential is a measure of the electron-pulling power of a single electrode. In a galvanic cell, the electrodes pull in opposite directions, so the overall pulling power of the cell, the cell's standard emf, is the *difference* of the standard potentials of the two electrodes (Fig. 12.6). That difference is always written as

Standard potentials are also called *standard electrode potentials*. Because they are always written for reduction half-reactions, they are also sometimes called *standard reduction potentials*.

$$E° = E°(\text{electrode on right of cell diagram}) - E°(\text{electrode on left of cell diagram}) \qquad \textbf{(3a)}$$

or, more succinctly,

$$E° = E_R° - E_L° \qquad \textbf{(3b)}$$

Note that, because the right side of the cell diagram corresponds to reduction, $E° = E°(\text{for reduction}) - E°(\text{for oxidation})$ where both values of $E°$ are the standard reduction potentials.

If $E° > 0$, then the corresponding cell reaction is spontaneous under standard conditions (that is, as explained in Section 9.3, $K > 1$) and the electrode on the right of the cell diagram serves as the cathode. For example, for the cell

$$Fe(s)|Fe^{2+}(aq)\|Ag^{+}(aq)|Ag(s) \quad \text{corresponding to} \quad 2\,Ag^{+}(aq) + Fe(s) \longrightarrow 2\,Ag(s) + Fe^{2+}(aq)$$

we write

$$E° = E°(Ag^{+}/Ag) - E°(Fe^{2+}/Fe)$$

and find $E° = +1.24$ V at 25°C. Because $E° > 0$, the cell reaction has $K > 1$, with products dominant at equilibrium, and iron metal can reduce silver ions. If we had written the cell in the opposite order,

$$Ag(s)|Ag^{+}(aq)\|Fe^{2+}(aq)|Fe(s) \quad \text{corresponding to} \quad 2\,Ag(s) + Fe^{2+}(aq) \longrightarrow 2\,Ag^{+}(aq) + Fe(s)$$

we would have written

$$E° = E°(Fe^{2+}/Fe) - E°(Ag^{+}/Ag)$$

and would have found $E° = -1.24$ V. We would have come to the same conclusion as before: for this reaction $K < 1$, with reactants dominant at equilibrium, and iron has a tendency to reduce silver.

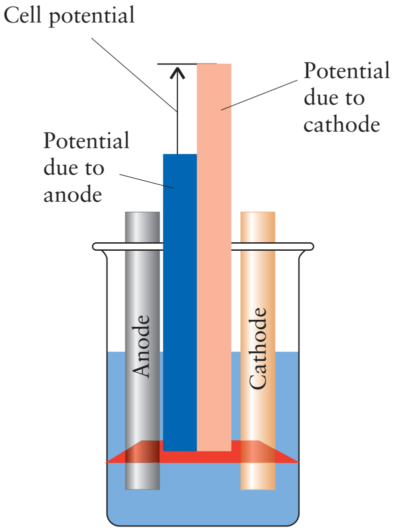


FIGURE 12.6 The cell emf can be thought of as the difference of the two potentials produced by the two electrodes.

A problem with compiling a list of standard potentials is that we know only the *overall* emf of the cell, not the contribution of a single electrode. A voltmeter placed between the two electrodes of a galvanic cell measures the *difference* of their potentials, not the individual values. To provide numerical values for individual standard potentials, we arbitrarily set the standard potential of one particular electrode, the hydrogen electrode, equal to zero at all temperatures:

$$2\,H^{+}(g) + 2\,e^{-} \longrightarrow H_2(g) \qquad E° = 0$$

In redox couple notation, $E°(H^+/H_2) = 0$ at all temperatures. A hydrogen electrode in its standard state, with hydrogen gas at 1 bar and the hydrogen ions present at 1 $mol{\cdot}L^{-1}$ (strictly, unit activity), is called a **standard hydrogen electrode** (SHE). The standard hydrogen electrode is then used to define the standard potentials of all other electrodes:

> The standard potential of a couple is the standard emf of a cell (including the sign) in which the couple forms the right-hand electrode in the cell diagram and a hydrogen electrode forms the left-hand electrode in the cell diagram.

For example, for the cell

$$Pt(s)|H_2(g)|H^+(aq)\|Cu^{2+}(aq)|Cu(s)$$

we find that the standard emf is 0.34 V with the copper electrode the cathode, and so $E° = +0.34$ V. Because the hydrogen electrode contributes zero to the standard emf of the cell, the emf is attributed entirely to the copper electrode, and we write

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

We can take this analysis a little farther. Because the cell reaction

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

is spontaneous in the direction written (under standard conditions), we can consider the oxidizing ability of $Cu^{2+}(aq)$, as represented by the reduction half-reaction $Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$, to be greater than the oxidizing ability of $H^+(aq)$, as represented by $2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$. Consequently, Cu^{2+} ions can be reduced to metallic copper by hydrogen gas under standard conditions. In general (Fig. 12.7),

> The more *positive* the potential, the greater the electron-pulling power of the reduction half-reaction and, therefore, the more strongly *oxidizing* the redox couple (the stronger the tendency for the half-reaction to occur as a reduction).

Now consider the cell

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

and the corresponding cell reaction

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

The standard emf is measured as 0.76 V and the hydrogen electrode is found to be the cathode: therefore, this emf is reported as −0.76 V. Because the entire emf is attributed to the zinc electrode, we write

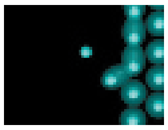
$$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s) \qquad E°(Zn^{2+}/Zn) = -0.76\text{ V}$$

The negative standard potential means that the Zn^{2+}/Zn electrode is the anode in a cell with H^+/H_2 as the other electrode and, therefore, that the *reverse* of the cell reaction, specifically

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

is spontaneous under standard conditions. We can conclude that the reducing ability of Zn(s) in the half-reaction $Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$ is greater than the reducing ability of $H_2(g)$ in the half-reaction $H_2(g) \rightarrow 2\,H^+(aq) + 2\,e^-$. Consequently, zinc metal can reduce H^+ ions in acidic solution to hydrogen gas under standard conditions. In general (Fig. 12.8),

> The more *negative* the potential, the greater the electron-donating power of the oxidation half-reaction and therefore the more strongly *reducing* the redox couple (that is, the stronger the tendency for the half-reaction to occur as an oxidation).



Animation: **Figure 12.7 Reduction at a cathode**

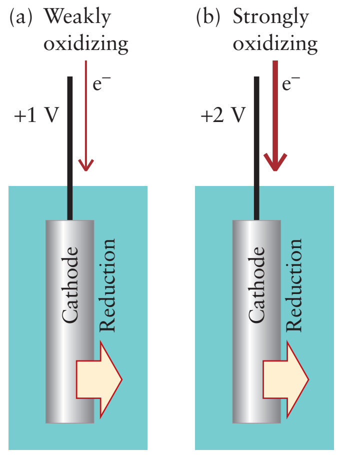
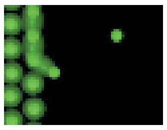


FIGURE 12.7 (a) A couple that has a small positive potential has a weak electron-pulling power (is a weak acceptor of electrons) relative to hydrogen ions and hence is a weak oxidizing agent. (b) A couple with a high positive potential has strong pulling power (is a strong acceptor of electrons) and is a strong oxidizing agent.



Animation: **Figure 12.8 Oxidation at an anode**

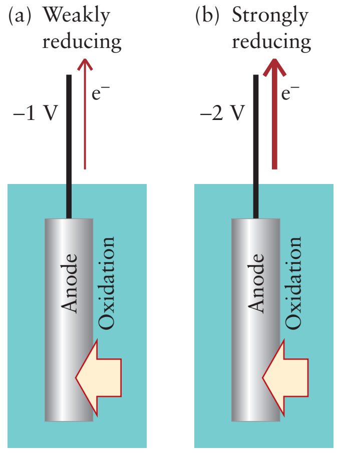


FIGURE 12.8 (a) A couple that has a small negative potential has a poor pushing power (is a weak donor of electrons) relative to hydrogen and, hence, is a weak reducing agent. (b) A couple with a large negative potential has strong pushing power (is a strong donor of electrons) and is a strong reducing agent.

TABLE 12.1 Standard Potentials at 25°C*

Species	Reduction half-reaction	$E°$ (V)
Oxidized form is strongly oxidizing		
F_2/F^-	$F_2(g) + 2\,e^- \longrightarrow 2\,F^-(aq)$	+2.87
Au^+/Au	$Au^+(aq) + e^- \longrightarrow Au(s)$	+1.69
Ce^{4+}/Ce^{3+}	$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-,H^+/Mn^{2+},H_2O$	$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	+1.51
Cl_2/Cl^-	$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$	+1.36
$Cr_2O_7^{2-},H^+/Cr^{3+},H_2O$	$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$	+1.33
$O_2,H^+/H_2O$	$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$	+1.23; +0.82 at pH = 7
Br_2/Br^-	$Br_2(l) + 2\,e^- \longrightarrow 2\,Br^-(aq)$	+1.09
$NO_3^-,H^+/NO,H_2O$	$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow NO(g) + 2\,H_2O(l)$	+0.96
Ag^+/Ag	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
Fe^{3+}/Fe^{2+}	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
I_2/I^-	$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$	+0.54
$O_2,H_2O/OH^-$	$O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq)$	+0.40; +0.82 at pH = 7
Cu^{2+}/Cu	$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$	+0.34
$AgCl/Ag,Cl^-$	$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
H^+/H_2	$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$	0, by definition
Fe^{3+}/Fe	$Fe^{3+}(aq) + 3\,e^- \longrightarrow Fe(s)$	−0.04
$O_2,H_2O/HO_2^-,OH^-$	$O_2(g) + H_2O(l) + 2\,e^- \longrightarrow HO_2^-(aq) + OH^-(aq)$	−0.08
Pb^{2+}/Pb	$Pb^{2+}(aq) + 2\,e^- \longrightarrow Pb(s)$	−0.13
Sn^{2+}/Sn	$Sn^{2+}(aq) + 2\,e^- \longrightarrow Sn(s)$	−0.14
Fe^{2+}/Fe	$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$	−0.44
Zn^{2+}/Zn	$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$	−0.76
$H_2O/H_2\ OH^-$	$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$	−0.83; −0.42 at pH = 7
Al^{3+}/Al	$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$	−1.66
Mg^{2+}/Mg	$Mg^{2+}(aq) + 2\,e^- \longrightarrow Mg(s)$	−2.36
Na^+/Na	$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
K^+/K	$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
Li^+/Li	$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05
Reduced form is strongly reducing		

* For a more extensive table, see Appendix 2B.

Notice that, in Appendix 2B, standard potentials are listed both by numerical value and alphabetically, to make it easy to find the one you want.

Table 12.1 lists a number of standard electrode potentials measured at 25°C (the only temperature we consider here); a longer list can be found in Appendix 2B. The standard potentials of elements vary in a complicated way through the periodic table (Fig. 12.9). However, the most negative—the most strongly reducing—are usually found toward the left of the periodic table, and the most positive—the most strongly oxidizing—are found toward the upper right.

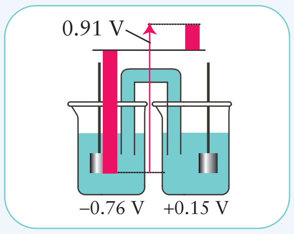
EXAMPLE 12.5 **Sample exercise: Determining the standard potential of an electrode**

The standard potential of a zinc electrode is −0.76 V, and the standard emf of the cell

$$Zn(s)\,|\,Zn^{2+}(aq)\,\|\,Sn^{4+}(aq),Sn^{2+}(aq)\,|\,Pt(s)$$

is +0.91 V. What is the standard potential of the Sn^{4+}/Sn^{2+} electrode?

SOLUTION We can determine the standard potential of an electrode by measuring the emf of a standard cell in which the other electrode has a known standard potential and applying Eq. 3.

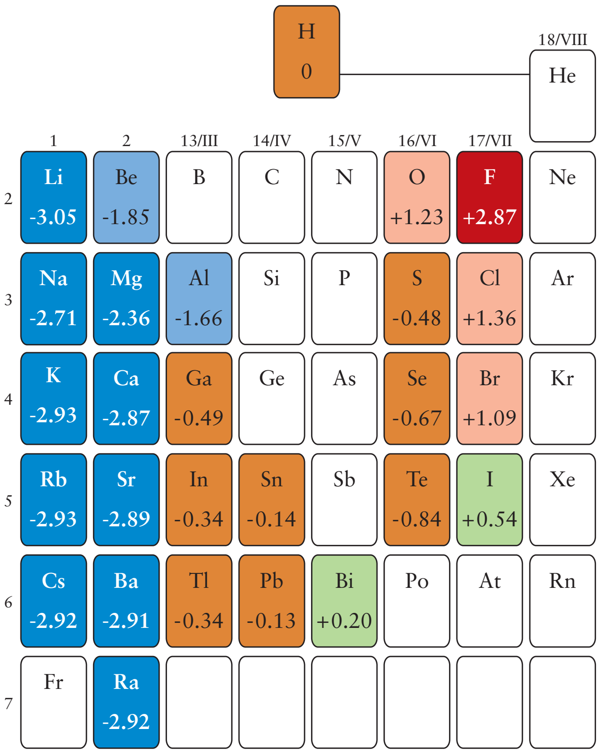


From Eq. 3, $E° = E_R° - E_L°$,

$$E° = E°(Sn^{4+}/Sn^{2+}) - E°(Zn^{2+}/Zn) = +0.91\text{ V}$$

Rearrange Eq. 3 into $E_R° = E° + E_L°$.

$$E°(Sn^{4+}/Sn^{2+}) = E° + E°(Zn^{2+}/Zn) = 0.91\text{ V} - 0.76\text{ V} = +0.15\text{ V}$$



	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
				H 0				He
2	Li -3.05	Be -1.85	B	C	N	O +1.23	F +2.87	Ne
3	Na -2.71	Mg -2.36	Al -1.66	Si	P	S -0.48	Cl +1.36	Ar
4	K -2.93	Ca -2.87	Ga -0.49	Ge	As	Se -0.67	Br +1.09	Kr
5	Rb -2.93	Sr -2.89	In -0.34	Sn -0.14	Sb	Te -0.84	I +0.54	Xe
6	Cs -2.92	Ba -2.91	Tl -0.34	Pb -0.13	Bi +0.20	Po	At	Rn
7	Fr	Ra -2.92						

FIGURE 12.9 The variation of standard potentials through the main groups of the periodic table. Note that the most negative values are in the *s* block and that the most positive values are close to fluorine.

SELF-TEST 12.6A The standard potential of the Ag^+/Ag electrode is +0.80 V, and the standard emf of the cell $Pt(s)|I_2(s)|I^-(aq)\|Ag^+(aq)|Ag(s)$ is +0.26 V at the same temperature. What is the standard potential of the I_2/I^- electrode?

[***Answer:*** +0.54 V]

SELF-TEST 12.6B The standard potential of the Fe^{2+}/Fe electrode is −0.44 V and the standard emf of the cell $Fe(s)|Fe^{2+}(aq)\|Pb^{2+}(aq)|Pb(s)$ is +0.31 V. What is the standard potential of the Pb^{2+}/Pb electrode?

In some cases, we find that available tables of data do not contain the standard potential that we need but do contain closely related values for the same element; for instance, we might require the standard potential of the Ce^{4+}/Ce couple, whereas we know only the values for the Ce^{3+}/Ce and Ce^{4+}/Ce^{3+} couples. In such cases, the potential of a couple cannot be determined by adding or subtracting the standard potentials directly. Instead, we calculate the values of $\Delta G°$ for each half-reaction and combine them into the $\Delta G°$ for the desired half-reaction. We then convert that value of $\Delta G°$ into the corresponding standard potential by using Eq. 2.

EXAMPLE 12.6 Calculating the standard potential of a couple from two related couples

Use the information in Appendix 2B to determine the standard potential for the redox couple Ce^{4+}/Ce, for which the reduction half-reaction is

$$Ce^{4+}(aq) + 4\,e^- \longrightarrow Ce(s) \qquad \text{(B)}$$

STRATEGY Use the alphabetical listing in Appendix 2B to find half-reactions that can be combined to give the desired half-reaction. Combine these half-reactions and their Gibbs free energies of reaction. Convert the Gibbs free energies into standard potentials by using Eq. 2 and then simplify the resulting expressions.

SOLUTION

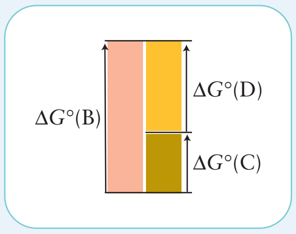
From the data in Appendix 2B,

$$Ce^{3+}(aq) + 3\,e^- \longrightarrow Ce(s) \qquad E° = -2.48\ \text{V} \qquad \text{(C)}$$

$$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq) \qquad E° = +1.61\ \text{V} \qquad \text{(D)}$$

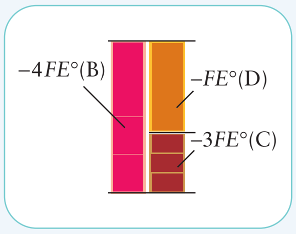
Add the reaction Gibbs free energies to get the overall reaction Gibbs free energy.

$$\Delta G°(B) = \Delta G°(C) + \Delta G°(D)$$



From $\Delta G_r° = -nFE°$,

$$-4FE°(B) = -3FE°(C) + \{-FE°(D)\}$$

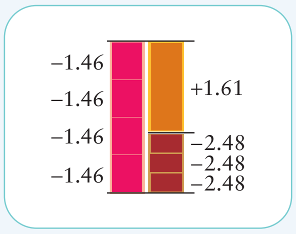


Divide by $-4F$.

$$E°(B) = \frac{3E°(C) + E°(D)}{4}$$

Insert the data.

$$E°(B) = \frac{3(-2.48\text{ V}) + 1.61\text{ V}}{4} = -1.46\text{ V}$$



Notice that this value is not the same as the sum of the potentials for half-reactions C and D.

SELF-TEST 12.7A Use the data in Appendix 2B to calculate the standard potential of the couple $Au^{3+}(aq)/Au^{+}(aq)$.

[*Answer:* +1.26 V]

SELF-TEST 12.7B Use the data in Appendix 2B to calculate the standard potential of the couple $Mn^{3+}(aq)/Mn(s)$.

> ***The standard potential of an electrode is the standard emf of a cell in which the electrode on the left in the cell diagram is a hydrogen electrode. A metal with a negative standard potential has a thermodynamic tendency to reduce hydrogen ions in solution; the ions of a metal with a positive standard potential have a tendency to be reduced by hydrogen gas.***

12.7 The Electrochemical Series

When redox couples are ordered by their standard potentials, we have a list of oxidizing and reducing agents ordered by their strengths. As we have seen, *the more negative the standard potential of a couple, the greater its reducing strength.* Only a couple with a negative potential can reduce hydrogen ions under standard conditions. A couple with a positive potential, such as Au^{3+}/Au, cannot reduce hydrogen ions under standard conditions (Fig. 12.10).

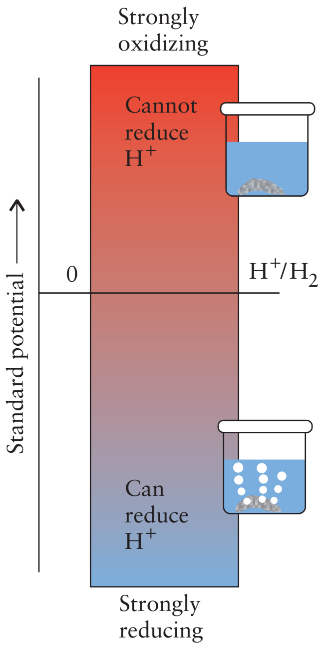


FIGURE 12.10 The significance of standard potentials. Only couples with negative standard potentials (and hence lying below hydrogen in the electrochemical series) can reduce hydrogen ions under standard conditions. The reducing power increases as the standard potential becomes more negative.

When Table 12.1 is viewed as a table of relative strengths of oxidizing and reducing agents, it is called the **electrochemical series**. The species on the left of each equation in Table 12.1 are potentially oxidizing agents. They can themselves be reduced. Species on the right of the equations are potentially reducing agents. An oxidized species in the list (on the left of the equation) has a tendency to oxidize a reduced species that lies below it. For example, Cu^{2+} ions oxidize zinc metal. A reduced species (on the right of the equation) has a tendency to reduce an oxidized species that lies above it. For example, zinc metal reduces H^{+} ions.

The higher the position of a species on the left side of an equation in Table 12.1, the greater its oxidizing strength. For example, F_2 is a strong oxidizing agent, whereas Li^+ is a very, very poor oxidizing agent. It also follows that, the lower the standard potential, the greater the reducing strength of the reduced species on the right side of an equation in Table 12.1. For example, lithium metal is the strongest reducing agent in the table.

SELF-TEST 12.8A Can lead produce zinc metal from aqueous zinc sulfate under standard conditions?

[***Answer:*** No, because lead lies above zinc in Table 12.1.]

SELF-TEST 12.8B Can chlorine gas oxidize water to oxygen gas under standard conditions in basic solution?

We can use the electrochemical series to predict the thermodynamic tendency for a reaction to take place under standard conditions. A cell reaction that is spontaneous under standard conditions (that is, has $K > 1$) has $\Delta G° < 0$ and therefore the corresponding cell has $E° > 0$. The standard emf is positive when $E_R° > E_L°$; that is, when the standard potential for the reduction half-reaction is more positive than that for the oxidation half-reaction.

EXAMPLE 12.7 Predicting the spontaneous direction of a redox reaction under standard conditions

Which is the more powerful oxidizing agent under standard conditions, an acidified aqueous permanganate solution or an acidified aqueous dichromate solution? Specify the cell for the spontaneous reaction of the two couples by writing a cell diagram that under standard conditions has a positive emf. Determine the standard emf of the cell and write the net ionic equation for the spontaneous cell reaction.

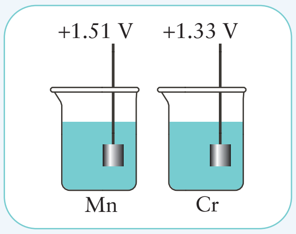
STRATEGY Find the standard potentials of the two reduction half-reactions in Appendix 2B. The couple with the more positive potential will act as an oxidizing agent (and be the site of reduction). That couple will be the right-hand electrode in the cell diagram corresponding to the spontaneous cell reaction. To calculate the standard emf of the cell, subtract the standard potential of the oxidation half-reaction (the one with the less-positive standard potential) from that of the reduction half-reaction. To write the cell reaction, follow the procedure in Toolbox 12.2.

SOLUTION

Find the two standard potentials in Appendix 2B.

$$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l) \qquad E° = +1.51\text{ V}$$

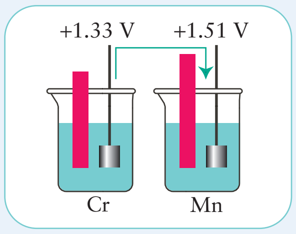
$$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l) \qquad E° = +1.33\text{ V}$$



The half-reaction with the more positive value of $E°$ occurs at the cathode in a spontaneous reaction.

$$E°(MnO_4^-,H^+/Mn^{2+},H_2O) > E°(Cr_2O_7^{2-},H^+/Cr^{3+},H_2O)$$

Therefore, MnO_4^- is a stronger oxidizing agent than $Cr_2O_7^{2-}$ in acidic solution and so serves as the cathode.

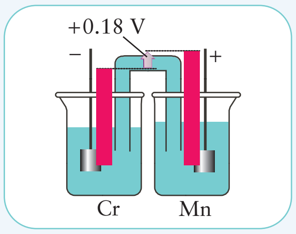


Find the standard emf from $E° = E°(\text{for reduction}) - E°(\text{for oxidation})$.

$$E° = 1.51\text{ V} - 1.33\text{ V} = +0.18\text{ V}$$

Write the cell diagram with the cathode on the right-hand side.

$$Pt(s)\,|\,Cr_2O_7^{2-}(aq),Cr^{3+}(aq),H^+(aq)\,||\,H^+(aq),MnO_4^-(aq),Mn^{2+}(aq)\,|\,Pt(s)$$



To construct the spontaneous cell reaction, combine the two half-reactions, leaving the permanganate half-reaction as a reduction and reversing the dichromate half-reaction. To match numbers of electrons, multiply the manganese half-reaction by 6 and the chromium half-reaction by 5:

$$10\ Cr^{3+}(aq) + 35\ H_2O(l) \longrightarrow 5\ Cr_2O_7{}^{2-}(aq) + 70\ H^+(aq) + 30\ e^-$$

$$6\ MnO_4{}^-(aq) + 48\ H^+(aq) + 30\ e^- \longrightarrow 6\ Mn^{2+}(aq) + 24\ H_2O(l)$$

Their net sum gives the spontaneous cell reaction:

$$6\ MnO_4{}^-(aq) + 11\ H_2O(l) + 10\ Cr^{3+}(aq) \longrightarrow 6\ Mn^{2+}(aq) + 22\ H^+(aq) + 5\ Cr_2O_7{}^{2-}(aq)$$

SELF-TEST 12.9A Which metal, zinc or nickel, is the stronger reducing agent in aqueous solution under standard conditions? Evaluate the standard emf of the appropriate cell, specify the cell with a cell diagram, and write the net ionic equation for the spontaneous reaction.

[*Answer:* Zinc; +0.53 V; $Zn(s)|Zn^{2+}(aq)||Ni^{2+}(aq)|Ni(s)$; $Zn(s) + Ni^{2+}(aq) \rightarrow Zn^{2+}(aq) + Ni(s)$]

SELF-TEST 12.9B Which is the stronger oxidizing agent, Cu^{2+} or Ag^+, in aqueous solution under standard conditions? Evaluate the standard emf of the appropriate cell, specify the cell with a cell diagram, and write the net ionic equation for the corresponding cell reaction.

The oxidizing and reducing power of a redox couple determines its position in the electrochemical series. The strongest oxidizing agents are at the top left of the table; the strongest reducing agents are at the bottom right of the table.

12.8 Standard Potentials and Equilibrium Constants

One of the most useful applications of standard potentials is in the calculation of equilibrium constants from electrochemical data. The techniques that we develop here can be applied to any kind of reaction, including neutralization and precipitation reactions as well as redox reactions, provided that they can be expressed as the difference of two reduction half-reactions.

We saw in Section 9.3 that the standard reaction Gibbs free energy, $\Delta G_r°$, is related to the equilibrium constant of the reaction by $\Delta G_r° = -RT \ln K$. In this chapter, we have seen that the standard reaction Gibbs free energy is related to the standard emf of a galvanic cell by $\Delta G_r° = -nFE°$, with n a pure number. When we combine the two equations, we get

$$nFE° = RT \ln K \tag{4}$$

This expression can be rearranged to allow us to calculate the equilibrium constant from the cell emf:

$$\ln K = \frac{nFE°}{RT} \tag{5)*}$$

Because the magnitude of K increases exponentially with $E°$, a reaction with a large positive $E°$ has $K \gg 1$. A reaction with a large negative $E°$ has $K \ll 1$.

A note on good practice: Equation 5 was derived on the basis of the "molar" convention for writing the reaction Gibbs free energy; that means that the n must be interpreted as a pure number. That convention keeps the units straight: $FE°$ has the units joules per mole, so does RT, so the ratio $FE°/RT$ is a pure number and, with n a pure number, the right hand side is a pure number too (as it must be, if it is to be equal to a logarithm).

The fact that we can calculate $E°$ from standard potentials allows us to calculate equilibrium constants for any reaction that can be expressed as two half-reactions. The reaction does not need to be spontaneous nor does it have to be a redox reaction. Toolbox 12.3 summarizes the steps and Example 12.8 shows the steps in action.

TOOLBOX 12.3 HOW TO CALCULATE EQUILIBRIUM CONSTANTS FROM ELECTROCHEMICAL DATA

CONCEPTUAL BASIS

The equilibrium constant of a reaction is an exponential function of the standard emf of the corresponding cell. We can expect a cell reaction with a large positive emf to have a strong tendency to take place, and therefore to produce a high proportion of products at equilibrium. Therefore, we expect $K > 1$ when $E° > 0$ (and often $K \gg 1$). The opposite is true for a cell reaction with a negative standard emf.

PROCEDURE

The procedure for calculating an equilibrium constant from electrochemical data is as follows.

Step 1 Write the balanced equation for the reaction. Then find two reduction half-reactions in Appendix 2B that combine to give that equation. Reverse one of the half-reactions and add them together.

Step 2 Identify the numerical (unitless) value of n from the change in oxidation numbers or by examining the half-reactions (after multiplication by appropriate factors) for the number of electrons transferred in the balanced equation.

Step 3 To obtain $E°$, subtract the standard potential of the half-reaction that was reversed (oxidation) from the standard potential of the half-reaction that was left as a reduction: $E° = E°(\text{for reduction}) - E°(\text{for oxidation})$. Alternatively, write a cell diagram for the reaction; in that case, $E° = E_R° - E_L°$.

Step 4 Use the relation $\ln K = nFE°/RT$ to calculate the value of K.

At 25.00°C (298.15 K), $RT/F = 0.025\ 693$ V; so, at that temperature,

$$\ln K = \frac{nE°}{0.025\ 693\ \text{V}}$$

This procedure is illustrated in Example 12.8.

EXAMPLE 12.8 Sample exercise: Calculating the equilibrium constant for a reaction

Calculate the equilibrium constant at 25.00°C for the reaction

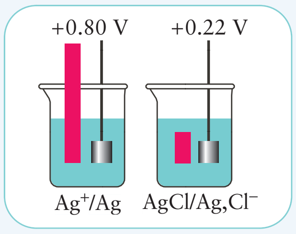
$$AgCl(s) \longrightarrow Ag^+(aq) + Cl^-(aq)$$

The equilibrium constant for this reaction is actually the solubility product, $K_{sp} = [Ag^+][Cl^-]$, for silver chloride (Section 11.8).

SOLUTION Because silver chloride is almost insoluble, we expect K to be very small (and $E°$ to be negative). Follow the procedure in Toolbox 12.3.

Step 1 Find the two reduction half-reactions required for the cell reaction.

$$\text{R: } AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq) \qquad E° = +0.22\ \text{V}$$
$$\text{L: } Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad E° = +0.80\ \text{V}$$



Reverse the second half-reaction.

$$Ag(s) \longrightarrow Ag^+(aq) + e^-$$

Add this equation to the reduction half-reaction and cancel species that appear on both sides of the equation.

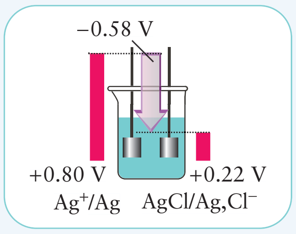
$$AgCl(s) \longrightarrow Ag^+(aq) + Cl^-(aq)$$

Step 2 From the half-reactions note the number of electrons transferred.

$$n = 1$$

Step 3 Find $E°$ from $E° = E°(\text{for reduction}) - E°(\text{for oxidation})$.

$$E° = 0.22\ \text{V} - 0.80\ \text{V} = -0.58\ \text{V}$$



From $\ln K = nFE°/RT = nE°/(RT/F)$,	$\ln K_{sp} = \frac{(1) \times (-0.58\text{ V})}{0.025\,693\text{ V}} = -\frac{0.58}{0.025\,693}$
Take the antilogarithm (e^x) of $\ln K_{sp}$.	$K_{sp} = e^{-0.58/0.025\,693} = 1.6 \times 10^{-10}$

The value of K_{sp} is the same as that listed in Table 11.4. Many of the solubility products listed in tables were determined from emf measurements and calculations like this one.

SELF-TEST 12.10A Use Appendix 2B to calculate the solubility product of mercury(I) chloride, Hg_2Cl_2.

[*Answer:* 2.6×10^{-18}]

SELF-TEST 12.10B Use the tables in Appendix 2B to calculate the solubility product of cadmium hydroxide, $Cd(OH)_2$.

The equilibrium constant of a reaction can be calculated from standard potentials by combining the equations for the half-reactions to give the cell reaction of interest and determining the standard potential of the corresponding cell.

12.9 The Nernst Equation

As a reaction proceeds toward equilibrium, the concentrations of its reactants and products change and ΔG approaches zero. Therefore, as reactants are consumed in a working electrochemical cell, the cell potential also decreases until finally it reaches zero. A "dead" battery is one in which the cell reaction has reached equilibrium. At equilibrium, a cell generates zero potential difference across its electrodes and the reaction can no longer do work. To describe this behavior quantitatively, we need to find how the cell emf varies with the concentrations of species in the cell.

HOW DO WE DO THAT?

To establish how the emf of a cell depends on concentration, we first note that the emf is proportional to the reaction Gibbs free energy (Eq. 2). We already know how ΔG_r varies with composition:

$$\Delta G_r = \Delta G_r° + RT \ln Q$$

where Q is the reaction quotient for the cell reaction (Eq. 5 of Section 9.3). Because $\Delta G_r = -nFE$ and $\Delta G_r° = -nFE°$, it follows at once that

$$-nFE = -nFE° + RT \ln Q$$

At this point, we divide through by $-nF$ to get an expression for E in terms of Q.

The equation for the concentration dependence of the cell emf that we have derived,

$$E = E° - \frac{RT}{nF} \ln Q \qquad (6)^*$$

is called the **Nernst equation** for the German electrochemist Walther Nernst, who first derived it. At 298.15 K, $RT/F = 0.025\,693$ V; so at that temperature the Nernst equation takes the form

$$E = E° - \frac{0.025\,693\text{ V}}{n} \ln Q$$

with n unitless. It is sometimes convenient to use this equation with common logarithms, in which case we make use of the relation $\ln x = 2.303 \log x$. At 298.15 K,

$$E = E° - \frac{2.303\,RT}{nF} \log Q = E° - \frac{0.05917\text{ V}}{n} \log Q$$

The Nernst equation is widely used to estimate the emf of cells under nonstandard conditions. In biology it is used, among other things, to estimate the potential difference across biological cell membranes, such as those of neurons.

EXAMPLE 12.9 Using the Nernst equation to predict an emf

Calculate the emf at 25°C of a Daniell cell in which the concentration of Zn^{2+} ions is $0.10\ mol\cdot L^{-1}$ and that of the Cu^{2+} ions is $0.0010\ mol\cdot L^{-1}$.

STRATEGY First, write the balanced equation for the cell reaction and the corresponding expression for Q, and note the value of n. Then determine $E°$ from the standard potentials in Table 12.1 or Appendix 2B. Determine the value of Q for the stated conditions. Calculate the emf by substituting these values into the Nernst equation, Eq. 6. At 25.00°C, $RT/F = 0.025\,693$ V.

SOLUTION The Daniell cell and the corresponding cell reaction are

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

Set up the reaction quotient.

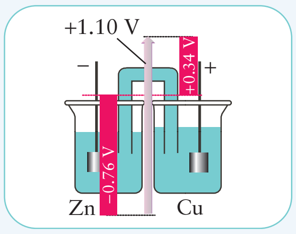
$$Q = \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}} = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{0.10}{0.0010}$$

From the balanced equation, note the value of n.

$$n = 2$$

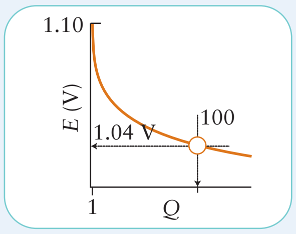
Determine the value of $E° = E_R° - E_L°$.

$$E° = 0.34 - (-0.76)\ V = +1.10\ V$$



From $E = E° - (RT/nF)\ln Q$,

$$E = 1.10\ V - \frac{0.025\,693\ V}{2}\ln\frac{0.10}{0.0010}$$
$$= 1.10\ V - 0.059\ V = +1.04\ V$$



SELF-TEST 12.11A Calculate the emf of the cell $Zn(s)|Zn^{2+}(aq, 1.50\ mol\cdot L^{-1})\|Fe^{2+}(aq, 0.10\ mol\cdot L^{-1})|Fe(s)$.

[***Answer:*** +0.29 V]

SELF-TEST 12.11B Calculate the emf of the concentration cell $Ag(s)|Ag^{+}(aq, 0.0010\ mol\cdot L^{-1})\|Ag^{+}(aq, 0.010\ mol\cdot L^{-1})|Ag(s)$.

An important application of the Nernst equation is the measurement of concentration. In a **concentration cell**, the two electrodes are identical except for their concentrations. For such a cell, $E° = 0$ and at 25°C the potential corresponding to the cell reaction is related to Q by $E = -(0.025693\ V/n)\ln Q$. For example, a concentration cell having two Ag^{+}/Ag electrodes is

$$Ag(s)|Ag^{+}(aq, L)\|Ag^{+}(aq, R)|Ag(s) \qquad Ag^{+}(aq, R) \longrightarrow Ag^{+}(aq, L)$$

The cell reaction has $n = 1$ and $Q = [Ag^{+}]_L/[Ag^{+}]_R$. If the concentration of Ag^{+} in the right-hand electrode is $1\ mol\cdot L^{-1}$, Q is equal to $[Ag^{+}]_L$, and the Nernst equation is

$$E = -(0.025693\ V)\ln[Ag^{+}]_L$$

Therefore, by measuring E, we can infer the concentration of Ag^+ in the left-hand electrode compartment. If the concentration of Ag^+ ions in the left-hand electrode is less than that in the right, then $E > 0$ for the cell as specified and the right-hand electrode will be found to be the cathode.

EXAMPLE 12.10 Using the Nernst equation to find a concentration

Each electrode compartment of a galvanic cell contains a silver electrode and 10.0 mL of 0.10 M $AgNO_3(aq)$; they are connected by a salt bridge. You now add 10.0 mL of 0.10 M NaCl(aq) to the left-hand electrode compartment. Almost all the silver precipitates as silver chloride but a little remains in solution as a saturated solution of AgCl. The measured emf is $E = +0.42$ V. What is the concentration of Ag^+ in the saturated solution?

STRATEGY The cell is a concentration cell in which the concentration of Ag^+ in one compartment is determined by the solubility of AgCl. Use the Nernst equation, Eq. 6, to find the concentration of Ag^+ in the compartment with the precipitate. The standard emf of the cell is 0 (in their standard states the electrodes are identical). At 25.00°C, $RT/F = 0.025\,693$ V.

SOLUTION The cell and the corresponding cell reaction are

$$\mathrm{Ag(s)}|\mathrm{Ag^+(aq, L)}||\mathrm{Ag^+(aq, R)}|\mathrm{Ag(s)} \qquad \mathrm{Ag^+(aq, R)} \longrightarrow \mathrm{Ag^+(aq, L)}$$

Set up the reaction quotient, Q.

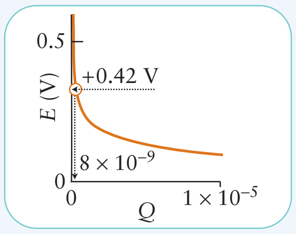
$$Q = \frac{[\mathrm{Ag^+}]_\mathrm{L}}{[\mathrm{Ag^+}]_\mathrm{R}} = \frac{[\mathrm{Ag^+}]_\mathrm{L}}{0.10}$$

From the balanced equation note the value of n.

$$n = 1$$

From $E = -(RT/nF)\ln Q$ rearranged into $\ln Q = -E/(RT/nF)$,

$$\ln Q = \frac{-0.42\ \mathrm{V}}{0.025\,693\ \mathrm{V}} = -16.34$$



From $Q = e^{\ln Q}$,

$$Q = e^{-16.34}$$

From $[\mathrm{Ag^+}]_\mathrm{L} = Q[\mathrm{Ag^+}]_\mathrm{R}$,

$$[\mathrm{Ag^+}]_\mathrm{L} = e^{-16.34} \times 0.10 = 8.0 \times 10^{-9}$$

That is, the concentration of Ag^+ ions in the saturated solution is 8.0 nmol·L^{-1}.

SELF-TEST 12.12A Calculate the molar concentration of Y^{3+} in a saturated solution of YF_3 by using a cell constructed with two yttrium electrodes. The electrolyte in one compartment is 1.0 M $Y(NO_3)_3(aq)$. In the other compartment you have prepared a saturated solution of YF_3. The measured cell potential is +0.34 V at 298 K.

[*Answer:* 8.3×10^{-18} mol·L^{-1}]

SELF-TEST 12.12B Calculate the emf of a cell constructed with two copper electrodes. The electrolyte in one compartment is 1.0 M $AgNO_3(aq)$. In the other compartment NaOH has been added to a $AgNO_3$ solution until the pH = 12.5 at 298 K.

The dependence of emf on composition is expressed by the Nernst equation, Eq. 6.

12.10 Ion-Selective Electrodes

An important application of the Nernst equation is the measurement of pH (and, through pH, acidity constants). The pH of a solution can be measured electrochemically with a device called a pH meter. The technique makes use of a cell in which one electrode is sensitive to the H_3O^+ concentration and another electrode serves as a reference. An electrode sensitive to the concentration of a particular ion is called an **ion-selective electrode**.

One combination of electrodes that could be used to determine pH is a hydrogen electrode connected through a salt bridge to a *calomel electrode*. The reduction half-reaction for the calomel electrode is

Calomel is the common name for mercury(I) chloride, Hg_2Cl_2.

$$Hg_2Cl_2(s) + 2\,e^- \longrightarrow 2\,Hg(l) + 2\,Cl^-(aq) \quad E° = +0.27\text{ V}$$

The overall cell reaction is

$$Hg_2Cl_2(s) + H_2(g) \longrightarrow 2\,H^+(aq) + 2\,Hg(l) + 2\,Cl^-(aq) \quad Q = \frac{[H^+]^2[Cl^-]^2}{P_{H_2}}$$

Provided that the pressure of hydrogen is 1 bar, we can write the reaction quotient as $Q = [H^+]^2[Cl^-]^2$. To find the concentration of hydrogen ions, we write the Nernst equation:

$$E = E° - \{\tfrac{1}{2}(0.0257\text{ V}) \times \ln [H^+]^2[Cl^-]^2\}$$

We apply $\ln (ab) = \ln a + \ln b$,

$$E = E° - \{\tfrac{1}{2}(0.0257\text{ V}) \times \ln [Cl^-]^2\} - \{\tfrac{1}{2}(0.0257\text{ V}) \times \ln [H^+]^2\}$$

and then use $\ln a^x = x \ln a$ to obtain

$$E = E° - \{(0.0257\text{ V}) \times \ln [Cl^-]\} - \{(0.0257\text{ V}) \times \ln [H^+]\}$$

The Cl^- concentration of a calomel electrode is fixed at the time of manufacture by saturating the solution with KCl, and so $[Cl^-]$ is a constant. We can therefore combine the first two terms on the right into a single constant, $E' = E° - (0.0257\text{ V}) \times \ln [Cl^-]$. Then, because $\ln x = 2.303 \log x$,

$$\begin{aligned} E &= E' - 2.303 \times (0.0257\text{ V}) \times \log [H^+] \\ &= E' + (0.0592\text{ V}) \times \text{pH} \end{aligned}$$

Therefore, by measuring the cell emf, E, we can determine the pH. The value of E' is established by calibrating the cell, which requires measuring E for a solution of known pH.

A **glass electrode**, a thin-walled glass bulb containing an electrolyte, is much easier to use than a hydrogen electrode and has a potential that varies linearly with the pH of the solution outside the glass bulb (Fig. 12.11). Often there is a calomel electrode built into the probe that makes contact with the test solution through a miniature salt bridge. A pH meter therefore usually has only one probe, which forms a complete electrochemical cell once it is dipped into a solution. The meter is calibrated with a buffer of known pH, and the measured cell emf is then automatically converted into the pH of the solution, which is displayed.

Commercially available electrodes used in *pX meters* are sensitive to other ions, such as Na^+, Ca^{2+}, NH_4^+, CN^-, or S^{2-}. They are used to monitor industrial processes and in pollution control.

The pH or concentrations of ions can be measured by using an electrode that responds selectively to only one species of ion.

FIGURE 12.11 A glass electrode in a protective plastic sleeve (left) is used to measure pH. It is used in conjunction with a calomel electrode (right) in pH meters such as this one.

ELECTROLYTIC CELLS

Redox reactions that have a positive Gibbs free energy of reaction are not spontaneous, but an electric current can be used to make them take place. For example, there is no common spontaneous chemical reaction in which fluorine is a product, and so the element cannot be isolated by any common chemical reaction. It was not until 1886 that the French chemist Henri Moissan found a way to force the formation of fluorine by passing an electric current through an anhydrous molten mixture of potassium fluoride and hydrogen fluoride. Fluorine is still prepared commercially by the same process.

In this part of Chapter 12, we study **electrolysis**, the process of driving a reaction in a nonspontaneous direction by using an electric current. First, we see how electrochemical cells are constructed for electrolysis and how to predict the potential needed to bring electrolysis about. Then, we examine the products of electrolysis and see how to predict the amount of products to expect for a given flow of electric current.

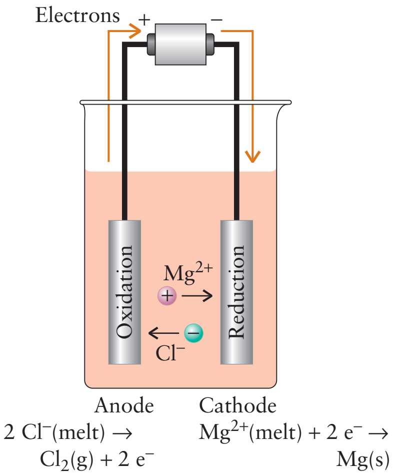


FIGURE 12.12 A schematic representation of the electrolytic cell used in the Dow process for magnesium. The electrolyte is molten magnesium chloride. As the current generated by the external source passes through the cell, magnesium ions are reduced to magnesium metal at the cathode and chloride ions are oxidized to chlorine gas at the anode.

The anode of an electrolytic cell is labeled + and the cathode −, the opposite of a galvanic cell.

12.11 Electrolysis

An electrochemical cell in which electrolysis takes place is called an **electrolytic cell**. The arrangement of components in electrolytic cells is different from that in galvanic cells. Typically, the two electrodes share the same compartment, there is only one electrolyte, and concentrations and pressures are far from standard. As in all electrochemical cells, the current is carried through the electrolyte by the ions present. For example, when copper metal is refined electrolytically, the anode is impure copper, the cathode is pure copper, and the electrolyte is an aqueous solution of $CuSO_4$. As the Cu^{2+} ions in solution are reduced and deposited as Cu atoms at the cathode, more Cu^{2+} ions migrate toward the cathode to take their place, and in turn their concentration is restored by Cu^{2+} produced by oxidation of copper metal at the anode.

Figure 12.12 shows schematically the layout of an electrolytic cell used for the commercial production of magnesium metal from molten magnesium chloride (the *Dow process*). As in a galvanic cell, oxidation takes place at the anode and reduction takes place at the cathode, electrons travel through the external wire from anode to cathode, cations move through the electrolyte toward the cathode, and anions move toward the anode. But unlike the spontaneously generated current in a galvanic cell, a current must be supplied by an external electrical power source for reaction to occur. That power source can be a galvanic cell, which provides the current that drives electrons through the wire in a predetermined direction. The result is to force oxidation at one electrode and reduction at the other. For example, the following half-reactions are made to take place in the Dow process:

$$\text{Anode reaction:}\quad 2\ \text{Cl}^-(\text{melt}) \longrightarrow \text{Cl}_2(\text{g}) + 2\ \text{e}^-$$
$$\text{Cathode reaction:}\quad \text{Mg}^{2+}(\text{melt}) + 2\ \text{e}^- \longrightarrow \text{Mg}(\text{l})$$

where "melt" signifies the molten salt. A rechargeable battery functions as a galvanic cell when it is doing work and as an electrolytic cell when it is being recharged.

To drive a reaction in a nonspontaneous direction, the external supply must generate a potential difference greater than the potential difference that would be produced by the reverse reaction. For example,

$$2\ \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\ \text{H}_2\text{O}(\text{l}) \qquad E = +1.23\ \text{V at pH} = 7\text{, spontaneous}$$

To achieve the nonspontaneous reaction

$$2\ \text{H}_2\text{O}(\text{l}) \longrightarrow 2\ \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \qquad E = -1.23\ \text{V at pH} = 7\text{, nonspontaneous}$$

we must apply at least 1.23 V from the external source to overcome the reaction's natural pushing power in the opposite direction. In practice, the applied potential difference must usually be substantially greater than the cell emf to reverse a spontaneous cell reaction and achieve a significant rate of product formation. The additional potential difference, which varies with the type of electrode, is called the **overpotential**. For platinum electrodes, the overpotential for the production of water from hydrogen and oxygen is about 0.6 V; so about 1.8 V (0.6

+1.23 V) is actually required to electrolyze water when platinum electrodes are used. Much contemporary research on electrochemical cells involves attempts to reduce the overpotential and hence to increase the efficiency of electrolytic processes.

When carrying out an electrolysis in solution, we must consider the possibility that other species present might be oxidized or reduced by the electric current. For example, suppose that we want to electrolyze water to produce hydrogen and oxygen. Because pure water does not carry a current, we must add an ionic solute with ions that are less easily oxidized or reduced than water:

$$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l) \qquad E = +0.82\text{ V at pH} = 7$$

To reverse this half-reaction and bring about the oxidation of water, we need an applied potential difference of at least 0.82 V. Suppose the added salt is sodium chloride. When Cl^- ions are present at 1 $mol{\cdot}L^{-1}$ in water, is it possible that they, and not the water, will be oxidized? From Table 12.1, the standard potential for the reduction of chlorine is +1.36 V:

$$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq) \qquad E° = +1.36\text{ V}$$

To reverse this reaction and oxidize chloride ions, we have to supply at least 1.36 V. Because only 0.82 V is needed to force the oxidation of water but 1.36 V is needed to force the oxidation of Cl^-, it appears that oxygen should be the product at the anode. However, the overpotential for oxygen production can be very high, and in practice chlorine also might be produced. At the cathode, we want the half-reaction $2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$ to take place. At pH = 7, the potential required for the reduction of hydrogen ions is 0.41 V. Hydrogen, rather than sodium metal, will be produced at the cathode, because the potential required to reduce sodium ions is significantly higher (+2.71 V).

EXAMPLE 12.11 **Sample exercise: Deciding which species will be produced at an electrode**

Suppose that an aqueous solution with pH = 7 and containing I^- ions at 1 $mol{\cdot}L^{-1}$ is being electrolyzed. Will O_2 or I_2 be produced at the anode?

SOLUTION From Table 12.1,

$$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq) \qquad E° = +0.54\text{ V}$$

so we know that at least 0.54 V is needed to oxidize I^-. We have seen that at least 0.82 V is needed to oxidize water:

$$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l) \qquad E = +0.82\text{ V at pH} = 7$$

Therefore, provided that the overpotentials are similar, we expect I^- ions to be oxidized in preference to water.

SELF-TEST 12.13A Predict the products resulting from the electrolysis of 1 M $AgNO_3(aq)$.
[*Answer:* Cathode, Ag; anode, O_2]

SELF-TEST 12.13B Predict the products resulting from the electrolysis of 1 M NaBr(aq).

The potential supplied to an electrolytic cell must be at least as great as that of the cell reaction to be reversed. If there is more than one reducible species in solution, the species with the greater potential for reduction is preferentially reduced. The same principle applies to oxidation.

12.12 The Products of Electrolysis

Now we shall see how to calculate the amount of product formed by a given amount of electricity (**1**). The calculation is based on observations made by Michael Faraday (Fig.12.13) and summarized—in more modern language than he used—as follows:

FIGURE 12.13 Michael Faraday (1791–1867).

Lab Video: Figure 12.14 Electroplating copper

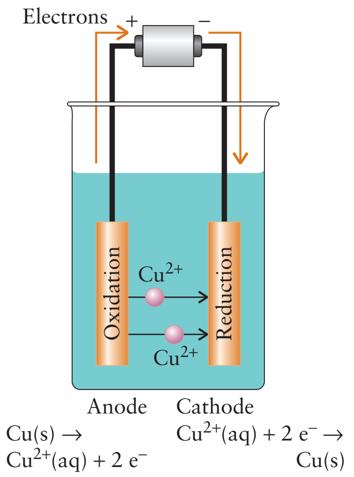
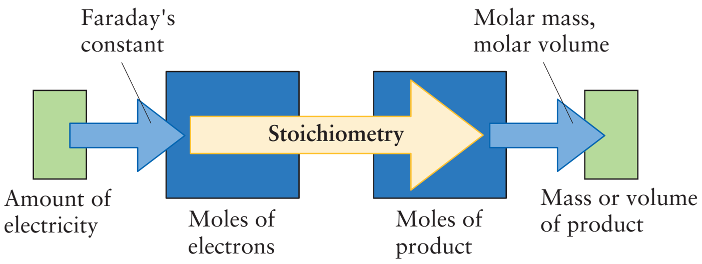


FIGURE 12.14 A schematic representation showing the electrolytic process for refining copper. The anode is impure copper. The Cu^{2+} ions produced by oxidation of the anode migrate to the cathode, where they are reduced to pure copper metal. A similar arrangement is used for electroplating objects.



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Faraday's law of electrolysis: The amount of product formed or reactant consumed by an electric current is stoichiometrically equivalent to the amount of electrons supplied.

Once we know the amount (in moles) of product formed, we can calculate the masses of the products or, if they are gases, their volumes.

EXAMPLE 12.12 Sample exercise: Calculating how much copper can be produced by electrolysis

Copper is refined electrolytically by using an impure form of copper metal called blister copper as the anode in an electrolytic cell (Fig. 12.14). The current supply drives the oxidation of the blister copper to copper(II) ions, Cu^{2+}, which are then reduced to pure copper metal at the cathode:

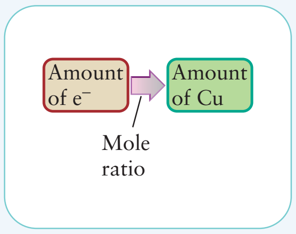
$$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$$

What amount of copper (in moles) can be produced by using 4.0 mol e^-?

SOLUTION

From 2 mol $e^- \simeq$ 1 mol Cu,

$$\text{Amount of Cu (mol)} = (4.0\ \text{mol } e^-) \times \frac{1\ \text{mol Cu}}{2\ \text{mol } e^-}$$
$$= 2.0\ \text{mol Cu}$$



SELF-TEST 12.14A What amount (in moles) of Al(s) can be produced from Al_2O_3 if 5.0 mol e^- is supplied?

[***Answer:*** 1.7 mol Al]

SELF-TEST 12.14B What amount (in moles) of Cr(s) can be produced from CrO_3 if 12.0 mol e^- is supplied?

In this context, Q is the charge supplied: don't confuse it with the reaction quotient Q!

The quantity, Q, of electricity passed through the electrolysis cell is measured in coulombs. It is determined by measuring the current, I, and the time, t, for which the current flows and is calculated from

$$\text{Charge supplied (C)} = \text{current (A)} \times \text{time (s)} \qquad \text{or} \qquad Q = It \qquad (7)$$

For example, because 1 A·s = 1 C, if 2.00 A is passed for 125 s, the charge supplied to the cell is

$$Q = (2.00\ \text{A}) \times (125\ \text{s}) = 250.\ \text{A·s} = 250.\ \text{C}$$

To determine the amount of electrons supplied by a given charge, we use Faraday's constant, F, the magnitude of the charge per mole of electrons (Section 12.4). Because the charge supplied is nF, where n is the amount of electrons (in moles), and $Q = nF$, it follows that

$$n = \frac{Q}{F} = \frac{It}{F} \qquad (8)^*$$

So, by measuring the current and the time for which it flows, we can determine the amount of electrons supplied. By combining the amount of electrons supplied with the mole ratio from the stoichiometry of the electrode reaction, we can deduce the amount of product obtained (see **1**).

TOOLBOX 12.4 HOW TO PREDICT THE RESULT OF ELECTROLYSIS

CONCEPTUAL BASIS

The number of electrons required to reduce a species is related to the stoichiometric coefficients in the reduction half-reaction. The same is true of oxidation. Therefore, we can set up a stoichiometric relation between the reduced or oxidized species and the amount of electrons supplied. The amount of electrons required is calculated from the current and the length of time for which the current flows.

PROCEDURE

To determine the amount of product that can be produced

Step 1 Identify the stoichiometric relation between electrons and the species of interest from the applicable half-reaction.

Step 2 Calculate the amount (in moles) of electrons supplied from Eq. 8, $n = It/F$. Use the stoichiometric relation from step 1 to convert n into the amount of substance. If required, use the molar mass to convert into mass (or molar volume to convert into volume).

This procedure is illustrated in Example 12.13

To determine the time required for a given amount of product to be produced

Step 1 Identify the stoichiometric relation between electrons and the species of interest from the applicable half-reaction.

Step 2 If required, use the molar mass to convert mass into amount (in moles). Use the stoichiometric relation from step 1 to convert the amount of substance into the amount of electrons passed, n (in moles).

Step 3 Substitute n, the current, and Faraday's constant into Eq. 8 rearranged to $t = Fn/I$ and solve for time.

This procedure is illustrated in Example 12.14.

EXAMPLE 12.13 Sample exercise: Calculating the amount of product formed by electrolysis

Aluminum is produced by electrolysis of its oxide dissolved in molten cryolite (Na_3AlF_6). Find the mass of aluminum that can be produced in 1.00 day (d) in an electrolytic cell operating continuously at 1.00×10^5 A. The cryolite does not react.

SOLUTION We use the first procedure in Toolbox 12.4.

Step 1 Write the half-reaction for the reduction and find the amount of electrons required to reduce 1 mol metal.

$$Al^{3+}(melt) + 3\,e^- \longrightarrow Al(l)$$

$$3\text{ mol e}^- \simeq 1\text{ mol Al}$$

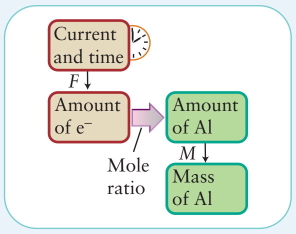
Step 2 From $n = It/F$, using $M(Al) = 26.98\text{ g·mol}^{-1}$, 3600 s = 1 h, and 24 h = 1 d,

$$m_{Al} = n_{e^-} \times \frac{1\text{ mol Al}}{3\text{ mol e}^-} \times \frac{26.98\text{ g Al}}{1\text{ mol Al}}$$

$$= \frac{(1.00 \times 10^5\text{ C·s}^{-1}) \times (24.0 \times 3600\text{ s})}{9.65 \times 10^4\text{ C·(mol e}^-)^{-1}}$$

$$\times \frac{1\text{ mol Al}}{3\text{ mol e}^-} \times \frac{26.98\text{ g Al}}{1\text{ mol Al}}$$

$$= 8.05 \times 10^5\text{ g Al}$$



The mass produced corresponds to 805 kg. The fact that the production of 1 mol Al requires 3 mol e⁻ accounts for the very high consumption of electricity characteristic of aluminum-production plants.

Self-Test 12.15A Determine the mass (in grams) of magnesium metal that can be obtained from molten magnesium chloride, by using a current of 7.30 A for 2.11 h. What volume of chlorine gas at 25°C and 1.00 atm will be produced at the anode?

[*Answer:* 6.98 g; 7.03 L]

Self-Test 12.15B What mass of chromium metal can be obtained from a 1 M solution of CrO_3 in dilute sulfuric acid, by using a current of 6.20 A for 6.00 h?

EXAMPLE 12.14 **Sample exercise: Calculating the time required to produce a given mass of product**

How many hours are required to plate 25.00 g of copper metal from 1.00 M $CuSO_4(aq)$ by using a current of 3.00 A?

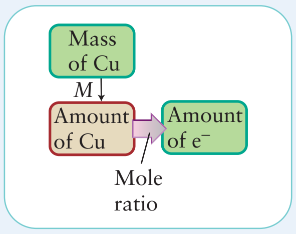
SOLUTION We use the second procedure in Toolbox 12.4.

Step 1 Find the stoichiometric relation between electrons and the species of interest from the half-reaction for the electrolysis.

$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$;
therefore, $2\ \text{mol e}^- \simeq 1\ \text{mol Cu}$

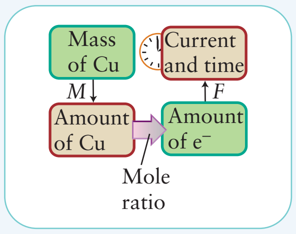
Step 2 To find $n(e^-)$ convert grams of Cu into moles of Cu and moles of Cu into moles of e^-.

$$n_{e^-} = (25.00\ \text{g Cu}) \times \left(\frac{1\ \text{mol Cu}}{63.54\ \text{g Cu}}\right) \times \left(\frac{2\ \text{mol e}^-}{1\ \text{mol Cu}}\right)$$
$$= \frac{25.00 \times 2}{63.54}\ \text{mol e}^-$$



Step 3 Convert seconds to hours and use $t = Fn/I$.

$$t = \frac{9.6485 \times 10^4\ \text{C}\cdot(\text{mol e}^-)^{-1}}{3.00\ \text{C}\cdot\text{s}^{-1}} \times \left(\frac{25.00 \times 2}{63.54}\ \text{mol e}^-\right) \times \left(\frac{1\ \text{h}}{3600\ \text{s}}\right)$$
$$= 7.0\ \text{h}$$



SELF-TEST 12.16A Determine the time, in hours, required to electroplate 7.00 g of magnesium metal from molten magnesium chloride, by using a current of 7.30 A.

[*Answer:* 2.12 h]

SELF-TEST 12.16B How many hours are required to plate 12.00 g of chromium metal from a 1 M solution of CrO_3 in dilute sulfuric acid, by using a current of 6.20 A?

The amount of product in an electrolysis reaction is calculated from the stoichiometry of the half-reaction and the current and time for which the current flows.

THE IMPACT ON MATERIALS

Electrochemical cells play important roles in both the purification and the preservation of metallic materials. Redox reactions are used throughout the chemical industry to extract metals from their ores. However, redox reactions also corrode the artifacts that industry produces. What redox reactions achieve, redox reactions can destroy.

12.13 Applications of Electrolysis

We have already described the refining of copper and the electrolytic extraction of aluminum, magnesium, and fluorine. Another important industrial application of electrolysis is the production of sodium metal by the *Downs process*, the electrolysis of molten rock salt (Fig. 12.15):

Cathode reaction: $2\,Na^+(melt) + 2\,e^- \longrightarrow 2\,Na(l)$
Anode reaction: $2\,Cl^-(melt) \longrightarrow Cl_2(g) + 2\,e^-$

Sodium chloride is plentiful as the mineral rock salt, but the solid does not conduct electricity, because the ions are locked into place. Sodium chloride must be molten for electrolysis to occur. The electrodes in the cell are made of inert materials such as carbon, and the cell is designed to keep the sodium and chlorine produced by the electrolysis out of contact with each other and away from air. In a modification of the Downs process, the electrolyte is an aqueous solution of sodium chloride (see Section 14.7). The products of this *chloralkali process* are chlorine and aqueous sodium hydroxide.

Electroplating is the electrolytic deposition of a thin film of metal on an object. The object to be electroplated (either metal or graphite-coated plastic) constitutes the cathode, and the electrolyte is an aqueous solution of a salt of the plating metal. Metal is deposited on the cathode by reduction of ions in the electrolyte solution. These cations are supplied either by the added salt or from oxidation of the anode, which is made of the plating metal (Fig. 12.16).

Electrolysis is used industrially to produce aluminum and magnesium; to extract metals from their salts; to prepare chlorine, fluorine, and sodium hydroxide; to refine copper; and in electroplating.

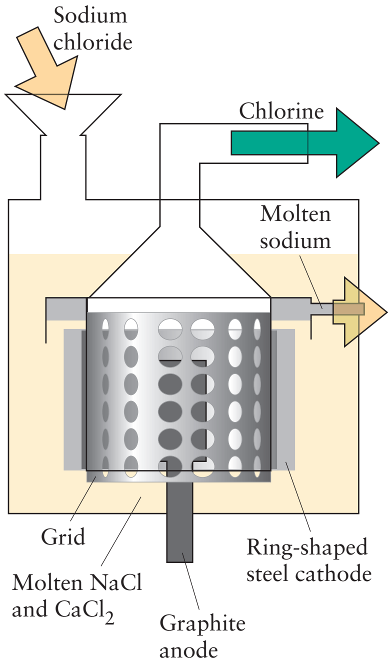


FIGURE 12.15 In the Downs process, molten sodium chloride is electrolyzed with a graphite anode (at which the Cl^- ions are oxidized to chlorine) and a steel cathode (at which the Na^+ ions are reduced to sodium). The sodium and chlorine are kept apart by the hoods surrounding the electrodes. Calcium chloride is present to lower the melting point of sodium chloride to an economical temperature.

12.14 Corrosion

Corrosion is the unwanted oxidation of a metal. It cuts short the lifetimes of steel products such as bridges and automobiles, and replacing corroded metal parts costs billions of dollars a year. Corrosion is an electrochemical process, and the electrochemical series is a source of insight into why corrosion occurs and how to prevent it.

The main culprit in corrosion is water. One half-reaction that we have to take into account is

$$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq) \qquad E^\circ = -0.83\text{ V}$$

This standard potential is for an OH^- concentration of 1 mol·L^{-1}, which corresponds to pH = 14, a strongly basic solution. However, from the Nernst equation, we can calculate that, at pH = 7, this couple has $E = -0.42$ V. Any metal with a standard potential more negative than -0.42 V can therefore reduce water at pH = 7: that is, at this pH, any such metal can be oxidized by water. Because $E^\circ = -0.44$ V for $Fe^{2+}(aq) + 2\,e^- \rightarrow Fe(s)$, iron has only a very slight tendency to be oxidized by water at pH = 7. For this reason, iron can be used for pipes in water supply systems and can be stored in oxygen-free water without rusting (Fig. 12.17).

When iron is exposed to damp air, with both oxygen and water present, the half-reaction

$$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l) \qquad E^\circ = +1.23\text{ V}$$

FIGURE 12.16 Chromium plating lends decorative flair as well as electrochemical protection to the steel of this motorcycle. Large quantities of electricity are needed for chromium plating because six electrons are required to produce each atom of chromium from chromium(VI) oxide.

FIGURE 12.17 Iron nails stored in oxygen-free water (left) do not rust, because the oxidizing power of water itself is weak. When oxygen is present (as a result of air dissolving in the water, right), oxidation is thermodynamically spontaneous and rust soon forms.

must be taken into account. The potential of this half-reaction at pH = 7 is +0.82 V, which lies well above the value for iron. Hence, iron can reduce oxygen in aqueous solution at pH = 7. In other words, oxygen and water can jointly oxidize iron metal to iron(II) ions. They can also subsequently work together to oxidize the iron(II) ions to iron(III), because $E° = +0.77$ V for $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$.

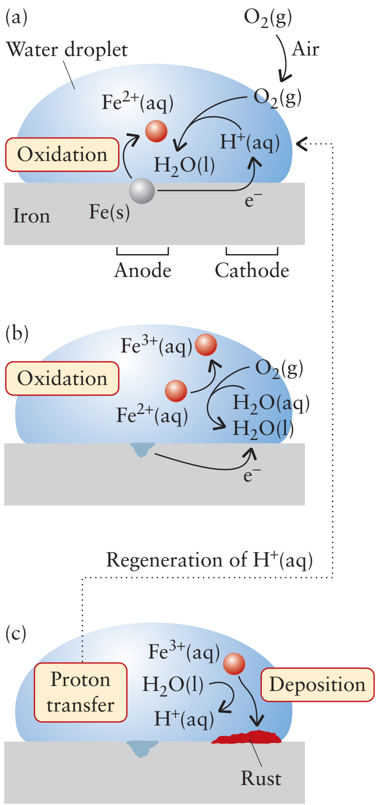


FIGURE 12.18 The mechanism of rust formation in a drop of water. (a) Oxidation of the iron occurs at a location out of contact with the oxygen of the air. The surface of the metal acts as an anode in a tiny galvanic cell, with the metal at the outer edge of the drop serving as the cathode. (b) Further oxidation of Fe^{2+} results in the formation of Fe^{3+} ions. (c) Protons are removed from H_2O as oxide ions combine with Fe^{3+} ions to deposit as rust. These protons are recycled, as indicated by the dotted line.

Let's look in more detail at the processes. A drop of water on the surface of iron can act as the electrolyte for corrosion in a tiny electrochemical cell (Fig. 12.18). At the edge of the drop, dissolved oxygen oxidizes the iron in the process

$$\begin{array}{lr} & 2\,Fe(s) \longrightarrow 2\,Fe^{2+}(aq) + 4\,e^- \\ & O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l) \\ \hline \text{Overall:} & 2\,Fe(s) + O_2(g) + 4\,H^+(aq) \longrightarrow 2\,Fe^{2+}(aq) + 2\,H_2O(l) \end{array} \qquad \textbf{(E)}$$

The electrons withdrawn from the metal by this oxidation can be restored from another part of the conducting metal—in particular, from iron lying beneath the oxygen-poor region in the center of the drop. The iron atoms there give up their electrons to the iron atoms at the edge of the drop, form Fe^{2+} ions, and drift away into the surrounding water. This process results in the formation of tiny pits in the surface of the iron. The Fe^{2+} ions are then oxidized further to Fe^{3+} by the dissolved oxygen:

$$\begin{array}{lr} & 2\,Fe^{2+}(aq) \longrightarrow 2\,Fe^{3+}(aq) + 2\,e^- \\ & \tfrac{1}{2}\,O_2(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2O(l) \\ \hline \text{Overall:} & 2\,Fe^{2+}(aq) + \tfrac{1}{2}\,O_2(g) + 2\,H^+(aq) \longrightarrow 2\,Fe^{3+}(aq) + H_2O(l) \end{array} \qquad \textbf{(F)}$$

These ions then precipitate as a hydrated iron(III) oxide, $Fe_2O_3{\cdot}H_2O$, the brown, insoluble substance that we call *rust*. The oxide ions can be regarded as coming from deprotonation of water molecules and as immediately forming the hydrated solid by precipitation with the Fe^{3+} ions produced in reaction F:

$$4\,H_2O(l) + 2\,Fe^{3+}(aq) \longrightarrow 6\,H^+(aq) + Fe_2O_3{\cdot}H_2O(s) \qquad \textbf{(G)}$$

This step restores the $H^+(aq)$ ions needed for reaction E, and so hydrogen ions function as a catalyst. The removal of Fe^{3+} ions from solution drives the reaction forward. The overall process is the sum of reactions E, F, and G:

$$2\,Fe(s) + \tfrac{3}{2}\,O_2(g) + H_2O(l) \longrightarrow Fe_2O_3{\cdot}H_2O(s)$$

Water is more highly conducting when it has dissolved ions, and the formation of rust is then accelerated. That is one reason why the salt air of coastal cities and salt used for de-icing highways is so damaging to exposed metal.

Because corrosion is electrochemical, we can use our knowledge of redox reactions to combat it. The simplest way to prevent corrosion is to protect the surface of the metal from exposure to air and water by painting. A method that achieves greater protection is to **galvanize** the metal, coating it with an unbroken film of zinc (Fig. 12.19). Zinc lies below iron in the electrochemical series; so, if a scratch exposes the metal beneath, the more strongly reducing zinc releases electrons to the iron. As a result, the zinc, not the iron, is oxidized. The zinc itself survives exposure on the unbroken surface because it is **passivated**, protected from further reaction, by a protective oxide. In general, the oxide of any metal that takes up more space than does the metal that it replaces acts as a **protective oxide**, an oxide that protects the metal from further oxidation. Zinc and chromium both form low-density protective oxides that can protect iron from oxidation.

It is not possible to galvanize large metal structures, such as ships, underground pipelines, gasoline storage tanks, and bridges, but **cathodic protection** can be used. For example, a block of a more strongly reducing metal than iron, typically zinc or magnesium, can be buried in moist soil and connected to an underground pipeline (Fig. 12.20). The block of magnesium is oxidized preferentially and supplies electrons to the iron for the reduction of oxygen. The block, which is called a **sacrificial anode**, protects the pipeline and is inexpensive to replace. For similar reasons, auto-

FIGURE 12.19 Steel girders are galvanized by immersion in a bath of molten zinc.

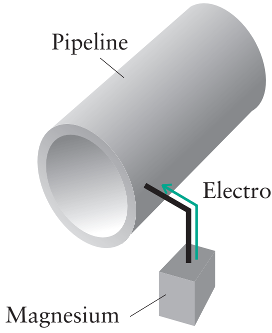


FIGURE 12.20 In the cathodic protection of a buried pipeline or other large metal construction, the artifact is connected to a number of buried blocks of metal, such as magnesium or zinc. The sacrificial anodes (the magnesium block in this illustration) supply electrons to the pipeline (the cathode of the cell), thereby preserving it from oxidation.

mobiles generally have negative ground systems as part of their electrical circuitry, which means that the body of the car is connected to the anode of the battery. The decay of the anode in the battery is the sacrifice that helps preserve the vehicle itself.

A common means of protecting the steel bodies of automobiles and trucks is through *cationic electrodeposition* coatings. In this process, coating containing a sacrificial metal is sprayed on the automobile body as a primer. The coating greatly reduces corrosion of the vehicle body. For many years lead was the only metal that could provide corrosion protection and also be applied in this manner. However, lead is toxic and concerns for environmental pollution stimulated research into alternative metals for cationic electrodeposition coatings. Eventually it was discovered that yttrium also offered corrosion resistance and, in fact, is twice as effective as lead. Yet yttrium is nontoxic and has an oxide that is a ceramic. Thus, the oxide is insoluble in water and cannot be spread through the environment through waterways.

Self-Test 12.17A Which of the following procedures helps to prevent the corrosion of an iron rod in water: (a) decreasing the concentration of oxygen in the water; (b) painting the rod?

[*Answer:* Both]

Self-Test 12.17B Which of the following elements can act as a sacrificial anode for iron: (a) copper; (b) aluminum; (c) tin?

The corrosion of iron is accelerated by the presence of oxygen, moisture, and salt. Corrosion can be inhibited by coating the surface with paint or zinc or by using cathodic protection.

12.15 Practical Cells

An important application of galvanic cells is their use as the portable power sources called batteries. An ideal battery should be inexpensive, portable, safe to use, and environmentally benign. It should also maintain a potential difference that is stable with the passage of time (Table 12.2). Both the mass and the volume of a battery are critical parameters. The electrolyte in a battery uses as little water as possible, both to reduce leakage of the electrolyte and to keep the mass low. Much of the research on batteries deals with raising the *specific energy*, the Gibbs free energy of reaction per kilogram (typically expressed in kilowatt-hours per kilogram, kW·h·kg^{-1}).

$1\ \text{kW·h} = (10^3\ \text{J·s}^{-1}) \times (3600\ \text{s}) = 3.6 \times 10^6\ \text{J} = 3.6\ \text{MJ}$ exactly.

A **primary cell** is a galvanic cell with the reactants sealed inside at manufacture. It cannot be recharged; when it runs down, it is discarded. A **fuel cell** is like a primary cell, but the reactants are continuously supplied (Box 12.1).

A *dry cell* is the primary cell used in most common applications, such as portable CD players, remote controls, and flashlights (Fig. 12.21). Its familiar

TABLE 12.2 Reactions in Commercial Batteries[*]

Primary cells	
dry	$Zn(s)\mid ZnCl_2(aq), NH_4Cl(aq)\mid MnO(OH)(s)\mid MnO_2(s)\mid graphite$, 1.5 V Anode: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$ followed by $Zn^{2+}(aq) + 4\,NH_3(aq) \longrightarrow [Zn(NH_3)_4]^{2+}(aq)$ Cathode: $MnO_2(s) + H_2O(l) + e^- \longrightarrow MnO(OH)(s) + OH^-(aq)$ followed by $NH_4^+(aq) + OH^-(aq) \longrightarrow H_2O(l) + NH_3(aq)$
alkaline	$Zn(s)\mid ZnO(s)\mid OH^-(aq)\mid Mn(OH)_2(s)\mid MnO_2(s)\mid graphite$, 1.5 V Anode: $Zn(s) + 2\,OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2\,e^-$ Cathode: $MnO_2(s) + 2\,H_2O(l) + 2\,e^- \longrightarrow Mn(OH)_2(s) + 2\,OH^-(aq)$
silver	$Zn(s)\mid ZnO(s)\mid KOH(aq)\mid Ag_2O(s)\mid Ag(s)\mid steel$, 1.6 V Anode: $Zn(s) + 2\,OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2\,e^-$ Cathode: $Ag_2O(s) + H_2O(l) + 2\,e^- \longrightarrow 2\,Ag(s) + 2\,OH^-(aq)$
Secondary cells	
lead–acid	$Pb(s)\mid PbSO_4(s)\mid H^+(aq), HSO_4^-(aq)\mid PbO_2(s)\mid PbSO_4(s)\mid Pb(s)$, 2 V Anode: $Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2\,e^-$ Cathode: $PbO_2(s) + 3\,H^+(aq) + HSO_4^-(aq) + 2\,e^- \longrightarrow PbSO_4(s) + 2\,H_2O(l)$
nicad	$Cd(s)\mid Cd(OH)_2(s)\mid KOH(aq)\mid Ni(OH)_3(s)\mid Ni(OH)_2(s)\mid Ni(s)$, 1.25 V Anode: $Cd(s) + 2\,OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2\,e^-$ Cathode: $2\,Ni(OH)_3(s) + 2\,e^- \longrightarrow 2\,Ni(OH)_2(s) + 2\,OH^-(aq)$
NiMH	$M(s)\mid MH(s)\mid KOH(aq)\mid NiOOH(s)\mid Ni(OH)_2(s)\mid Ni(s)$, 1.2 V Anode: $MH(s)$[†] $+ OH^-(aq) \longrightarrow M(s) + H_2O(l) + e^-$ Cathode: $NiOOH(s) + H_2O(l) + e^- \longrightarrow Ni(OH)_2(s) + OH^-$
sodium–sulfur	$Na(l)\mid Na^+$(ceramic electrolyte),S^{2-}(ceramic electrolyte)$\mid S_8(l)$, 2.2 V Anode: $2\,Na(l) \longrightarrow 2\,Na^+$(electrolyte) $+ 2\,e^-$ Cathode: $S_8(l) + 16\,e^- \longrightarrow 8\,S^{2-}$(electrolyte)

[*] Cell notation is described in Section 12.5.

[†] The metal in a nickel–metal hydride battery is usually a complex alloy of several metals, such as Cr, Ni, Co, V, Ti, Fe, and Zr.

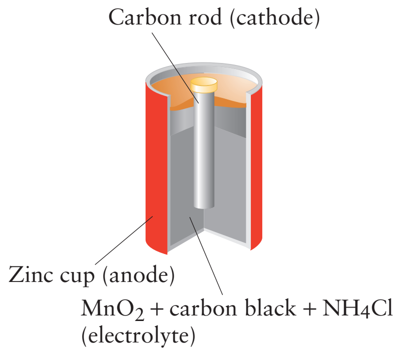


FIGURE 12.21 A commercial dry cell. The dry cell is also called the Leclanché cell, for Georges Leclanché, the French engineer who invented it in about 1866. The electrolyte is a moist paste.

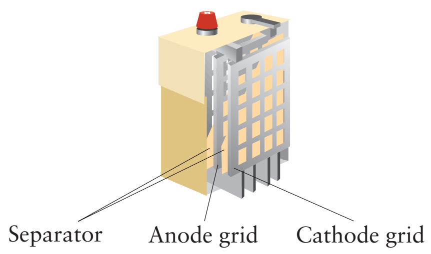


FIGURE 12.22 A lead–acid battery consists of a number of cells in series. A series of six cells produces about 12 V.

cylindrical zinc container serves as the anode; in the center is the cathode, a carbon rod. The interior of the container is lined with paper that serves as the porous barrier. The electrolyte is a moist paste of ammonium chloride, manganese(IV) oxide, finely granulated carbon, and an inert filler, usually starch. The ammonia provided by the ammonium ions forms the complex ion $Zn(NH_3)_4^{2+}$ with the Zn^{2+} ions and prevents their buildup and a consequent reduction of the potential.

Two primary cells that provide a more stable and longer-lasting potential than the dry cell are the alkaline cell and silver cell. An *alkaline cell* is similar to a dry cell but uses an alkaline electrolyte, with which the zinc electrode does not readily react when the battery is not in use. As a result, alkaline cells have longer lives than dry cells. They are used in smoke detectors and backup power supplies. A *silver cell* has a cathode made of Ag_2O. The relatively high emf of a silver cell, with its solid reactants and products, is maintained with great reliability over long periods of time and the cell can be manufactured in very small sizes. These features make it desirable for medical implants such as pacemakers, for hearing aids, and for cameras.

Secondary cells are galvanic cells that must be charged before they can be used; this type of cell is normally rechargeable. The batteries used in portable computers and automobiles are secondary cells. In the charging process, an external source of electricity reverses the spontaneous cell reaction and creates a nonequilibrium mixture of reactants. After charging, the cell can again produce electricity.

The *lead–acid cell* of an automobile battery is a secondary cell that contains several grids that act as electrodes (Fig. 12.22). Although it has a low specific energy, because the total surface area of these grids is large, the battery can generate large currents for short periods, such as the time needed for starting an engine. The electrodes are initially a hard lead–antimony alloy covered with a paste of lead(II) sulfate. The electrolyte is dilute sulfuric acid. During the first charging, some of the lead(II) sulfate is reduced to lead on one of the electrodes; that electrode will act as the anode during discharge. Simultaneously, during charging, lead(II) sulfate is

BOX 12.1 FRONTIERS OF CHEMISTRY: FUEL CELLS

Few places are more inhospitable to life than outer space. Any habitat, including a spacecraft, needs a source of electrical power, and astronauts need enough water for drinking and washing. Because the mass of a spacecraft must be kept as low as possible, most batteries—which usually provide energy from the oxidation of a metal—would be too heavy. Electricity can be obtained from combustion reactions by burning a fuel to create heat, which runs a generator. However, producing electricity from burning fuels is very inefficient because energy is wasted as heat.

The problem was solved by Francis Bacon, a British scientist and engineer, who developed an idea proposed by Sir William Grove in 1839. A fuel cell generates electricity directly from a chemical reaction, as in a battery, but uses reactants that are supplied continuously, as in an engine. A fuel cell that runs on hydrogen and oxygen is currently installed on the space shuttle (see Fig. L.1). An advantage of this fuel cell is that the only product of the cell reaction, water, can be used for life support.

In a simple version of a fuel cell, a fuel such as hydrogen gas is passed over a platinum electrode, oxygen is passed over the other, similar electrode, and the electrolyte is aqueous potassium hydroxide. A porous membrane separates the two electrode compartments. Many varieties of fuel cells are possible, and in some the electrolyte is a solid polymer membrane or a ceramic (see Section 14.22). Three of the most promising fuel cells are the alkali fuel cell, the phosphoric acid fuel cell, and the methanol fuel cell.

The hydrogen–oxygen cell used in the space shuttle is called an alkali fuel cell, because it has an alkaline electrolyte:

Anode: $2\ H_2(g) + 4\ OH^-(aq) \longrightarrow 4\ H_2O(l) + 4\ e^-$

Electrolyte: $KOH(aq)$

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

Although its cost prohibits its use in many applications, the alkali fuel cell is the primary fuel cell used in the aerospace industry.

If an acid electrolyte is used, water is produced only at the cathode. An example is the phosphoric acid fuel cell:

Anode: $2\ H_2(g) \longrightarrow 4\ H^+(aq) + 4\ e^-$

Electrolyte: $H_3PO_4(aq)$

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

This fuel cell has shown promise for combined heat and power systems (CHP systems). In such systems, the waste heat is used to heat buildings or to do work. Efficiency in a CHP plant can reach 80%. These plants could replace heating plants and power sources in colleges and universities, hotels, and apartment buildings.

Although hydrogen gas is an attractive fuel, it has disadvantages for mobile applications: it is difficult to store and dangerous to handle. One possibility for portable fuel cells is to store the hydrogen in carbon nanotubes. Carbon nanofibers in herringbone patterns have been shown to store huge amounts of hydrogen and to result in energy densities twice that of gasoline. Another option is the use of organometallic materials or inorganic hydrides, such as sodium aluminum hydride, $NaAlH_4$, doped with titanium.

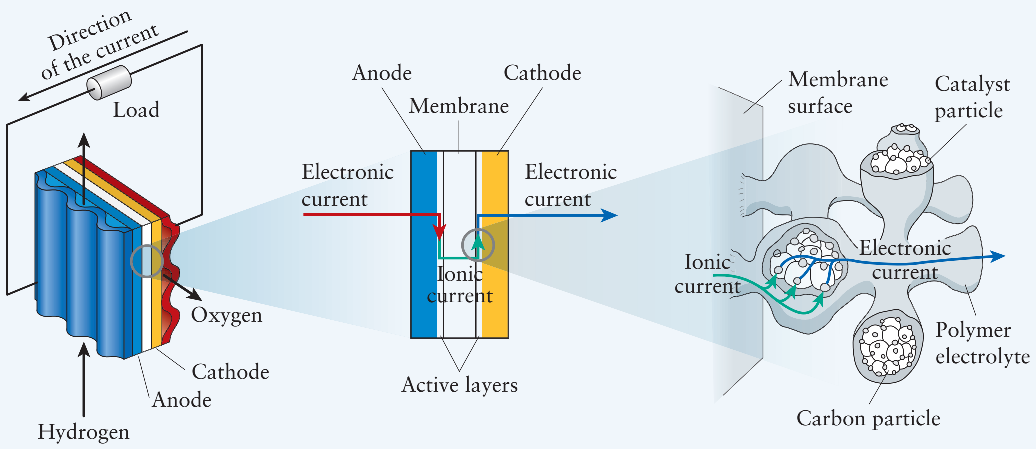
Until these materials have been developed, one attractive fuel is methanol, which is easy to handle and is rich in hydrogen atoms:

Anode: $CH_3OH(l) + 6\ OH^-(aq) \longrightarrow 5\ H_2O(l) + CO_2(g) + 6\ e^-$

Electrolyte: polymeric materials

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

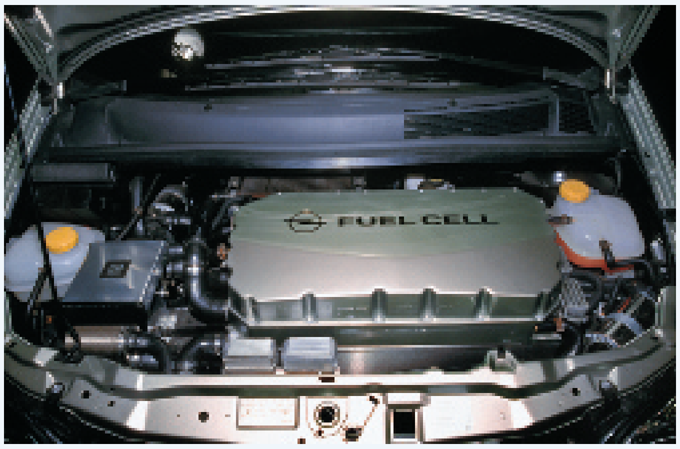
A disadvantage of methanol, however, is the phenomenon of "electro-osmotic drag" in which protons moving through the



This proton exchange membrane is used in both hydrogen and methanol fuel cells, in which a catalyst at the anode produces hydrogen from the methanol. Because the membrane allows the protons, but not the electrons, to travel through it, the protons flow through the porous membrane to the cathode, where they combine with oxygen to form water, while the electrons flow through an external circuit.

(continued)

BOX 12.1 FRONTIERS OF CHEMISTRY: FUEL CELLS *(continued)*



This automobile is powered by a hydrogen fuel cell with a proton exchange membrane. Its operation is pollution free, because the only product of the combustion is water.

polymer proton-exchange electrolyte membrane that separates the anode and cathode carry water and methanol with them into the cathode compartment. In the cathode, the potential is sufficient to oxidize CH_3OH to CO_2, thereby reducing the efficiency of the cell. One solution might be to find a material for the cathode that is selective to oxygen reduction so that any methanol that leaks in is not oxidized.

An exciting emerging technology is the biofuel cell. A biofuel cell is like a conventional fuel cell; however, in place of a platinum catalyst, it uses enzymes or even whole organisms. The electricity will be extracted through organic molecules that can support the transfer of electrons. One application will be as the power source for medical implants, such as pacemakers, perhaps by using the glucose present in the bloodstream as the fuel.

HOW MIGHT YOU CONTRIBUTE?

Fuel cell technologies developed for aerospace have the potential to change the way we live. Automobiles powered by hydrogen fuel cells are already being manufactured (see illustration below). However, there are many obstacles that must be overcome before fuel cells reach their potential to provide us with pollution-free energy. The hydrogen fuel cells are the most attractive, because of their use of a renewable fuel. Hydrogen can be obtained from the water in the oceans. The challenge is to extract it from seawater by using solar energy and to find safe means of transportation and storage. Many practical problems with fuel cells also need to be solved, such as controlling corrosion by electrolytes and reducing the cell size and operating temperature.

Related Exercises: 12.67–12.70.

For Further Reading: Breakthrough Technologies Institute, “The Online Fuel Cell Information Center,” http://www.fuelcells.org/. M. Jacoby, “Filling up with Hydrogen,” *Chemical and Engineering News,* vol. 83, August 22, 2005, pp. 42–47. P. Weiss, “Pocket sockets,” *Science News,* vol. 162, September 7, 2002, pp. 155–156. E. Willcocks, “Fuel cells go mobile,” *Chemistry in Britain,* January 2003, p. 27.

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oxidized to lead(IV) oxide on the electrode that will later act as the cathode during discharge. The lead–acid cell, which has a potential of 2 V, is used in a series of six cells to provide a 12-V source of power for starting the engine in most vehicles and as the main power source in electric vehicles.

Hybrid vehicles make use of the rechargeable *nickel–metal hydride (NiMH) cell* to supplement energy provided by burning gasoline. In this type of battery, hydrogen is stored in the form of a metal hydride, using a heterogeneous alloy of several metals, commonly including titanium, vanadium, chromium, and nickel. The advantages include low mass, high energy density, long shelf life, high current load capability, rapid charging, and good capacity (long time between charges). Because the materials are nontoxic, disposal of the batteries does not generate environmental problems.

The *lithium-ion cell* is used in laptop computers, because it can be recharged many times. This type of battery has an electrolyte consisting of polypropylene oxide or polyethylene oxide mixed with molten lithium salts and then allowed to cool. The resulting rubbery materials serve as good conductors of Li^+ ions. The low mass density of lithium gives it the highest available energy density, and lithium’s very negative electrode potential provides an emf as high as 4 V.

A *sodium–sulfur cell* is one of the more startling batteries (Fig. 12.23). It has liquid reactants (sodium and sulfur) and a solid electrolyte (a porous aluminum oxide ceramic); it must operate at a temperature of about 320°C; and it is highly dangerous in case of breakage. Because sodium has a low density, these cells have a very high specific energy. Their most common application is to power electric

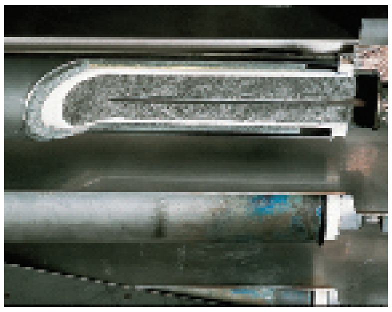


FIGURE 12.23 A sodium–sulfur battery used in an electric vehicle.

vehicles. Once the vehicle is operating, the heat generated by the battery is sufficient to maintain the temperature.

> ***Practical galvanic cells can be classified as primary cells (reactants are sealed inside in a charged state), secondary cells (can be recharged), and fuel cells.***

SKILLS YOU SHOULD HAVE MASTERED

☐ 1 Balance chemical equations for redox reactions by the half-reaction method (Toolbox 12.1 and Examples 12.1 and 12.2).

☐ 2 Estimate the reaction Gibbs free energy from a cell emf (Example 12.3).

☐ 3 Write the cell diagram for a redox reaction (Self-Test 12.4).

☐ 4 Write the chemical equation for a cell reaction, given the cell diagram (Toolbox 12.2 and Example 12.4).

☐ 5 Determine the standard potential of an electrode from a cell emf (Example 12.5).

☐ 6 Calculate the standard potential of a redox couple from two others relating to different oxidation states (Example 12.6).

☐ 7 Predict the spontaneous direction of a redox reaction by using the electrochemical series (Example 12.7).

☐ 8 Calculate the equilibrium constant for a reaction from the standard cell emf (Toolbox 12.3 and Example 12.8).

☐ 9 Use the Nernst equation to predict a cell emf (Examples 12.9 and 12.10).

☐ 10 Predict the likely products of electrolysis of an aqueous solution from standard potentials (Example 12.11).

☐ 11 Calculate the amount of product produced from electrolysis or the time required for electrolysis (Toolbox 12.4 and Examples 12.12, 12.13, and 12.14).

☐ 12 Describe corrosion and means for protecting iron from corrosion (Section 12.14).

☐ 13 Describe the operation of commercial practical cells (Section 12.15).

EXERCISES

Assume a temperature of 25°C (298 K) for the following exercises unless instructed otherwise.

Redox Equations

12.1 The following redox reaction is used in acidic solution in the Breathalyzer test to determine the level of alcohol in the blood:

$$H^+(aq) + Cr_2O_7^{2-}(aq) + C_2H_5OH(aq) \longrightarrow Cr^{3+}(aq) + C_2H_4O(aq) + H_2O(l)$$

(a) Identify the elements undergoing changes in oxidation state and indicate the initial and final oxidation numbers for these elements. (b) Write and balance the oxidation half-reaction. (c) Write and balance the reduction half-reaction. (d) Combine the half-reactions to produce a balanced redox equation.

12.2 The following redox reaction between persulfate ions and chromium ions is carried out in aqueous acidic solution:

$$O_3SOOSO_3^{2-}(aq) + Cr^{3+}(aq) \longrightarrow HSO_4^-(aq) + Cr_2O_7^{2-}(aq)$$

(a) Identify the elements undergoing changes in oxidation state and indicate the initial and final oxidation numbers for these elements. (b) Write and balance the oxidation half-reaction. (c) Write and balance the reduction half-reaction. (d) Combine the half-reactions to produce a balanced redox equation.

12.3 Balance each of the following skeletal equations by using oxidation and reduction half-reactions. All the reactions take place in acidic solution. Identify the oxidizing agent and reducing agent in each reaction.
(a) Reaction of thiosulfate ion with chlorine gas:
$Cl_2(g) + S_2O_3^{2-}(aq) \rightarrow Cl^-(aq) + SO_4^{2-}(aq)$
(b) Action of the permanganate ion on sulfurous acid:
$MnO_4^-(aq) + H_2SO_3(aq) \rightarrow Mn^{2+}(aq) + HSO_4^-(aq)$
(c) Reaction of hydrosulfuric acid with chlorine:
$H_2S(aq) + Cl_2(g) \rightarrow S(s) + Cl^-(aq)$
(d) Reaction of chlorine in water:
$Cl_2(g) \rightarrow HClO(aq) + Cl^-(aq)$

12.4 Balance each of the following skeletal equations by using oxidation and reduction half-reactions. All the reactions take place in acidic solution. Identify the oxidizing agent and reducing agent in each reaction.
(a) Conversion of iron(II) into iron(III) by dichromate ion:
$Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow Fe^{3+}(aq) + Cr^{3+}(aq)$
(b) Formation of acetic acid from ethanol by the action of permanganate ion:
$C_2H_5OH(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + CH_3COOH(aq)$
(c) Reaction of iodide with nitric acid:
$I^-(aq) + NO_3^-(aq) \rightarrow I_2(aq) + NO(g)$
(d) Reaction of arsenic(III) sulfide with nitric acid:
$As_2S_3(s) + NO_3^-(aq) \rightarrow H_3AsO_4(aq) + S(s) + NO(g)$

12.5 Balance each of the following skeletal equations by using oxidation and reduction half-reactions. All the reactions take place in basic solution. Identify the oxidizing agent and reducing agent in each reaction.
(a) Action of ozone on bromide ions:
$O_3(aq) + Br^-(aq) \rightarrow O_2(g) + BrO_3^-(aq)$
(b) Reaction of bromine in water:
$Br_2(l) \rightarrow BrO_3^-(aq) + Br^-(aq)$
(c) Formation of chromate ions from chromium(III) ions:
$Cr^{3+}(aq) + MnO_2(s) \rightarrow Mn^{2+}(aq) + CrO_4^{2-}(aq)$
(d) Reaction of elemental phosphorus to form phosphine, PH_3, a poisonous gas with the odor of decaying fish:
$P_4(s) \rightarrow H_2PO_2^-(aq) + PH_3(g)$

12.6 Balance each of the following skeletal equations by using oxidation and reduction half-reactions. All the reactions take place in basic solution. Identify the oxidizing agent and reducing agent in each reaction.
(a) Production of chlorite ions from dichlorine heptoxide:
$\text{Cl}_2\text{O}_7\text{(g)} + \text{H}_2\text{O}_2\text{(aq)} \rightarrow \text{ClO}_2^{-}\text{(aq)} + \text{O}_2\text{(g)}$
(b) Action of permanganate ions on sulfide ions:
$\text{MnO}_4^{-}\text{(aq)} + \text{S}^{2-}\text{(aq)} \rightarrow \text{S(s)} + \text{MnO}_2\text{(s)}$
(c) Reaction of hydrazine with chlorate ions:
$\text{N}_2\text{H}_4\text{(g)} + \text{ClO}_3^{-}\text{(aq)} \rightarrow \text{NO(g)} + \text{Cl}^{-}\text{(aq)}$
(d) Reaction of plumbate ions and hypochlorite ions:
$\text{Pb(OH)}_4^{2-}\text{(aq)} + \text{ClO}^{-}\text{(aq)} \rightarrow \text{PbO}_2\text{(s)} + \text{Cl}^{-}\text{(aq)}$

12.7 The compound P_4S_3 is oxidized by nitrate ions in acid solution to give phosphoric acid, sulfate ions, and nitric oxide, NO. Write the balanced equation for each half-reaction and the overall equation for the reaction.

12.8 Iron(II) hydrogen phosphite, FeHPO_3, is oxidized by hypochlorite ions in basic solution. The products are chloride ion, phosphate ion, and iron(III) hydroxide. Write the balanced equation for each half-reaction and the overall equation for the reaction.

Galvanic Cells

12.9 Write the half-reactions and the balanced equation for the cell reaction for each of the following galvanic cells:
(a) $\text{Ni(s)}|\text{Ni}^{2+}\text{(aq)}\|\text{Ag}^{+}\text{(aq)}|\text{Ag(s)}$
(b) $\text{C(gr)}|\text{H}_2\text{(g)}|\text{H}^{+}\text{(aq)}\|\text{Cl}^{-}\text{(aq)}|\text{Cl}_2\text{(g)}|\text{Pt(s)}$
(c) $\text{Cu(s)}|\text{Cu}^{2+}\text{(aq)}\|\text{Ce}^{4+}\text{(aq)},\text{Ce}^{3+}\text{(aq)}|\text{Pt(s)}$
(d) $\text{Pt(s)}|\text{O}_2\text{(g)}|\text{H}^{+}\text{(aq))}\|\text{OH}^{-}\text{(aq)}|\text{O}_2\text{(g)}|\text{Pt(s)}$
(e) $\text{Pt(s)}|\text{Sn}^{4+}\text{(aq)},\text{Sn}^{2+}\text{(aq)}\|\text{Cl}^{-}\text{(aq)}|\text{Hg}_2\text{Cl}_2\text{(s)}|\text{Hg(l)}$

12.10 Write the half-reactions and the balanced equation for the cell reaction for each of the following galvanic cells:
(a) $\text{Cu(s)}|\text{Cu}^{2+}\text{(aq)}\|\text{Cu}^{+}\text{(aq)}|\text{Cu(s)}$
(b) $\text{Cr(s)}|\text{Cr}^{2+}\text{(aq)}\|\text{Au}^{3+}\text{(aq)}|\text{Au(s)}$
(c) $\text{Ag(s)}|\text{AgI(s)}|\text{I}^{-}\text{(aq)}\|\text{Cl}^{-}\text{(aq)}|\text{AgCl(s)}|\text{Ag(s)}$
(d) $\text{Hg(l)}|\text{Hg}_2\text{Cl}_2\text{(s)}|\text{Cl}^{-}\text{(aq)}\|\text{Cl}^{-}\text{(aq)}|\text{AgCl(s)}|\text{Ag(s)}$
(e) $\text{Hg(l)}|\text{Hg}_2^{2+}\text{(aq)}\|\text{MnO}_4^{-}\text{(aq)},\text{Mn}^{2+}\text{(aq)},\text{H}^{+}\text{(aq)}|\text{Pt(s)}$

12.11 Write the half-reactions, the balanced equation for the cell reaction, and the cell diagram for each of the following skeletal equations:
(a) $\text{Ni}^{2+}\text{(aq)} + \text{Zn(s)} \rightarrow \text{Ni(s)} + \text{Zn}^{2+}\text{(aq)}$
(b) $\text{Ce}^{4+}\text{(aq)} + \text{I}^{-}\text{(aq)} \rightarrow \text{I}_2\text{(s)} + \text{Ce}^{3+}\text{(aq)}$
(c) $\text{Cl}_2\text{(g)} + \text{H}_2\text{(g)} \rightarrow \text{HCl(aq)}$
(d) $\text{Au}^{+}\text{(aq)} \rightarrow \text{Au(s)} + \text{Au}^{3+}\text{(aq)}$

12.12 Write the half-reactions, the balanced equation for the cell reaction, and the cell diagram for each of the following skeletal equations:
(a) $\text{Mn(s)} + \text{Ti}^{2+}\text{(aq)} \rightarrow \text{Mn}^{2+}\text{(aq)} + \text{Ti(s)}$
(b) $\text{Fe}^{3+}\text{(aq)} + \text{H}_2\text{(g)} \rightarrow \text{Fe}^{2+}\text{(aq)} + \text{H}^{+}\text{(aq)}$
(c) $\text{Cu}^{+}\text{(aq)} \rightarrow \text{Cu(s)} + \text{Cu}^{2+}\text{(aq)}$
(d) $\text{MnO}_4^{-}\text{(aq)} + \text{H}^{+}\text{(aq)} + \text{Cl}^{-}\text{(aq)} \rightarrow$
$\text{Cl}_2\text{(g)} + \text{Mn}^{2+}\text{(aq)} + \text{H}_2\text{O(l)}$

12.13 Write the half-reactions and devise a galvanic cell (write a cell diagram) to study each of the following reactions:
(a) $\text{AgBr(s)} \rightleftharpoons \text{Ag}^{+}\text{(aq)} + \text{Br}^{-}\text{(aq)}$, a solubility equilibrium
(b) $\text{H}^{+}\text{(aq)} + \text{OH}^{-}\text{(aq)} \rightarrow \text{H}_2\text{O(l)}$, the Brønsted neutralization reaction
(c) $\text{Cd(s)} + 2\ \text{Ni(OH)}_3\text{(s)} \rightarrow \text{Cd(OH)}_2\text{(s)} + 2\ \text{Ni(OH)}_2\text{(s)}$, the reaction in the nickel–cadmium cell

12.14 Write balanced half-reactions and devise a galvanic cell (write a cell diagram) to study each of the following reactions:
(a) $\text{AgNO}_3\text{(aq)} + \text{KI(aq)} \rightarrow \text{AgI(s)} + \text{KNO}_3\text{(aq)}$, a precipitation reaction
(b) $\text{H}_3\text{O}^{+}\text{(aq, concentrated)} \rightarrow \text{H}_3\text{O}^{+}\text{(aq, dilute)}$
(c) $\text{Zn(s)} + \text{Ag}_2\text{O(s)} \rightarrow \text{ZnO(s)} + 2\ \text{Ag(s)}$, the reaction in a silver cell

12.15 (a) Write balanced reduction half-reactions for the redox reaction of an acidified solution of potassium permanganate and iron(II) chloride. (b) Write the balanced equation for the cell reaction and devise a galvanic cell to study the reaction (write its cell diagram).

12.16 (a) Write balanced reduction half-reactions for the redox reaction between sodium dichromate and mercury(I) nitrate in an acidic solution. (b) Write the balanced equation for the cell reaction and devise a galvanic cell to study the reaction (write its cell diagram).

12.17 Predict the standard emf of each of the following galvanic cells:
(a) $\text{Pt(s)}|\text{Cr}^{3+}\text{(aq)},\text{Cr}^{2+}\text{(aq)}\|\text{Cu}^{2+}\text{(aq)}|\text{Cu(s)}$
(b) $\text{Ag(s)}|\text{AgI(s)}|\text{I}^{-}\text{(aq)}\|\text{Cl}^{-}\text{(aq)}|\text{AgCl(s)}|\text{Ag(s)}$
(c) $\text{Hg(l)}|\text{Hg}_2\text{Cl}_2\text{(s)}|\text{Cl}^{-}\text{(aq)}\|\text{Hg}_2^{2+}\text{(aq)}|\text{Hg(l)}$
(d) $\text{C(gr)}|\text{Sn}^{4+}\text{(aq)},\text{Sn}^{2+}\text{(aq)}\|\text{Pb}^{4+}\text{(aq)},\text{Pb}^{2+}\text{(aq)}|\text{Pt(s)}$

12.18 Predict the standard emf of each of the following galvanic cells:
(a) $\text{Pt(s)}|\text{Fe}^{3+}\text{(aq)},\text{Fe}^{2+}\text{(aq)}\|\text{Ag}^{+}\text{(aq)}|\text{Ag(s)}$
(b) $\text{U(s)}|\text{U}^{3+}\text{(aq)}\|\ \text{V}^{2+}\text{(aq)}|\text{V(s)}$
(c) $\text{Sn(s)}|\text{Sn}^{2+}\text{(aq)}\|\text{Sn}^{4+}\text{(aq)},\text{Sn}^{2+}\text{(aq)}|\text{Pt(s)}$
(d) $\text{Cu(s)}|\text{Cu}^{2+}\text{(aq)}\|\text{Au}^{+}\text{(aq)}|\text{Au(s)}$

12.19 For each reaction that is spontaneous under standard conditions, write a cell diagram, determine the standard cell emf, and calculate $\Delta G°$ for the reaction:
(a) $2\ \text{NO}_3^{-}\text{(aq)} + 8\ \text{H}^{+}\text{(aq)} + 6\ \text{Hg(l)} \rightarrow$
$3\ \text{Hg}_2^{2+}\text{(aq)} + 2\ \text{NO(g)} + 4\ \text{H}_2\text{O(l)}$
(b) $2\ \text{Hg}^{2+}\text{(aq)} + 2\ \text{Br}^{-}\text{(aq)} \rightarrow \text{Hg}_2^{2+}\text{(aq)} + \text{Br}_2\text{(l)}$
(c) $\text{Cr}_2\text{O}_7^{2-}\text{(aq)} + 14\ \text{H}^{+}\text{(aq)} + 6\ \text{Pu}^{3+}\text{(aq)} \rightarrow$
$6\ \text{Pu}^{4+}\text{(aq)} + 2\ \text{Cr}^{3+}\text{(aq)} + 7\ \text{H}_2\text{O(l)}$

12.20 Predict the standard cell emf and calculate the standard reaction Gibbs free energy for galvanic cells having the following cell reactions:
(a) $3\ \text{Zn(s)} + 2\ \text{Bi}^{3+}\text{(aq)} \rightarrow 3\ \text{Zn}^{2+}\text{(aq)} + 2\ \text{Bi(s)}$
(b) $2\ \text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\ \text{H}_2\text{O(l)}$ in acidic solution
(c) $2\ \text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\ \text{H}_2\text{O(l)}$ in basic solution
(d) $3\ \text{Au}^{+}\text{(aq)} \rightarrow 2\ \text{Au(s)} + \text{Au}^{3+}\text{(aq)}$

12.21 A student was given a standard $\text{Cu(s)}|\text{Cu}^{2+}\text{(aq)}$ half-cell and another half-cell containing an unknown metal M immersed in 1.00 M $\text{M(NO}_3)_2\text{(aq)}$. When the copper was connected as the anode at 25°C, the cell emf was found to be -0.689 V. What is the reduction potential for the unknown M^{2+}/M couple?

12.22 A student was given a standard $\text{Fe(s)}|\text{Fe}^{2+}\text{(aq)}$ half-cell and another half-cell containing an unknown metal M immersed in 1.00 M $\text{MNO}_3\text{(aq)}$. When these two half-cells were connected at 25°C, the complete cell functioned as a galvanic cell with $E = +1.24$ V. The reaction was allowed to continue overnight and the two electrodes were weighed. The iron electrode was found to be lighter and the unknown metal electrode was heavier. What is the standard potential of the unknown M^{+}/M couple?

12.23 Arrange the following metals in order of increasing strength as reducing agents for species in aqueous solution: (a) Cu, Zn, Cr, Fe; (b) Li, Na, K, Mg; (c) U, V, Ti, Al; (d) Ni, Sn, Au, Ag.

12.24 Arrange the following species in order of increasing strength as oxidizing agents for species in aqueous solution: (a) Co^{2+}, Cl_2, Ce^{4+}, In^{3+}; (b) NO_3^-, ClO_4^-, HBrO, $Cr_2O_7^{2-}$, all in acidic solution; (c) O_2, O_3, HClO, and HBrO, all in acidic solution; (d) O_2, O_3, ClO^-, BrO^-, all in basic solution.

12.25 Suppose that each of the following pairs of redox couples are joined to form a galvanic cell that generates a current under standard conditions. Identify the oxidizing agent and the reducing agent, write a cell diagram, and calculate the standard cell emf. (a) Co^{2+}/Co and Ti^{3+}/Ti^{2+}; (b) La^{3+}/La and U^{3+}/U; (c) H^+/H_2 and Fe^{3+}/Fe^{2+}; (d) $O_3/O_2,OH^-$ and Ag^+/Ag.

12.26 Suppose that each of the following pairs of redox couples are joined to form a galvanic cell that generates a current under standard conditions. Identify the oxidizing agent and the reducing agent, write a cell diagram, and calculate the standard cell emf. (a) Pt^{2+}/Pt and $AgF/Ag,F^-$, (b) Cr^{3+}/Cr^{2+} and I_3^-/I^-; (c) H^+/H_2 and Ni^{2+}/Ni; (d) $O_3/O_2,OH^-$ and $O_3,H^+/O_2$.

12.27 Identify the reactions with $K > 1$ in the following list and, for each such reaction, identify the oxidizing agent and calculate the standard cell emf.

(a) $Cl_2(g) + 2\,Br^-(aq) \rightarrow 2\,Cl^-(aq) + Br_2(l)$

(b) $MnO_4^-(aq) + 8\,H^+(aq) + 5\,Ce^{3+}(aq) \rightarrow 5\,Ce^{4+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l)$

(c) $2\,Pb^{2+}(aq) \rightarrow Pb(s) + Pb^{4+}(aq)$

(d) $2\,NO_3^-(aq) + 4\,H^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2\,NO_2(g) + 2\,H_2O(l)$

12.28 Identify the reactions with $K > 1$ among the following reactions and, for each such reaction, write balanced reduction and oxidation half-reactions. For those reactions, show that $K > 1$ by calculating the standard Gibbs free energy of the reaction. Use the smallest whole-number coefficients to balance the equations.

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

(b) $Al(s) + Pb^{2+}(aq) \rightarrow ?$

(c) $Hg_2^{2+}(aq) + Ce^{3+}(aq) \rightarrow ?$

(d) $Zn(s) + Sn^{2+}(aq) \rightarrow ?$

(e) $O_2(g) + H^+(aq) + Hg(l) \rightarrow ?$

12.29 (a) Using data available in Appendix 2B, write the disproportionation reaction for $Au^+(aq)$. (b) From the appropriate standard potentials, determine whether Au^+ will disproportionate spontaneously in aqueous solution under standard conditions.

12.30 (a) Using data available in Appendix 2B, write the disproportionation reaction for Sn^{2+}. (b) From the appropriate standard potentials, determine whether Sn^{2+} will spontaneously disproportionate in aqueous solution under standard conditions.

12.31 Using data available in Appendix 2B, calculate the standard potential for the half-reaction $U^{4+}(aq) + 4\,e^- \rightarrow U(s)$.

12.32 Using data available in Appendix 2B, calculate the standard potential for the half-reaction $Ti^{3+}(aq) + 3\,e^- \rightarrow Ti(s)$.

12.33 Determine the equilibrium constants for the following reactions:

(a) $Mn(s) + Ti^{2+}(aq) \rightleftharpoons Mn^{2+}(aq) + Ti(s)$

(b) $In^{3+}(aq) + U^{3+}(aq) \rightleftharpoons In^{2+}(aq) + U^{4+}(aq)$

12.34 Determine the equilibrium constants for the following reactions:

(a) $2\,Fe^{3+}(aq) + H_2(g) \rightleftharpoons 2\,Fe^{2+}(aq) + 2\,H^+(aq)$

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

12.35 Calculate the reaction quotient, *Q*, for the cell reaction, given the measured values of the cell emf. Balance the chemical equations by using the smallest whole-number coefficients.

(a) $Pt(s)|Sn^{4+}(aq),Sn^{2+}(aq)\|Pb^{4+}(aq),Pb^{2+}(aq)|C(gr)$, $E = +1.33$ V.

(b) $Pt(s)|O_2(g)|H^+(aq)\|Cr_2O_7^{2-}(aq),H^+(aq),Cr^{3+}(aq)|Pt(s)$, $E = +0.10$ V.

12.36 Calculate the reaction quotient, *Q*, for the cell reaction, given the measured values of the cell emf. Balance the chemical equations by using the smallest whole-number coefficients.

(a) $Ag(s)|Ag^+(aq)\|ClO_4^-(aq),H^+(aq),ClO_3^-(aq)|Pt(s)$, $E = +0.40$ V.

(b) $C(gr)|Cl_2(g)|Cl^-(aq)\|Au^{3+}(aq)|Au(s)$, $E = 0.00$ V.

12.37 Calculate *E* for each of the following concentration cells:

(a) $Cu(s)|Cu^{2+}(aq, 0.0010\ mol{\cdot}L^{-1})\|Cu^{2+}(aq, 0.010\ mol{\cdot}L^{-1})|Cu(s)$

(b) $Pt(s)|H_2(g, 1\ bar)|H^+(aq, pH = 4.0)\|H^+(aq, pH = 3.0)|H_2(g, 1\ bar)|Pt(s)$

12.38 Determine the unknown concentration of the ion in each of the following cells:

(a) $Pb(s)|Pb^{2+}(aq, ?)\|Pb^{2+}(aq, 0.10\ mol{\cdot}L^{-1})|Pb(s)$, $E = +0.050$ V.

(b) $Pt(s)|Fe^{3+}(aq, 0.10\ mol{\cdot}L^{-1}),Fe^{2+}(aq, 1.0\ mol{\cdot}L^{-1})\|Fe^{3+}(aq, ?),Fe^{2+}(aq, 0.0010\ mol{\cdot}L^{-1})|Pt(s)$, $E = +0.10$ V.

12.39 Determine the emf of each of the following cells:

(a) $Pt(s)|H_2(g, 1.0\ bar)|HCl(aq, 0.075\ \text{M})\|HCl(aq, 1.0\ mol{\cdot}L^{-1})|H_2(g, 1.0\ bar)|Pt(s)$

(b) $Zn(s)|Zn^{2+}(aq, 0.37\ mol{\cdot}L^{-1})\|Ni^{2+}(aq, 0.059\ mol{\cdot}L^{-1})|Ni(s)$

(c) $Pt(s)|Cl_2(g, 250\ Torr)|HCl(aq, 1.0\ \text{M})\|HCl(aq, 0.85\ \text{M})|H_2(g, 125\ Torr)|Pt(s)$

(d) $Sn(s)|Sn^{2+}(aq, 0.277\ mol{\cdot}L^{-1})\|Sn^{4+}(aq, 0.867\ mol{\cdot}L^{-1}),Sn^{2+}(aq, 0.55\ mol{\cdot}L^{-1})|Pt(s)$

12.40 Determine the emf of each of the following cells:

(a) $Cr(s)|Cr^{3+}(aq, 0.37\ mol{\cdot}L^{-1})\|Pb^{2+}(aq, 9.5 \times 10^{-3}\ mol{\cdot}L^{-1})|Pb(s)$

(b) $Pt(s)|H_2(g, 2.0\ bar)|H^+(pH = 3.5)\|Cl^-(aq, 0.75\ mol{\cdot}L^{-1})|Hg_2Cl_2(s)|Hg(l)$

(c) $C(gr)|Sn^{4+}(aq, 0.059\ mol{\cdot}L^{-1}),Sn^{2+}(aq, 0.059\ mol{\cdot}L^{-1})\|Fe^{3+}(aq, 0.15\ mol{\cdot}L^{-1}),Fe^{2+}(aq, 0.15\ mol{\cdot}L^{-1})|Pt(s)$

(d) $Ag(s)|AgI(s)|I^-(aq, 0.025\ mol{\cdot}L^{-1})\|Cl^-(aq, 0.67\ mol{\cdot}L^{-1})|AgCl(s)|Ag(s)$

12.41 Determine the unknown quantity in each of the following cells:

(a) $Pt(s)|H_2(g, 1.0\ bar)|H^+(pH = ?)\|Cl^-(aq, 1.0\ mol{\cdot}L^{-1})|Hg_2Cl_2(s)|Hg(l)$, $E = +0.33$ V.

(b) $C(gr)|Cl_2(g, 1.0\ bar)|Cl^-; (aq, ?)\|MnO_4^-(aq, 0.010\ mol{\cdot}L^{-1}),H^+(pH = 4.0),Mn^{2+}(aq, 0.10\ mol{\cdot}L^{-1})|Pt(s)$, $E = -0.30$ V.

12.42 Determine the unknown quantity in each of the following cells:
(a) Pt(s)|H_2(g, 1.0 bar)|H^+(pH = ?)‖Cl^-(aq, 1.0 mol·L^{-1})|AgCl(s)|Ag(s), $E = +0.30$ V.
(b) Pb(s)|Pb^{2+}(aq, ?)‖Ni^{2+}(aq, 0.10 mol·L^{-1})|Ni(s), $E = +0.040$ V.

12.43 A tin electrode in 0.015 M $Sn(NO_3)_2$(aq) is connected to a hydrogen electrode in which the pressure of H_2 is 1.0 bar. If the cell potential is 0.061 V at 25°C, what is the pH of the electrolyte at the hydrogen electrode?

12.44 A lead electrode in 0.010 M $Pb(NO_3)_2$(aq) is connected to a hydrogen electrode in which the pressure of H_2 is 1.0 bar. If the cell potential is 0.057 V at 25°C, what is the pH of the electrolyte at the hydrogen electrode?

12.45 (a) Using data from Appendix 2B, calculate the solubility product of Hg_2Cl_2. (b) Compare this number with the value listed in Table 11.4 and comment on the difference.

12.46 (a) The standard potential of the reduction of Ag_2CrO_4 to Ag(s) and chromate ions is +0.446 V. Write the balanced half-reaction for the reduction of silver chromate. (b) Using the data from part (a) and Appendix 2B, calculate the solubility product of Ag_2CrO_4(s).

12.47 Consider the cell Ag(s)|Ag^+(aq, 5.0 mmol·L^{-1})‖Ag^+(aq, 0.15 mol·L^{-1})|Ag(s). Can this cell do work? If so, what is the maximum work that it can perform (per mole of Ag)?

12.48 Consider the cell Ag(s)|Ag^+(aq, 2.1×10^{-4} mol·L^{-1})‖Pb^{2+}(aq, 0.10 mol·L^{-1})|Pb(s). (a) Can this cell do work? If so, what is the maximum work that it can perform (per mole of Pb)? (b) What is the value of ΔH for the cell reaction and what is the sign of ΔS?

12.49 Suppose the reference electrode for Table 12.1 were the standard calomel electrode, Hg_2Cl_2/Hg,Cl^-($[Cl^-]$ = 1.00 mol·L^{-1}) with its $E°$ set equal to 0. Under this system, what would be the potential for (a) the standard hydrogen electrode; (b) the standard Cu^{2+}/Cu redox couple?

12.50 Consider the question posed in Exercise 12.49 except that a saturated calomel electrode (the solution is saturated with KCl instead of having $[Cl^-]$ = 1.00 mol·L^{-1}) is used in place of the standard calomel electrode. How will this replacement change the answers given in Exercise 12.49? The solubility of KCl is 35 g/(100 mL H_2O).

Electrolysis

For the exercises in this section, base your answers on the potentials listed in Table 12.1 or Appendix 2B, with the exception of the reduction and oxidation of water at pH = 7:

$$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq) \qquad E = -0.42 \text{ V at pH} = 7$$

$$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l) \qquad E = +0.82 \text{ V at pH} = 7$$

Ignore other factors such as passivation and overpotential.

12.51 A 1.0 M $NiSO_4$(aq) solution was electrolyzed by using inert electrodes. Write (a) the cathode reaction; (b) the anode reaction. (c) With no overpotential or passivity at the electrodes, what is the minimum potential that must be supplied to the cell for the onset of electrolysis?

12.52 A 1.0 M KBr(aq) solution was electrolyzed by using inert electrodes. Write (a) the cathode reaction; (b) the anode reaction. (c) With no overpotential or passivity at the electrodes, what is the minimum potential that must be supplied to the cell for the onset of electrolysis?

12.53 Aqueous solutions of (a) Mn^{2+}; (b) Al^{3+}; (c) Ni^{2+}; (d) Au^{3+} with concentrations of 1.0 mol·L^{-1} are electrolyzed at pH = 7. Determine whether the metal ion or water will be reduced at the cathode.

12.54 The anode of an electrolytic cell was constructed from (a) Cr; (b) Pt; (c) Cu; (d) Ni. Determine whether oxidation of the electrode or of water will take place at the anode when the electrolyte consists of a 1.0 M solution of the oxidized metal ions at pH = 7.

12.55 A total charge of 4.5 kC is passed through an electrolytic cell. Determine the quantity of substance produced in each case: (a) the mass (in grams) of bismuth metal from a bismuth nitrate solution; (b) the volume (in liters at 273 K and 1.00 atm) of hydrogen gas from a sulfuric acid solution; (c) the mass of cobalt (in grams) from a cobalt(III) chloride solution.

12.56 A total charge of 96.5 kC is passed through an electrolytic cell. Determine the quantity of substance produced in each case: (a) the mass (in grams) of silver metal from a silver nitrate solution; (b) the volume (in liters at 273 K and 1.00 atm) of chlorine gas from a brine solution (concentrated aqueous sodium chloride solution); (c) the mass of copper (in grams) from a copper(II) chloride solution.

12.57 (a) How much time is required to electroplate 1.50 g of silver from a silver nitrate solution by using a current of 13.6 mA? (b) When the same current is used for the same length of time, what mass of copper can be electroplated from a copper(II) sulfate solution?

12.58 (a) When a current of 324 mA is used for 7.0 h, what volume (measured in liters at 298 K and 1.0 atm) of fluorine gas can be produced from a molten mixture of potassium and hydrogen fluorides? (b) With the same current and time period, how many liters of oxygen gas at 298 K and 1.0 atm can be produced from the electrolysis of water?

12.59 (a) What current is required to produce 2.5 g of chromium metal from chromium(VI) oxide in 12 h? (b) What current is required to produce 2.5 g of sodium metal from molten sodium chloride in the same period?

12.60 What current is required to electroplate 6.66 μg of gold in 30.0 min from a gold(III) chloride aqueous solution? (b) How much time is required to electroplate 6.66 μg of chromium from a potassium dichromate solution, by using a current of 100 mA?

12.61 When a ruthenium chloride solution was electrolyzed for 500 s with a 120-mA current, 31.0 mg of ruthenium was deposited. What is the oxidation number of ruthenium in the ruthenium chloride?

12.62 A 4.9-g sample of manganese was produced from a manganese nitrate aqueous solution when a current of 350 mA was passed for 13.7 h. What is the oxidation number of manganese in the manganese nitrate?

12.63 A current of 15.0 A electroplated 50.0 g of hafnium metal from an aqueous solution in 2.00 h. What is the oxidation number of hafnium in the solution?

12.64 A mass loss of 12.57 g occurred in 6.00 h at a titanium anode when a current of 4.70 A was used in an electrolytic cell. What is the oxidation number of the titanium in solution?

12.65 A metal forms the salt MCl_3. Electrolysis of the molten salt with a current of 0.700 A for 6.63 h produced 3.00 g of the metal. What is the molar mass of the metal?

12.66 Thomas Edison was faced with the problem of measuring the electricity that each of his customers had used. His first solution was to use a zinc "coulometer," an electrolytic cell in which the quantity of electricity is determined by measuring the mass of zinc deposited. Only some of the current used by the customer passed through the coulometer. (a) What mass of zinc would be deposited in 1 month (of 31 days) if 1.0 mA of current passed through the cell continuously? (b) An alternative solution to this problem is to collect the hydrogen produced by electrolysis and measure its volume. What volume would be collected at 298 K and 1.00 bar under the same conditions? (c) Which method would be more practical?

Impact on Materials

For Exercises 12.67–12.70, refer to Box 12.1.

12.67 The "aluminum–air fuel cell" is used as a reserve battery in remote locations. In this cell aluminum reacts with the oxygen in air in basic solution. (a) Write the oxidation and reduction half-reactions for this cell. (b) Calculate the standard cell potential. See Box 12.1.

12.68 A fuel cell in which hydrogen reacts with nitrogen instead of oxygen is proposed. (a) Write the chemical equation for the reaction in water, which produces aqueous ammonia. (b) What would be the maximum free energy output of the cell for the consumption of 28.0 kg nitrogen? (c) Is this type of fuel cell thermodynamically feasible? See Box 12.1.

12.69 The body functions as a kind of fuel cell that uses oxygen from the air to oxidize glucose:

$$C_6H_{12}O_6(aq) + 6\ O_2(g) \longrightarrow 6\ CO_2(g) + 6\ H_2O(l)$$

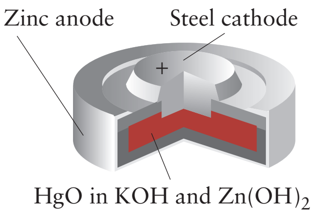
During normal activity, a person uses the equivalent of about 10 MJ of energy a day. Assume that this value represents ΔG, and estimate the average current through your body in the course of a day, assuming that all the energy that we use arises from the reduction of O_2 in the glucose oxidation reaction. See Box 12.1.

12.70 A photoelectrochemical cell is an electrochemical cell that uses light to carry out a chemical reaction. This type of cell is being considered for the production of hydrogen from water. The silicon electrodes in a photoelectrochemical cell react with water:

$$SiO_2(s) + 4\ H^+(aq) + 4\ e^- \longrightarrow Si(s) + 2\ H_2O(l) \qquad E° = -0.84\ V$$

Calculate the standard cell potential for the reaction between silicon and water in a cell that also produces hydrogen from water and write the balanced equation for the cell reaction. See Box 12.1.

12.71 What is (a) the electrolyte and (b) the oxidizing agent in the mercury cell shown here? (c) Write the overall cell reaction for a mercury cell.



12.72 What is (a) the electrolyte and (b) the oxidizing agent during discharge in a lead–acid battery? (c) Write the reaction that takes place at the cathode during the charging of the lead–acid battery.

12.73 Explain how a dry cell generates electricity.

12.74 The density of the electrolyte in a lead–acid battery is measured to assess its state of charge. Explain how the density indicates the state of charge of the battery.

12.75 (a) What is the electrolyte in a nickel–cadmium cell? (b) Write the reaction that takes place at the anode when the cell is being charged.

12.76 (a) Why are lead–antimony grids used as electrodes in the lead–acid battery rather than smooth plates? (b) What is the reducing agent in the lead–acid battery? (c) The lead–acid cell potential is about 2 V. How, then, does a car battery produce 12 V for its electrical system?

12.77 A chromium-plated steel bicycle handlebar is scratched. Will rusting of the iron in the steel be encouraged or retarded by the chromium?

12.78 A solution is prepared by dissolving 1 mol each of $Cu(NO_3)_2$, $Ni(NO_3)_2$, and $AgNO_3$ in 1.0 L of water. Using only data from Appendix 2B, identify the metals (if any) that when added to these solutions (a) will leave the Ni^{2+} ions unaffected but will cause Cu and Ag to plate out of solution; (b) will leave the Ni^{2+} and Cu^{2+} ions in solution but will cause Ag to plate out of solution; (c) will leave all three metals ions in solution; (d) will leave Ni^{2+} and Ag^+ ions in solution but will cause Cu to plate out of solution.

12.79 Suppose that 2.69 g of a silver salt (AgX) is dissolved in 550 mL of water. With a current of 3.5 A, 395.0 s was needed to plate out all the silver. (a) What is the mass percentage of silver in the salt? (b) What is the formula of the salt?

12.80 Three electrolytic cells containing solutions of $CuNO_3$, $Sn(NO_3)_2$, and $Fe(NO_3)_3$, respectively, are connected in series. A current of 3.5 A is passed through the cells until 3.05 g of copper has been deposited in the first cell. (a) What masses of tin and iron are deposited? (b) For how long did the current flow?

12.81 (a) What is the approximate chemical formula of rust? (b) What is the oxidizing agent in the formation of rust? (c) How does the presence of salt accelerate the rusting process?

12.82 (a) What is the electrolyte solution in the formation of rust? (b) How are steel (iron) objects protected by galvanizing and by sacrificial anodes? (c) Suggest two metals that could be used in place of zinc for galvanizing iron.

12.83 (a) Suggest two metals that could be used for the cathodic protection of a titanium pipeline. (b) What factors other than relative positions in the electrochemical series need to be considered in practice? (c) Often copper piping is connected to iron pipes in household plumbing systems. What is a possible effect of the copper on the iron pipes?

12.84 (a) Can aluminum be used for the cathodic protection of a steel underground storage container? (b) Which of the metals zinc, silver, copper, and magnesium cannot be used as a sacrificial anode in the protection of a buried iron pipeline? Explain your answer. (c) What is the electrolyte solution for the cathodic protection of an underground pipeline by a sacrificial anode?

Integrated Exercises

12.85 Volta discovered that when he used different metals in his "pile" some combinations had a stronger effect than others. From that information he constructed an electromotive series. How would Volta have ordered the following metals, if he put the most strongly reducing metal first: Fe, Ag, Au, Zn, Cu, Ni, Co, Al?

12.86 One stage in the extraction of gold from rocks involves dissolving the metal from the rock with a basic solution of sodium cyanide that has been thoroughly aerated. This stage results in the formation of soluble $Au(CN)_2^-$ ions. The next stage is to reduce gold to the metal by the addition of zinc dust, forming $Zn(CN)_4^{2-}$. Write the balanced equations for the half-reactions and the overall redox equation for both stages.

12.87 A galvanic cell has the following cell reaction: $M(s) + 2\,Zn^{2+}(aq) \rightarrow 2\,Zn(s) + M^{4+}(aq)$. The standard emf of the cell is +0.16 V. What is the standard potential of the M^{4+}/M redox couple?

12.88 Using data in Appendix 2B, calculate the standard potential for the half-reaction $Ti^{4+}(aq) + 4\,e^- \rightarrow Ti(s)$.

12.89 K_{sp} for $Cu(IO_3)_2$ is 1.4×10^{-7}. Using this value and data available in Appendix 2B, calculate $E°$ for the half-reaction $Cu(IO_3)_2(s) + 2\,e^- \rightarrow Cu(s) + 2\,IO_3^-(aq)$.

12.90 K_{sp} for $Ni(OH)_2$ is 6.5×10^{-18}. Using this value and data from Appendix 2B, calculate $E°$ for the half-reaction $Ni(OH)_2(s) + 2\,e^- \rightarrow Ni(s) + 2\,OH^-(aq)$.

12.91 A voltaic cell functions only when the electrical circuit is complete. In the external circuit the current is carried by the flow of electrons through a metal wire. Explain how the current is carried through the cell itself.

12.92 A technical handbook contains tables of thermodynamic quantities for common reactions. If you want to know whether a certain cell reaction has a positive standard emf, which of the following properties would give you that information directly (on inspection)? Which would not? Explain. (a) $\Delta G°$; (b) $\Delta H°$; (c) $\Delta S°$; (d) $\Delta U°$; (e) K.

12.93 Answer the following questions and, for each "yes" response, write a balanced cell reaction and calculate the standard cell emf. (a) Can the oxygen present in air oxidize silver metal in acidic solution? (b) Can the oxygen in air oxidize silver metal in basic solution?

12.94 What is the standard potential for the reduction of oxygen to water in (a) an acidic solution? (b) a basic solution? (c) Is MnO_4^- more stable in an acidic or a basic aerated solution (a solution saturated with oxygen gas at 1 atm)? Explain your conclusion.

12.95 (a) If you were to construct a concentration cell in which one half-cell contains 1.0 M $CrCl_3$ and the other half-cell 0.0010 M $CrCl_3$, and both electrodes were chromium, at which electrode would reduction spontaneously take place? How will each of the following changes affect the cell potential? Justify your answers. (b) Adding 100 mL pure water to the anode compartment. (c) Adding 100 mL 1.0 M NaOH(aq) to the cathode compartment ($Cr(OH)_3$ is insoluble). (d) Increasing the mass of the chromium electrode in the anode compartment.

12.96 Dental amalgam, a solid solution of silver and tin in mercury, is used for filling tooth cavities. Two of the reduction half-reactions that the filling can undergo are

$$3\,Hg_2^{2+}(aq) + 4\,Ag(s) + 6\,e^- \longrightarrow 2\,Ag_2Hg_3(s) \qquad E° = +0.85\text{ V}$$

$$Sn^{2+}(aq) + 3\,Ag(s) + 2\,e^- \longrightarrow Ag_3Sn(s) \qquad E° = -0.05\text{ V}$$

Suggest a reason why, when you accidentally bite on a piece of aluminum foil with a tooth containing a silver filling, you may feel pain. Write a balanced chemical equation to support your suggestion.

12.97 Suppose that 25.0 mL of a solution of Ag^+ ions of unknown concentration is titrated with 0.015 M KI(aq) at 25°C. A silver electrode is immersed in this solution, and its potential is measured relative to a standard hydrogen electrode. A total of 16.7 mL of KI(aq) was required to reach the stoichiometric point, when the potential was 0.325 V. (a) What is the molar concentration of Ag^+ in the solution? (b) Determine K_{sp} for AgI from these data.

12.98 Suppose that 35.0 mL of 0.012 M $Cu^+(aq)$ is titrated with 0.010 M KBr(aq) at 25°C. A copper electrode is immersed in this solution, and its potential is measured relative to a standard hydrogen electrode. What volume of the KBr solution must be added to reach the stoichiometric point and what will the potential be at that point? $K_{sp}(CuBr) = 5.2 \times 10^{-9}$.

12.99 Use the data in Appendix 2B and the fact that, for the half-reaction $F_2(g) + 2\,H^+(aq) + 2\,e^- \rightarrow 2\,HF(aq)$, $E° = +3.03$ V, to calculate the value of K_a for HF.

12.100 The following items are obtained from the stockroom for the construction of a galvanic cell: two 250-mL beakers and a salt bridge, a voltmeter with attached wires and clips, 200 mL of 0.0080 M $CrCl_3(aq)$, 200 mL of 0.12 M $CuSO_4(aq)$, a piece of copper wire, and a chrome-plated piece of metal. (a) Describe the construction of the galvanic cell. (b) Write the reduction half-reactions. (c) Write the overall cell reaction. (d) Write the cell diagram for the galvanic cell. (e) What is the expected cell emf?

12.101 (a) Considering the dependence of the Gibbs free energy of reaction on emf and on temperature, derive an equation for the temperature dependence of $E°$. (b) Use your equation to predict the standard emf for the formation of water from hydrogen and oxygen in a fuel cell at 80°C. Assume that $\Delta H°$ and $\Delta S°$ are independent of Temperature.

12.102 The standard cell potential ($E°$) for the reaction below is +0.63 V. What is the cell potential for this reaction at 275 K when $[Zn^{2+}] = 2.0 \times 10^{-4}\ mol \cdot L^{-1}$ and $[Pb^{2+}] = 1.0\ mol \cdot L^{-1}$? (See Exercise 12.101.)

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

12.103 In a neuron (a nerve cell), the concentration of K^+ ions inside the cell is about 20 to 30 times as great as that outside. What potential difference between the inside and the outside of the cell would you expect to measure if the difference is due only to the imbalance of potassium ions?

12.104 (a) The emf of the cell $Zn(s)|Zn^{2+}(aq, ?)\|Pb^{2+}(aq, 0.10\ mol \cdot L^{-1})|Pb(s)$ is +0.661 V. What is the molarity of Zn^{2+} ions? (b) Write an equation that gives the Zn^{2+} ion concentration as a function of emf, assuming that all other aspects of the cell remain constant.

12.105 Calculate the standard emf and the actual emf of the galvanic cell $Pt(s)|Fe^{3+}(aq, 0.20\ mol \cdot L^{-1}), Fe^{2+}(aq, 0.0010\ mol \cdot L^{-1})\|Ag^{+}(aq, 0.020\ mol \cdot L^{-1})|Ag(s)$. Explain the difference in values.

12.106 Electrochemistry is one of the main methods used to determine equilibrium constants that are either very large or very small. To measure the equilibrium constant for the reaction of $Fe(CN)_6^{4-}$ with $Na_2Cr_2O_7$, the following cell was built:

$$Pt|Fe(CN)_6^{3-}(aq, 0.00010\ mol \cdot L^{-1}), Fe(CN)_6^{4-}(aq, 1.0\ mol \cdot L^{-1}) \| H^{+}(aq, 1.0\ mol \cdot L^{-1}), Cr_2O_7^{2-}(aq, 0.1\ mol \cdot L^{-1}), Cr^{3+}(aq, 0.010\ mol \cdot L^{-1})|Pt \qquad E = 1.18\ V \text{ at } 298\ K$$

Write the cell reaction and determine its equilibrium constant.

12.107 The reduction of ClO_4^- can be conducted in either basic or acidic solutions. The two half-reactions are

$$\text{(1, acidic) } ClO_4^-(aq) + 2\ H^+(aq) + 2\ e^- \longrightarrow ClO_3^-(aq) + H_2O(l) \qquad E° = +1.23\ V$$

$$\text{(2, basic) } ClO_4^-(aq) + H_2O(l) + 2\ e^- \longrightarrow ClO_3^-(aq) + 2\ OH^-(l) \qquad E° = +0.36\ V$$

(a) Show how these processes are related by deriving an expression that gives the pH dependence of the emf for each half-reaction. (b) What is the potential of each reaction in neutral solution?

12.108 Calculate the standard potential of the Cu^+/Cu couple from those of the Cu^{2+}/Cu^+ and Cu^{2+}/Cu couples.

12.109 When a pH meter was standardized with a boric acid–borate buffer with a pH of 9.40, the cell emf was +0.060 V. When the buffer was replaced with a solution of unknown hydronium ion concentration, the cell emf was +0.22 V. What is the pH of the solution?

12.110 Show how a silver–silver chloride electrode (silver in contact with solid AgCl and a solution of Cl^- ions) and a hydrogen electrode can be used to measure (a) pH; (b) pOH.

12.111 What voltage range does a voltmeter need to have in order to measure pH in the range of 1 to 14 at 25°C if the voltage is zero when pH = 7?

12.112 The entropy change of a cell reaction can be determined from the change of the cell potential with temperature. (a) Show that $\Delta S° = nF(E_2° - E_1°)/(T_2 - T_1)$. Assume that $\Delta S°$ and $\Delta H°$ are constant over the temperature range considered. (b) Calculate $\Delta S°$ and $\Delta H°$ for the cell reaction $Hg_2Cl_2(s) + H_2(g) \rightarrow 2\ Hg(l) + 2\ H^+(aq) + 2\ Cl^-(aq)$, given that $E° = +0.2699$ V at 293 K and +0.2669 V at 303 K.

12.113 A silver concentration cell is constructed with the electrolyte at both electrodes being initially 0.10 M AgNO(aq) at 25°C. The electrolyte at one electrode is diluted by a factor of 10 five times and the emf measured each time. (a) Plot the emf of this cell on a graph as a function of $\ln[Ag^+]_{anode}$. (b) Calculate the value of the slope of the line. To what term in the Nernst equation does this value correspond? Is the value you determined from the plot consistent with the value you would calculate from the values in that term? If not consistent, calculate your percentage error. (c) What is the value of the *y*-intercept? To what term in the Nernst equation does this value correspond?

12.114 Consider the electroplating of a metal +1 cation from a solution of unknown concentration according to the half-reaction $M^+(aq) + e^- \rightarrow M(s)$, with a standard potential $E°$. When the half-cell is connected to an appropriate oxidation half-cell and current is passed through it, the M^+ cation begins plating out at E_1. To what value (E_2) must the applied potential be adjusted, relative to E_1, if 99.99% of the metal is to be removed from the solution?

12.115 Using only data given in Appendix 2B, calculate the acidity constant for HBrO.

12.116 The absolute magnitudes of the standard potentials of two metals M and X were determined to be

$$\text{(1) } M^+(aq) + e^- \longrightarrow M(s) \qquad |E°| = 0.25\ V$$

$$\text{(2) } X^{2+}(aq) + 2\ e^- \longrightarrow X(s) \qquad |E°| = 0.65\ V$$

When the two electrodes are connected, current flows from M to X in the external circuit. When the electrode corresponding to half-reaction 1 is connected to the standard hydrogen electrode (SHE), current flows from M to SHE. (a) What are the signs of $E°$ of the two half-reactions? (b) What is the standard cell potential for the cell constructed from these two electrodes?

12.117 An aqueous solution of Na_2SO_4 was electrolyzed for 30.0 min; 25.0 mL of oxygen was collected at the anode over water at 22°C at a total pressure of 722 Torr. Determine the current that was used to produce the gas. See Table 8.3 for the vapor pressure of water.

12.118 A brine solution is electrolyzed by using a current of 2.0 A. How much time is required to collect 20.0 L of chlorine if the gas is collected over water at 20.0°C and the total pressure is 770. Torr? Assume that the water is already saturated with chlorine, and so no more dissolves. See Table 8.3 for the vapor pressure of water.

Chemistry Connections

12.119 Many important biological reactions involve electron transfer. Because the pH of bodily fluids is close to 7, the

"biological standard potential" of an electrode, E^*, is measured at pH = 7.
(a) Calculate the biological standard potential for (i) the reduction of hydrogen ions to hydrogen gas; (ii) the reduction of nitrate ions to NO gas.
(b) Calculate the biological standard potential E^* for the reduction of the biomolecule NAD^+ to NADH in aqueous solution. The reduction half-reaction under thermodynamic standard conditions is $NAD^+(aq) + H^+(aq) + 2\,e^- \rightarrow NADH(aq)$, with $E° = -0.099$ V.
(c) The pyruvate ion, $CH_3C(=O)CO_2{}^-$, is formed during the metabolism of glucose in the body. The ion has a chain of three carbon atoms. The central carbon atom has a double bond to a terminal oxygen atom and one of the end carbon atoms is bonded to two oxygen atoms in a carboxylate group. Draw the Lewis structure of the pyruvate ion and assign a hybridization scheme to each carbon atom.
(d) During exercise the pyruvate ion is converted to lactate ion in the body by coupling to the half reaction for NADH given in part (b). For the half-reaction pyruvate $+ 2\,H^+ + 2\,e^- \rightarrow$ lactate, $E^* = -0.190$ V. Write the cell reaction for the spontaneous reaction that occurs between these two biological couples and calculate E^* and $E°$ for the overall reaction.
(e) Calculate the standard Gibbs free energy of reaction for the overall reaction in part (d).
(f) Calculate the equilibrium constant at 25°C for the overall reaction in part (d).