

Chapter 17

Electrochemistry



Figure 17.1 Electric vehicles are powered by batteries, devices that harness the energy of spontaneous redox reactions. (credit: modification of work by Robert Couse-Baker)

Chapter Outline

- 17.1 Review of Redox Chemistry
- 17.2 Galvanic Cells
- 17.3 Electrode and Cell Potentials
- 17.4 Potential, Free Energy, and Equilibrium
- 17.5 Batteries and Fuel Cells
- 17.6 Corrosion
- 17.7 Electrolysis

Introduction

Another chapter in this text introduced the chemistry of reduction-oxidation (redox) reactions. This important reaction class is defined by changes in oxidation states for one or more reactant elements, and it includes a subset of reactions involving the transfer of electrons between reactant species. Around the turn of the nineteenth century, chemists began exploring ways these electrons could be transferred *indirectly* via an external circuit rather than directly via intimate contact of redox reactants. In the two centuries since, the field of *electrochemistry* has evolved to yield significant insights on the fundamental aspects of redox chemistry as well as a wealth of technologies ranging from industrial-scale metallurgical processes to robust, rechargeable batteries for electric vehicles (**Figure 17.1**). In this chapter, the essential concepts of electrochemistry will be addressed.

17.1 Review of Redox Chemistry

By the end of this section, you will be able to:

- Describe defining traits of redox chemistry
- Identify the oxidant and reductant of a redox reaction
- Balance chemical equations for redox reactions using the half-reaction method

Since reactions involving electron transfer are essential to the topic of electrochemistry, a brief review of redox chemistry is provided here that summarizes and extends the content of an earlier text chapter (see chapter on reaction stoichiometry). Readers wishing additional review are referred to the text chapter on reaction stoichiometry.

Oxidation Numbers

By definition, a redox reaction is one that entails changes in *oxidation number* (or *oxidation state*) for one or more of the elements involved. The oxidation number of an element in a compound is essentially an assessment of how the electronic environment of its atoms is different in comparison to atoms of the pure element. By this description, *the oxidation number of an atom in an element is equal to zero*. For an atom in a compound, *the oxidation number is equal to the charge the atom would have in the compound if the compound were ionic*. Consequential to these rules, *the sum of oxidation numbers for all atoms in a molecule is equal to the charge on the molecule*. To illustrate this formalism, examples from the two compound classes, ionic and covalent, will be considered.

Simple ionic compounds present the simplest examples to illustrate this formalism, since by definition the elements' oxidation numbers are numerically equivalent to ionic charges. Sodium chloride, NaCl, is comprised of Na⁺ cations and Cl[−] anions, and so oxidation numbers for sodium and chlorine are, +1 and −1, respectively. Calcium fluoride, CaF₂, is comprised of Ca²⁺ cations and F[−] anions, and so oxidation numbers for calcium and fluorine are, +2 and −1, respectively.

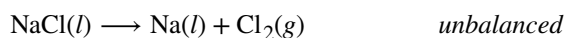
Covalent compounds require a more challenging use of the formalism. Water is a covalent compound whose molecules consist of two H atoms bonded separately to a central O atom via polar covalent O–H bonds. The shared electrons comprising an O–H bond are more strongly attracted to the more electronegative O atom, and so it acquires a partial negative charge in the water molecule (relative to an O atom in elemental oxygen). Consequently, H atoms in a water molecule exhibit partial positive charges compared to H atoms in elemental hydrogen. The sum of the partial negative and partial positive charges for each water molecule is zero, and the water molecule is neutral.

Imagine that the polarization of shared electrons within the O–H bonds of water were 100% complete—the result would be *transfer* of electrons from H to O, and water would be an ionic compound comprised of O^{2−} anions and H⁺ cations. And so, the oxidation numbers for oxygen and hydrogen in water are −2 and +1, respectively. Applying this same logic to carbon tetrachloride, CCl₄, yields oxidation numbers of +4 for carbon and −1 for chlorine. In the nitrate ion, NO₃[−], the oxidation number for nitrogen is +5 and that for oxygen is −2, summing to equal the 1− charge on the molecule:

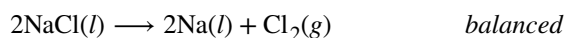
$$(1 \text{ N atom})\left(\frac{+5}{\text{N atom}}\right) + (3 \text{ O atoms})\left(\frac{-2}{\text{O atom}}\right) = +5 + -6 = -1$$

Balancing Redox Equations

The unbalanced equation below describes the decomposition of molten sodium chloride:



This reaction satisfies the criterion for redox classification, since the oxidation number for Na is decreased from +1 to 0 (it undergoes *reduction*) and that for Cl is increased from −1 to 0 (it undergoes *oxidation*). The equation in this case is easily balanced by inspection, requiring stoichiometric coefficients of 2 for the NaCl and Na:



Redox reactions that take place in aqueous solutions are commonly encountered in electrochemistry, and many involve water or its characteristic ions, $\text{H}^+(aq)$ and $\text{OH}^-(aq)$, as reactants or products. In these cases, equations representing the redox reaction can be very challenging to balance by inspection, and the use of a systematic approach called the *half-reaction method* is helpful. This approach involves the following steps:

1. Write skeletal equations for the oxidation and reduction half-reactions.
2. Balance each half-reaction for all elements except H and O.
3. Balance each half-reaction for O by adding H_2O .
4. Balance each half-reaction for H by adding H^+ .
5. Balance each half-reaction for charge by adding electrons.
6. If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.
7. Add the two half-reactions and simplify.
8. If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.

The examples below demonstrate the application of this method to balancing equations for aqueous redox reactions.

Example 17.1

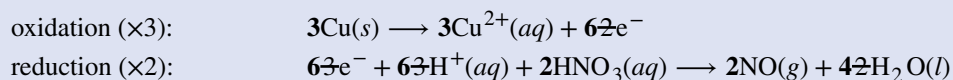
Balancing Equations for Redox Reactions in Acidic Solutions

Write the balanced equation representing reaction between solid copper and nitric acid to yield aqueous copper(II) ions and nitrogen monoxide gas.

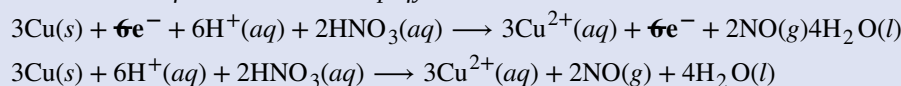
Solution

Following the steps of the half-reaction method:

1. Write skeletal equations for the oxidation and reduction half-reactions.
 oxidation: $\text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq)$
 reduction: $\text{HNO}_3(aq) \longrightarrow \text{NO}(g)$
2. Balance each half-reaction for all elements except H and O.
 oxidation: $\text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq)$
 reduction: $\text{HNO}_3(aq) \longrightarrow \text{NO}(g)$
3. Balance each half-reaction for O by adding H_2O .
 oxidation: $\text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq)$
 reduction: $\text{HNO}_3(aq) \longrightarrow \text{NO}(g) + 2\text{H}_2\text{O}(l)$
4. Balance each half-reaction for H by adding H^+ .
 oxidation: $\text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq)$
 reduction: $3\text{H}^+(aq) + \text{HNO}_3(aq) \longrightarrow \text{NO}(g) + 2\text{H}_2\text{O}(l)$
5. Balance each half-reaction for charge by adding electrons.
 oxidation: $\text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq) + 2\text{e}^-$
 reduction: $3\text{e}^- + 3\text{H}^+(aq) + \text{HNO}_3(aq) \longrightarrow \text{NO}(g) + 2\text{H}_2\text{O}(l)$
6. If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.



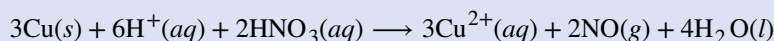
7. Add the two half-reactions and simplify.



8. If the reaction takes place in a basic medium, add OH^{-} ions the equation obtained in step 7 to neutralize the H^{+} ions (add in equal numbers to both sides of the equation) and simplify.

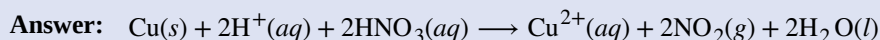
This step not necessary since the solution is stipulated to be acidic.

The balanced equation for the reaction in an acidic solution is then



Check Your Learning

The reaction above results when using relatively diluted nitric acid. If concentrated nitric acid is used, nitrogen dioxide is produced instead of nitrogen monoxide. Write a balanced equation for this reaction.



Example 17.2

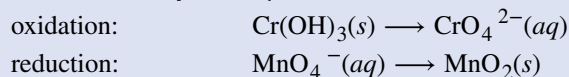
Balancing Equations for Redox Reactions in Basic Solutions

Write the balanced equation representing reaction between aqueous permanganate ion, MnO_4^{-} , and solid chromium(III) hydroxide, $\text{Cr}(\text{OH})_3$, to yield solid manganese(IV) oxide, MnO_2 , and aqueous chromate ion, CrO_4^{2-} . The reaction takes place in a basic solution.

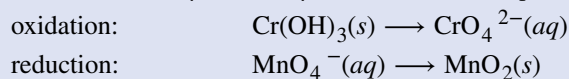
Solution

Following the steps of the half-reaction method:

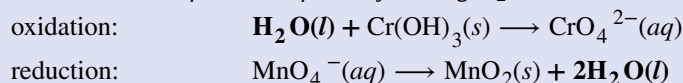
1. Write skeletal equations for the oxidation and reduction half-reactions.



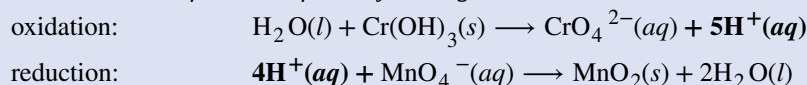
2. Balance each half-reaction for all elements except H and O.



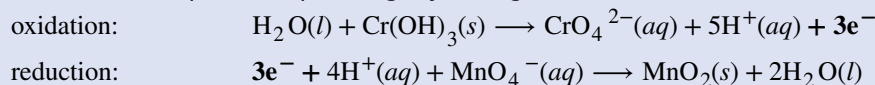
3. Balance each half-reaction for O by adding H_2O .



4. Balance each half-reaction for H by adding H^{+} .



5. Balance each half-reaction for charge by adding electrons.

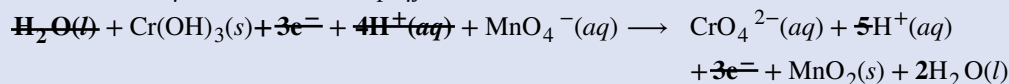


6. If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is

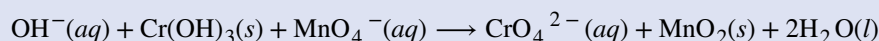
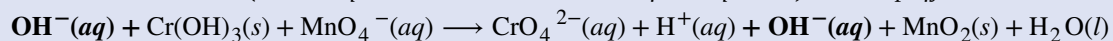
equal to the number produced in the other.

This step is not necessary since the number of electrons is already in balance.

7. Add the two half-reactions and simplify.

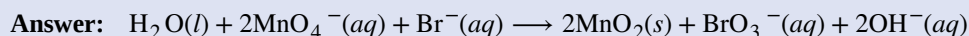


8. If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.



Check Your Learning

Aqueous permanganate ion may also be reduced using aqueous bromide ion, Br^- , the products of this reaction being solid manganese(IV) oxide and aqueous bromate ion, BrO_3^- . Write the balanced equation for this reaction occurring in a basic medium.



17.2 Galvanic Cells

By the end of this section, you will be able to:

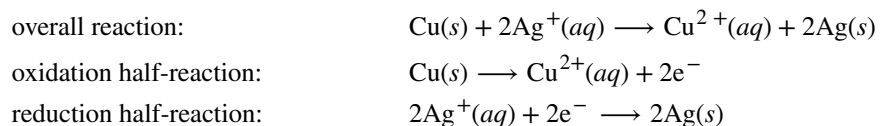
- Describe the function of a galvanic cell and its components
- Use cell notation to symbolize the composition and construction of galvanic cells

As demonstration of spontaneous chemical change, **Figure 17.2** shows the result of immersing a coiled wire of copper into an aqueous solution of silver nitrate. A gradual but visually impressive change spontaneously occurs as the initially colorless solution becomes increasingly blue, and the initially smooth copper wire becomes covered with a porous gray solid.



Figure 17.2 A copper wire and an aqueous solution of silver nitrate (left) are brought into contact (center) and a spontaneous transfer of electrons occurs, creating blue $\text{Cu}^{2+}(aq)$ and gray $\text{Ag}(s)$ (right).

These observations are consistent with (i) the oxidation of elemental copper to yield copper(II) ions, $\text{Cu}^{2+}(aq)$, which impart a blue color to the solution, and (ii) the reduction of silver(I) ions to yield elemental silver, which deposits as a fluffy solid on the copper wire surface. And so, *the direct transfer of electrons from the copper wire to the aqueous silver ions is spontaneous* under the employed conditions. A summary of this redox system is provided by these equations:



Consider the construction of a device that contains all the reactants and products of a redox system like the one here, but prevents physical contact between the reactants. Direct transfer of electrons is, therefore, prevented; transfer, instead, takes place indirectly through an external circuit that contacts the separated reactants. Devices of this sort are generally referred to as *electrochemical cells*, and those in which a spontaneous redox reaction takes place are called **galvanic cells** (or **voltaic cells**).

A galvanic cell based on the spontaneous reaction between copper and silver(I) is depicted in **Figure 17.3**. The cell is comprised of two **half-cells**, each containing the redox conjugate pair (“couple”) of a single reactant. The half-cell shown at the left contains the Cu(0)/Cu(II) couple in the form of a solid copper foil and an aqueous solution of copper nitrate. The right half-cell contains the Ag(I)/Ag(0) couple as solid silver foil and an aqueous silver nitrate solution. An external circuit is connected to each half-cell at its solid foil, meaning the Cu and Ag foil each function as an *electrode*. By definition, the **anode** of an electrochemical cell is the electrode at which oxidation occurs (in this case, the Cu foil) and the **cathode** is the electrode where reduction occurs (the Ag foil). The redox reactions in a galvanic cell occur only at the interface between each half-cell’s reaction mixture and its electrode. To keep the reactants separate while maintaining charge-balance, the two half-cell solutions are connected by a tube filled with inert electrolyte solution called a **salt bridge**. The spontaneous reaction in this cell produces Cu^{2+} cations in the anode half-cell and consumes Ag^+ ions in the cathode half-cell, resulting in a compensatory flow of inert ions from the salt bridge that maintains charge balance. Increasing concentrations of Cu^{2+} in the anode half-cell are balanced by an influx of NO_3^- from the salt bridge, while a flow of Na^+ into the cathode half-cell compensates for the decreasing Ag^+ concentration.

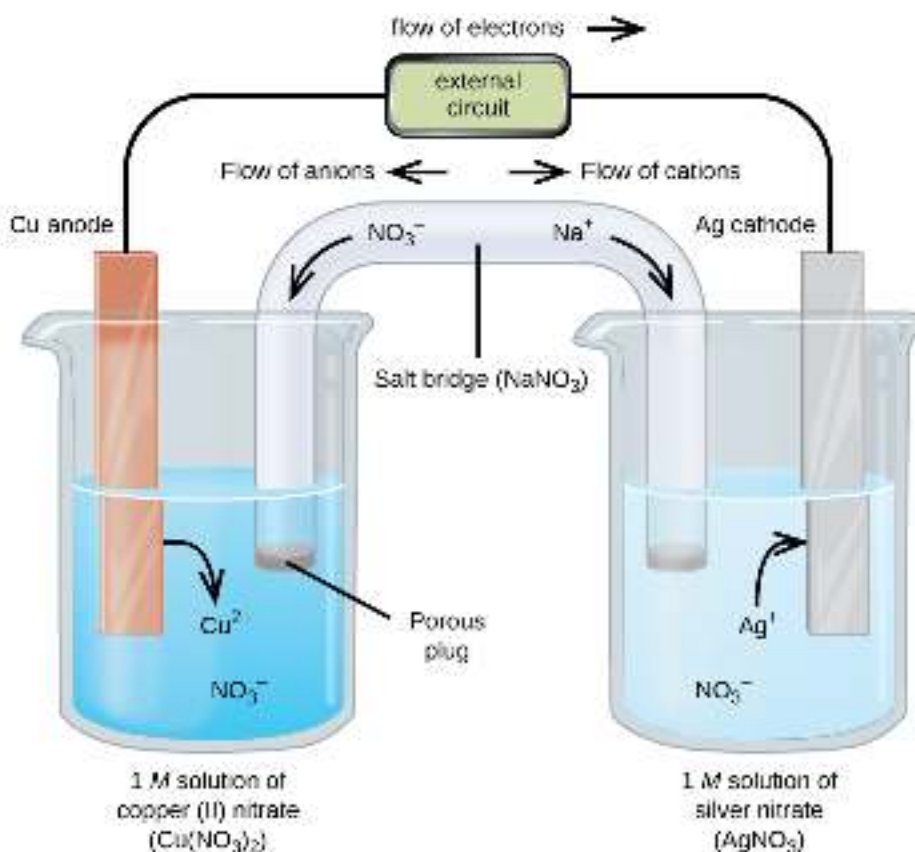


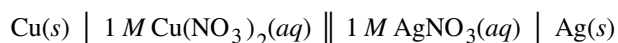
Figure 17.3 A galvanic cell based on the spontaneous reaction between copper and silver(I) ions.

Cell Notation

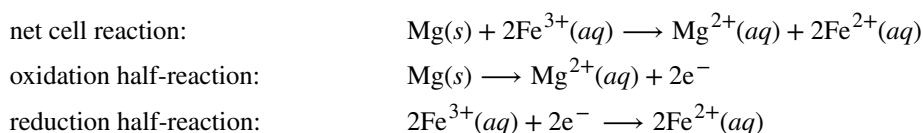
Abbreviated symbolism is commonly used to represent a galvanic cell by providing essential information on its composition and structure. These symbolic representations are called **cell notations** or **cell schematics**, and they are written following a few guidelines:

- The relevant components of each half-cell are represented by their chemical formulas or element symbols
- All interfaces between component phases are represented by vertical parallel lines; if two or more components are present in the same phase, their formulas are separated by commas
- By convention, the schematic begins with the anode and proceeds left-to-right identifying phases and interfaces encountered within the cell, ending with the cathode

A verbal description of the cell as viewed from anode-to-cathode is often a useful first-step in writing its schematic. For example, the galvanic cell shown in **Figure 17.3** consists of a solid copper anode immersed in an aqueous solution of copper(II) nitrate that is connected via a salt bridge to an aqueous silver(I) nitrate solution, immersed in which is a solid silver cathode. Converting this statement to symbolism following the above guidelines results in the cell schematic:



Consider a different galvanic cell (see **Figure 17.4**) based on the spontaneous reaction between solid magnesium and aqueous iron(III) ions:



In this cell, a solid magnesium anode is immersed in an aqueous solution of magnesium chloride that is connected via a salt bridge to an aqueous solution containing a mixture of iron(III) chloride and iron(II) chloride, immersed in which is a platinum cathode. The cell schematic is then written as



Notice the cathode half-cell is different from the others considered thus far in that its electrode is comprised of a substance (Pt) that is neither a reactant nor a product of the cell reaction. This is required when neither member of the half-cell's redox couple can reasonably function as an electrode, which must be electrically conductive and in a phase separate from the half-cell solution. In this case, both members of the redox couple are solute species, and so Pt is used as an **inert electrode** that can simply provide or accept electrons to redox species in solution. Electrodes constructed from a member of the redox couple, such as the Mg anode in this cell, are called **active electrodes**.

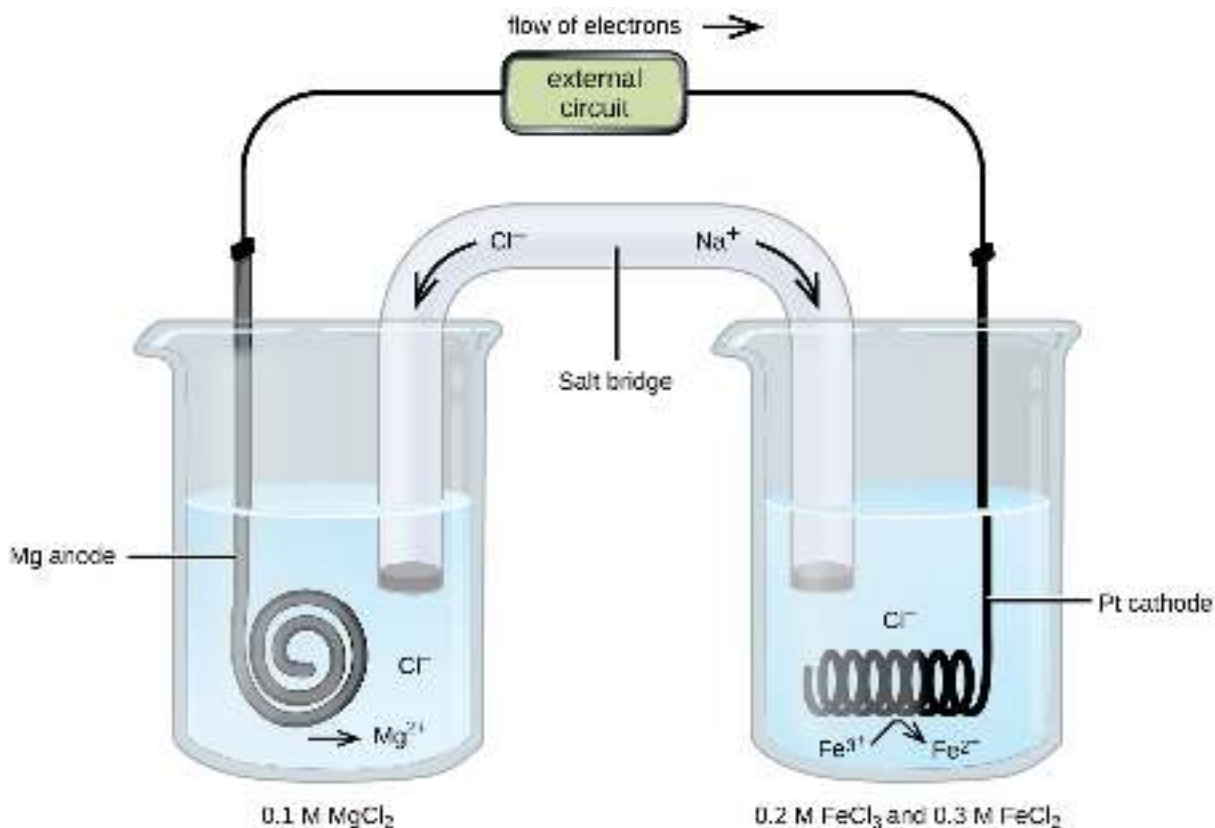


Figure 17.4 A galvanic cell based on the spontaneous reaction between magnesium and iron(III) ions.

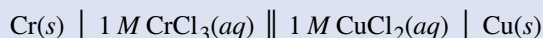
Example 17.3

Writing Galvanic Cell Schematics

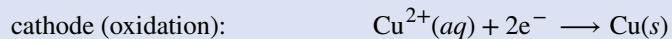
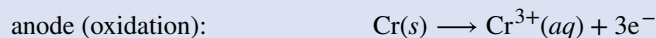
A galvanic cell is fabricated by connecting two half-cells with a salt bridge, one in which a chromium wire is immersed in a 1 M CrCl_3 solution and another in which a copper wire is immersed in 1 M CuCl_2 . Assuming the chromium wire functions as an anode, write the schematic for this cell along with equations for the anode half-reaction, the cathode half-reaction, and the overall cell reaction.

Solution

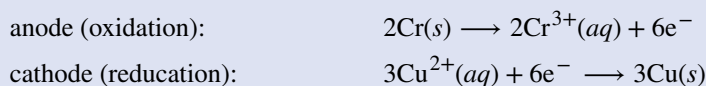
Since the chromium wire is stipulated to be the anode, the schematic begins with it and proceeds left-to-right, symbolizing the other cell components until ending with the copper wire cathode:



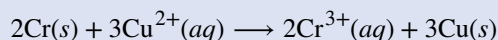
The half-reactions for this cell are



Multiplying to make the number of electrons lost by Cr and gained by Cu^{2+} equal yields

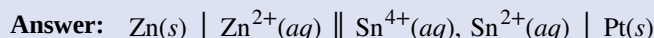
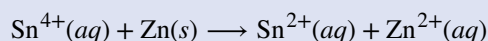


Adding the half-reaction equations and simplifying yields an equation for the cell reaction:



Check Your Learning

Omitting solute concentrations and spectator ion identities, write the schematic for a galvanic cell whose net cell reaction is shown below.



17.3 Electrode and Cell Potentials

By the end of this section, you will be able to:

- Describe and relate the definitions of electrode and cell potentials
- Interpret electrode potentials in terms of relative oxidant and reductant strengths
- Calculate cell potentials and predict redox spontaneity using standard electrode potentials

Unlike the spontaneous oxidation of copper by aqueous silver(I) ions described in section 17.2, immersing a copper wire in an aqueous solution of lead(II) ions yields no reaction. The two species, $\text{Ag}^{+}(aq)$ and $\text{Pb}^{2+}(aq)$, thus show a distinct difference in their redox activity towards copper: the silver ion spontaneously oxidized copper, but the lead ion did not. Electrochemical cells permit this relative redox activity to be quantified by an easily measured property, *potential*. This property is more commonly called *voltage* when referenced in regard to electrical applications, and it is a measure of energy accompanying the transfer of charge. Potentials are measured in the volt unit, defined as one joule of energy per one coulomb of charge, $V = J/C$.

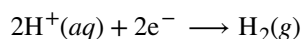
When measured for purposes of electrochemistry, a potential reflects the driving force for a specific type of charge transfer process, namely, the transfer of electrons between redox reactants. Considering the nature of potential in this context, it is clear that the potential of a single half-cell or a single electrode can't be measured; "transfer" of electrons requires both a donor and recipient, in this case a reductant and an oxidant, respectively. Instead, a half-cell potential may only be assessed relative to that of another half-cell. It is only the *difference in potential* between two half-cells that may be measured, and these measured potentials are called **cell potentials**, E_{cell} , defined as

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

where E_{cathode} and E_{anode} are the potentials of two different half-cells functioning as specified in the subscripts. As for other thermodynamic quantities, the **standard cell potential**, E°_{cell} , is a cell potential measured when both half-cells are under standard-state conditions (1 M concentrations, 1 bar pressures, 298 K):

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

To simplify the collection and sharing of potential data for half-reactions, the scientific community has designated one particular half-cell to serve as a universal reference for cell potential measurements, assigning it a potential of exactly 0 V. This half-cell is the **standard hydrogen electrode (SHE)** and it is based on half-reaction below:



A typical SHE contains an inert platinum electrode immersed in precisely 1 M aqueous H^{+} and a stream of bubbling H_2 gas at 1 bar pressure, all maintained at a temperature of 298 K (see **Figure 17.5**).

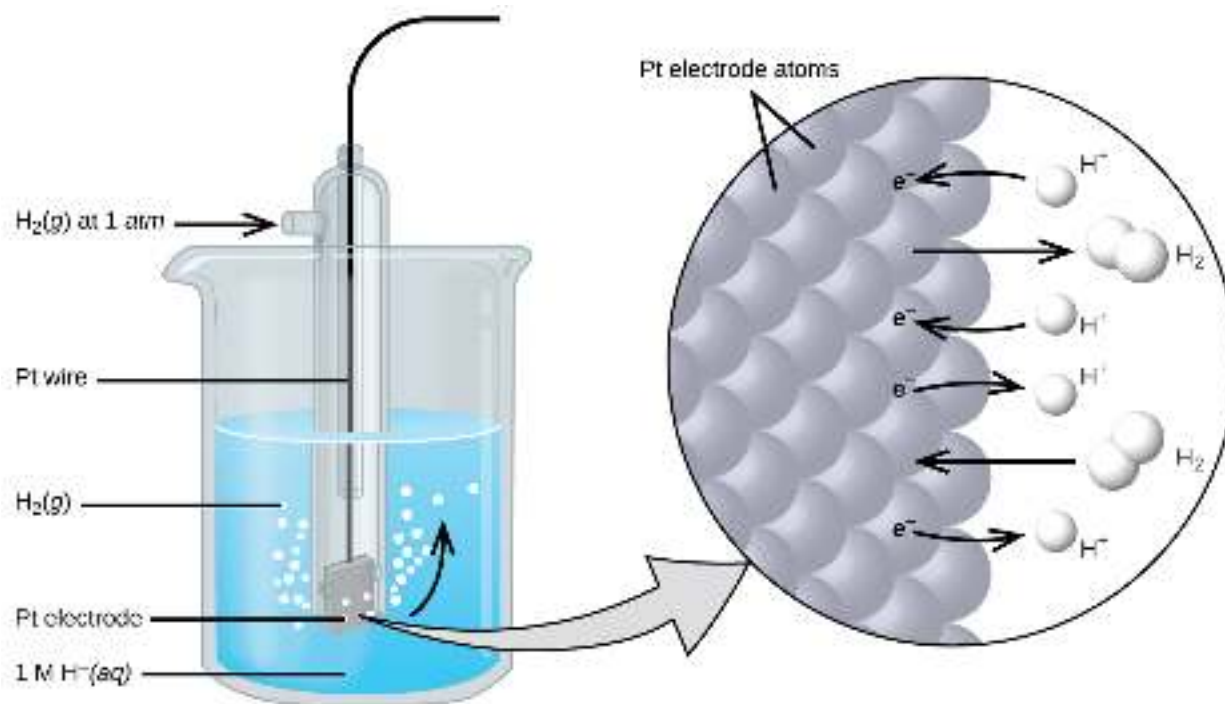


Figure 17.5 A standard hydrogen electrode (SHE).

The assigned potential of the SHE permits the definition of a conveniently measured potential for a single half-cell. The **electrode potential (E_X)** for a half-cell X is defined as *the potential measured for a cell comprised of X acting as cathode and the SHE acting as anode*:

$$\begin{aligned} E_{\text{cell}} &= E_X - E_{\text{SHE}} \\ E_{\text{SHE}} &= 0 \text{ V (defined)} \\ E_{\text{cell}} &= E_X \end{aligned}$$

When the half-cell X is under standard-state conditions, its potential is the **standard electrode potential, E°_X** . Since the definition of cell potential requires the half-cells function as cathodes, these potentials are sometimes called *standard reduction potentials*.

This approach to measuring electrode potentials is illustrated in **Figure 17.6**, which depicts a cell comprised of an SHE connected to a copper(II)/copper(0) half-cell under standard-state conditions. A voltmeter in the external circuit allows measurement of the potential difference between the two half-cells. Since the Cu half-cell is designated as the cathode in the definition of cell potential, it is connected to the red (positive) input of the voltmeter, while the designated SHE anode is connected to the black (negative) input. These connections insure that the sign of the measured potential will be consistent with the sign conventions of electrochemistry per the various definitions discussed above. A cell potential of +0.337 V is measured, and so

$$E^\circ_{\text{cell}} = E^\circ_{\text{Cu}} = +0.337 \text{ V}$$

Tabulations of E° values for other half-cells measured in a similar fashion are available as reference literature to permit calculations of cell potentials and the prediction of the spontaneity of redox processes.

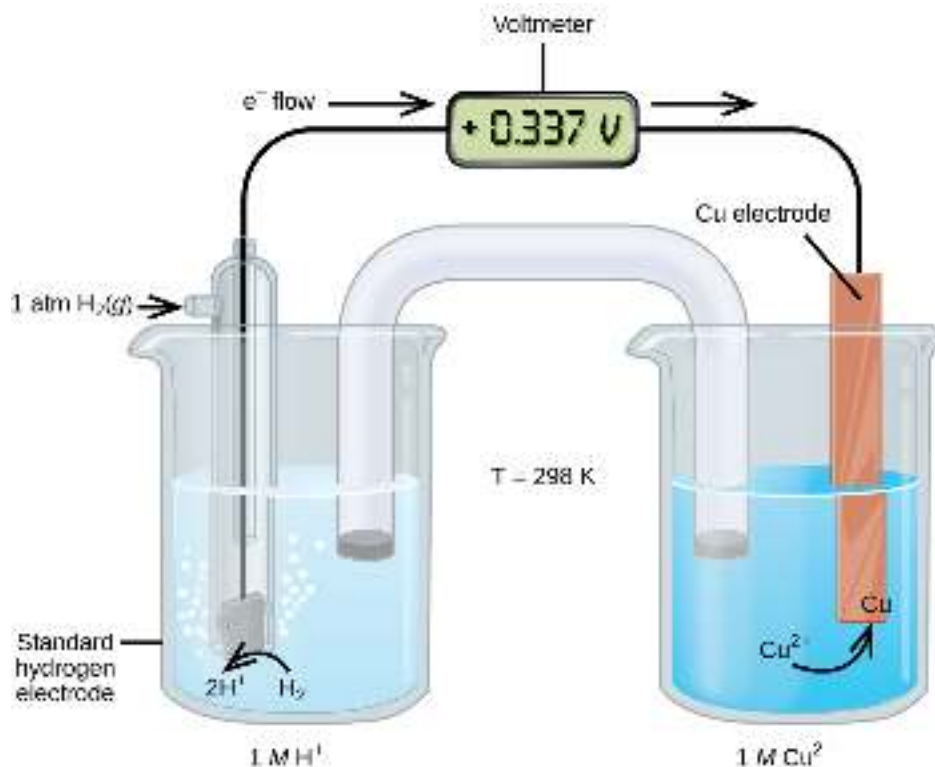


Figure 17.6 A cell permitting experimental measurement of the standard electrode potential for the half-reaction $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \longrightarrow \text{Cu}(\text{s})$

Table 17.1 provides a listing of standard electrode potentials for a selection of half-reactions in numerical order, and a more extensive alphabetical listing is given in **Appendix L**.

Selected Standard Reduction Potentials at 25 °C

Half-Reaction	E° (V)
$\text{F}_2(\text{g}) + 2\text{e}^{-} \longrightarrow 2\text{F}^{-}(\text{aq})$	+2.866
$\text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^{+}(\text{aq}) + 2\text{e}^{-} \longrightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	+1.69
$\text{MnO}_4^{-}(\text{aq}) + 8\text{H}^{+}(\text{aq}) + 5\text{e}^{-} \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	+1.507
$\text{Au}^{3+}(\text{aq}) + 3\text{e}^{-} \longrightarrow \text{Au}(\text{s})$	+1.498
$\text{Cl}_2(\text{g}) + 2\text{e}^{-} \longrightarrow 2\text{Cl}^{-}(\text{aq})$	+1.35827
$\text{O}_2(\text{g}) + 4\text{H}^{+}(\text{aq}) + 4\text{e}^{-} \longrightarrow 2\text{H}_2\text{O}(\text{l})$	+1.229
$\text{Pt}^{2+}(\text{aq}) + 2\text{e}^{-} \longrightarrow \text{Pt}(\text{s})$	+1.20
$\text{Br}_2(\text{aq}) + 2\text{e}^{-} \longrightarrow 2\text{Br}^{-}(\text{aq})$	+1.0873
$\text{Ag}^{+}(\text{aq}) + \text{e}^{-} \longrightarrow \text{Ag}(\text{s})$	+0.7996

Table 17.1

Selected Standard Reduction Potentials at 25 °C

Half-Reaction	E° (V)
$\text{Hg}_2^{2+}(aq) + 2e^- \longrightarrow 2\text{Hg}(l)$	+0.7973
$\text{Fe}^{3+}(aq) + e^- \longrightarrow \text{Fe}^{2+}(aq)$	+0.771
$\text{MnO}_4^-(aq) + 2\text{H}_2\text{O}(l) + 3e^- \longrightarrow \text{MnO}_2(s) + 4\text{OH}^-(aq)$	+0.558
$\text{I}_2(s) + 2e^- \longrightarrow 2\text{I}^-(aq)$	+0.5355
$\text{NiO}_2(s) + 2\text{H}_2\text{O}(l) + 2e^- \longrightarrow \text{Ni(OH)}_2(s) + 2\text{OH}^-(aq)$	+0.49
$\text{Cu}^{2+}(aq) + 2e^- \longrightarrow \text{Cu}(s)$	+0.34
$\text{Hg}_2\text{Cl}_2(s) + 2e^- \longrightarrow 2\text{Hg}(l) + 2\text{Cl}^-(aq)$	+0.26808
$\text{AgCl}(s) + e^- \longrightarrow \text{Ag}(s) + \text{Cl}^-(aq)$	+0.22233
$\text{Sn}^{4+}(aq) + 2e^- \longrightarrow \text{Sn}^{2+}(aq)$	+0.151
$2\text{H}^+(aq) + 2e^- \longrightarrow \text{H}_2(g)$	0.00
$\text{Pb}^{2+}(aq) + 2e^- \longrightarrow \text{Pb}(s)$	-0.1262
$\text{Sn}^{2+}(aq) + 2e^- \longrightarrow \text{Sn}(s)$	-0.1375
$\text{Ni}^{2+}(aq) + 2e^- \longrightarrow \text{Ni}(s)$	-0.257
$\text{Co}^{2+}(aq) + 2e^- \longrightarrow \text{Co}(s)$	-0.28
$\text{PbSO}_4(s) + 2e^- \longrightarrow \text{Pb}(s) + \text{SO}_4^{2-}(aq)$	-0.3505
$\text{Cd}^{2+}(aq) + 2e^- \longrightarrow \text{Cd}(s)$	-0.4030
$\text{Fe}^{2+}(aq) + 2e^- \longrightarrow \text{Fe}(s)$	-0.447
$\text{Cr}^{3+}(aq) + 3e^- \longrightarrow \text{Cr}(s)$	-0.744
$\text{Mn}^{2+}(aq) + 2e^- \longrightarrow \text{Mn}(s)$	-1.185
$\text{Zn(OH)}_2(s) + 2e^- \longrightarrow \text{Zn}(s) + 2\text{OH}^-(aq)$	-1.245
$\text{Zn}^{2+}(aq) + 2e^- \longrightarrow \text{Zn}(s)$	-0.7618
$\text{Al}^{3+}(aq) + 3e^- \longrightarrow \text{Al}(s)$	-1.662
$\text{Mg}^{2+}(aq) + 2e^- \longrightarrow \text{Mg}(s)$	-2.372
$\text{Na}^+(aq) + e^- \longrightarrow \text{Na}(s)$	-2.71
$\text{Ca}^{2+}(aq) + 2e^- \longrightarrow \text{Ca}(s)$	-2.868

Table 17.1

Selected Standard Reduction Potentials at 25 °C

Half-Reaction	E° (V)
$\text{Ba}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ba}(\text{s})$	-2.912
$\text{K}^+(\text{aq}) + \text{e}^- \longrightarrow \text{K}(\text{s})$	-2.931
$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$	-3.04

Table 17.1

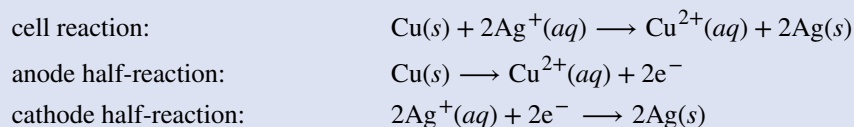
Example 17.4

Calculating Standard Cell Potentials

What is the standard potential of the galvanic cell shown in **Figure 17.3**?

Solution

The cell in **Figure 17.3** is galvanic, the spontaneous cell reaction involving oxidation of its copper anode and reduction of silver(I) ions at its silver cathode:



The standard cell potential computed as

$$\begin{aligned}
 E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\
 &= E^\circ_{\text{Ag}} - E^\circ_{\text{Cu}} \\
 &= 0.7996 \text{ V} - 0.34 \text{ V} \\
 &= +0.46 \text{ V}
 \end{aligned}$$

Check Your Learning

What is the standard cell potential expected if the silver cathode half-cell in **Figure 17.3** is replaced with a lead half-cell: $\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Pb}(\text{s})$?

Answer: -0.47 V

Interpreting Electrode and Cell Potentials

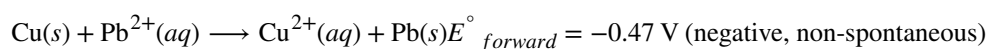
Thinking carefully about the definitions of cell and electrode potentials and the observations of spontaneous redox change presented thus far, a significant relation is noted. The previous section described the spontaneous oxidation of copper by aqueous silver(I) ions, but no observed reaction with aqueous lead(II) ions. Results of the calculations in **Example 17.4** have just shown *the spontaneous process is described by a positive cell potential while the nonspontaneous process exhibits a negative cell potential*. And so, with regard to the relative effectiveness (“strength”) with which aqueous Ag^+ and Pb^{2+} ions oxidize Cu under standard conditions, *the stronger oxidant is the one exhibiting the greater standard electrode potential, E°* . Since by convention electrode potentials are for reduction processes, an increased value of E° corresponds to an increased driving force behind the reduction of the species (hence increased effectiveness of its action as an *oxidizing agent* on some other species). Negative values for electrode potentials are simply a consequence of assigning a value of 0 V to the SHE, indicating the reactant of the half-reaction is a weaker oxidant than aqueous hydrogen ions.

Applying this logic to the numerically ordered listing of standard electrode potentials in **Table 17.1** shows this listing

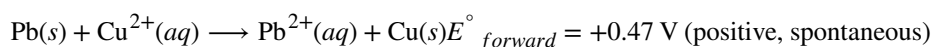
to be likewise in order of the oxidizing strength of the half-reaction's reactant species, decreasing from strongest oxidant (most positive E°) to weakest oxidant (most negative E°). Predictions regarding the spontaneity of redox reactions under standard state conditions can then be easily made by simply comparing the relative positions of their table entries. By definition, E°_{cell} is positive when $E^\circ_{\text{cathode}} > E^\circ_{\text{anode}}$, and so any redox reaction in which the oxidant's entry is above the reductant's entry is predicted to be spontaneous.

Reconsideration of the two redox reactions in **Example 17.4** provides support for this fact. The entry for the silver(I)/silver(0) half-reaction is above that for the copper(II)/copper(0) half-reaction, and so the oxidation of Cu by Ag^+ is predicted to be spontaneous ($E^\circ_{\text{cathode}} > E^\circ_{\text{anode}}$ and so $E^\circ_{\text{cell}} > 0$). Conversely, the entry for the lead(II)/lead(0) half-cell is beneath that for copper(II)/copper(0), and the oxidation of Cu by Pb^{2+} is nonspontaneous ($E^\circ_{\text{cathode}} < E^\circ_{\text{anode}}$ and so $E^\circ_{\text{cell}} < 0$).

Recalling the chapter on thermodynamics, the spontaneities of the forward and reverse reactions of a reversible process show a reciprocal relationship: if a process is spontaneous in one direction, it is non-spontaneous in the opposite direction. As an indicator of spontaneity for redox reactions, the potential of a cell reaction shows a consequential relationship in its arithmetic sign. The spontaneous oxidation of copper by lead(II) ions is *not* observed,



and so the reverse reaction, the oxidation of lead by copper(II) ions, is predicted to occur spontaneously:



Note that reversing the direction of a redox reaction effectively interchanges the identities of the cathode and anode half-reactions, and so the cell potential is calculated from electrode potentials in the reverse subtraction order than that for the forward reaction. In practice, a voltmeter would report a potential of -0.47 V with its red and black inputs connected to the Pb and Cu electrodes, respectively. If the inputs were swapped, the reported voltage would be $+0.47 \text{ V}$.

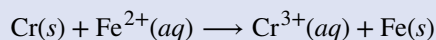
Example 17.5

Predicting Redox Spontaneity

Are aqueous iron(II) ions predicted to spontaneously oxidize elemental chromium under standard state conditions? Assume the half-reactions to be those available in **Table 17.1**.

Solution

Referring to the tabulated half-reactions, the redox reaction in question can be represented by the equations below:



The entry for the putative oxidant, Fe^{2+} , appears *above* the entry for the reductant, Cr, and so a spontaneous reaction is predicted per the quick approach described above. Supporting this predication by calculating the standard cell potential for this reaction gives

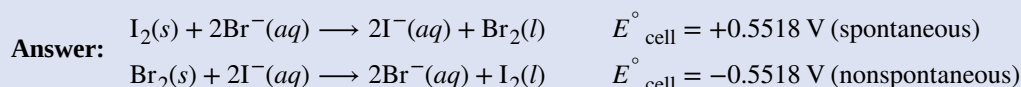
$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= E^\circ_{\text{Fe(II)}} - E^\circ_{\text{Cr}} \\ &= -0.447 \text{ V} - (-0.774 \text{ V}) = +0.297 \text{ V} \end{aligned}$$

The positive value for the standard cell potential indicates the process is spontaneous under standard state conditions.

Check Your Learning

Use the data in **Table 17.1** to predict the spontaneity of the oxidation of bromide ion by molecular iodine under standard state conditions, supporting the prediction by calculating the standard cell potential for the

reaction. Repeat for the oxidation of iodide ion by molecular bromine.



17.4 Potential, Free Energy, and Equilibrium

By the end of this section, you will be able to:

- Explain the relations between potential, free energy change, and equilibrium constants
- Perform calculations involving the relations between cell potentials, free energy changes, and equilibrium
- Use the Nernst equation to determine cell potentials under nonstandard conditions

So far in this chapter, the relationship between the cell potential and reaction *spontaneity* has been described, suggesting a link to the free energy change for the reaction (see chapter on thermodynamics). The interpretation of potentials as measures of oxidant *strength* was presented, bringing to mind similar measures of acid-base strength as reflected in equilibrium constants (see the chapter on acid-base equilibria). This section provides a summary of the relationships between potential and the related thermodynamic properties ΔG and K .

E° and ΔG°

The standard free energy change of a process, ΔG° , was defined in a previous chapter as the maximum work that could be performed by a system, w_{max} . In the case of a redox reaction taking place within a galvanic cell under standard state conditions, essentially all the work is associated with transferring the electrons from reductant-to-oxidant, w_{elec} :

$$\Delta G^\circ = w_{\text{max}} = w_{\text{elec}}$$

The work associated with transferring electrons is determined by the total amount of charge (coulombs) transferred and the cell potential:

$$\begin{aligned} \Delta G^\circ = w_{\text{elec}} &= -nFE^\circ_{\text{cell}} \\ \Delta G^\circ &= -nFE^\circ_{\text{cell}} \end{aligned}$$

where n is the number of moles of electrons transferred, F is **Faraday's constant**, and E°_{cell} is the standard cell potential. The relation between free energy change and standard cell potential confirms the sign conventions and spontaneity criteria previously discussed for both of these properties: spontaneous redox reactions exhibit positive potentials and negative free energy changes.

E° and K

Combining a previously derived relation between ΔG° and K (see the chapter on thermodynamics) and the equation above relating ΔG° and E°_{cell} yields the following:

$$\begin{aligned} \Delta G^\circ &= -RT \ln K = -nFE^\circ_{\text{cell}} \\ E^\circ_{\text{cell}} &= \left(\frac{RT}{nF}\right) \ln K \end{aligned}$$

This equation indicates redox reactions with large (positive) standard cell potentials will proceed far towards completion, reaching equilibrium when the majority of reactant has been converted to product. A summary of the relations between E° , ΔG° and K is depicted in **Figure 17.7**, and a table correlating reaction spontaneity to values of these properties is provided in **Table 17.2**.

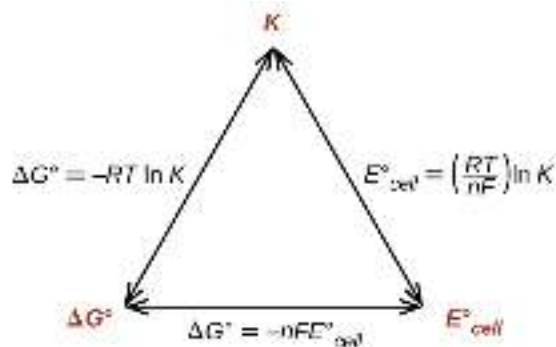


Figure 17.7 Graphic depicting the relation between three important thermodynamic properties.

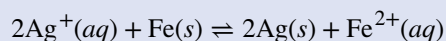
K	ΔG°	E°_{cell}	
> 1	< 0	> 0	Reaction is spontaneous under standard conditions Products more abundant at equilibrium
< 1	> 0	< 0	Reaction is non-spontaneous under standard conditions Reactants more abundant at equilibrium
$= 1$	$= 0$	$= 0$	Reaction is at equilibrium under standard conditions Reactants and products equally abundant

Table 17.2

Example 17.6

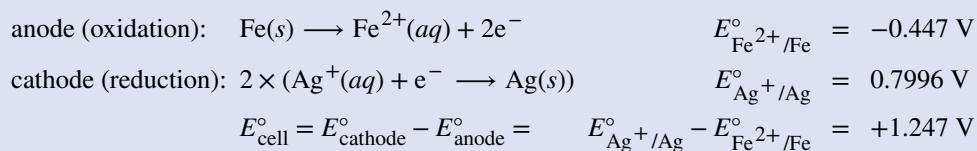
Equilibrium Constants, Standard Cell Potentials, and Standard Free Energy Changes

Use data from **Appendix L** to calculate the standard cell potential, standard free energy change, and equilibrium constant for the following reaction at 25 °C. Comment on the spontaneity of the forward reaction and the composition of an equilibrium mixture of reactants and products.



Solution

The reaction involves an oxidation-reduction reaction, so the standard cell potential can be calculated using the data in **Appendix L**.



With $n = 2$, the equilibrium constant is then

$$\begin{aligned}
 E_{\text{cell}}^{\circ} &= \frac{0.0592 \text{ V}}{n} \log K \\
 K &= 10^{n \times E_{\text{cell}}^{\circ} / 0.0592 \text{ V}} \\
 K &= 10^{2 \times 1.247 \text{ V} / 0.0592 \text{ V}} \\
 K &= 10^{42.128} \\
 K &= 1.3 \times 10^{42}
 \end{aligned}$$

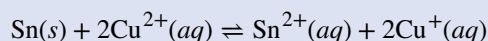
The standard free energy is then

$$\begin{aligned}
 \Delta G^{\circ} &= -nFE_{\text{cell}}^{\circ} \\
 \Delta G^{\circ} &= -2 \times 96,485 \frac{\text{C}}{\text{mol}} \times 1.247 \frac{\text{J}}{\text{C}} = -240.6 \frac{\text{kJ}}{\text{mol}}
 \end{aligned}$$

The reaction is spontaneous, as indicated by a negative free energy change and a positive cell potential. The K value is very large, indicating the reaction proceeds to near completion to yield an equilibrium mixture containing mostly products.

Check Your Learning

What is the standard free energy change and the equilibrium constant for the following reaction at room temperature? Is the reaction spontaneous?



Answer: Spontaneous; $n = 2$; $E_{\text{cell}}^{\circ} = +0.291 \text{ V}$; $\Delta G^{\circ} = -56.2 \frac{\text{kJ}}{\text{mol}}$; $K = 6.8 \times 10^9$.

Potentials at Nonstandard Conditions: The Nernst Equation

Most of the redox processes that interest science and society do not occur under standard state conditions, and so the potentials of these systems under nonstandard conditions are a property worthy of attention. Having established the relationship between potential and free energy change in this section, the previously discussed relation between free energy change and reaction mixture composition can be used for this purpose.

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

Notice the reaction quotient, Q , appears in this equation, making the free energy change dependent upon the composition of the reaction mixture. Substituting the equation relating free energy change to cell potential yields the **Nernst equation**:

$$\begin{aligned}
 -nFE_{\text{cell}} &= -nFE_{\text{cell}}^{\circ} + RT \ln Q \\
 E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q
 \end{aligned}$$

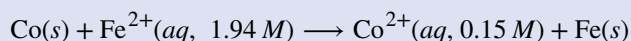
This equation describes how the potential of a redox system (such as a galvanic cell) varies from its standard state value, specifically, showing it to be a function of the number of electrons transferred, n , the temperature, T , and the reaction mixture composition as reflected in Q . A convenient form of the Nernst equation for most work is one in which values for the fundamental constants (R and F) and a factor converting from natural to base-10 logarithms have been included:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \ln Q$$

Example 17.7

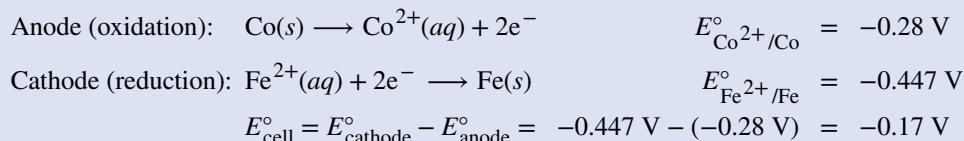
Predicting Redox Spontaneity Under Nonstandard Conditions

Use the Nernst equation to predict the spontaneity of the redox reaction shown below.



Solution

Collecting information from **Appendix L** and the problem,



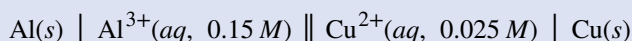
Notice the negative value of the standard cell potential indicates the process is not spontaneous under standard conditions. Substitution of the Nernst equation terms for the nonstandard conditions yields:

$$\begin{aligned}Q &= \frac{[\text{Co}^{2+}]}{[\text{Fe}^{2+}]} = \frac{0.15 \text{ M}}{1.94 \text{ M}} = 0.077 \\ E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \frac{0.0592 \text{ V}}{n} \log Q \\ E_{\text{cell}} &= -0.17 \text{ V} - \frac{0.0592 \text{ V}}{2} \log 0.077 \\ E_{\text{cell}} &= -0.17 \text{ V} + 0.033 \text{ V} = -0.014 \text{ V}\end{aligned}$$

The cell potential remains negative (slightly) under the specified conditions, and so the reaction remains nonspontaneous.

Check Your Learning

For the cell schematic below, identify values for n and Q , and calculate the cell potential, E_{cell} .



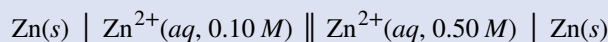
Answer: $n = 6$; $Q = 1440$; $E_{\text{cell}} = +1.97 \text{ V}$, spontaneous.

A **concentration cell** is constructed by connecting two nearly identical half-cells, each based on the same half-reaction and using the same electrode, varying only in the concentration of one redox species. The potential of a concentration cell, therefore, is determined only by the difference in concentration of the chosen redox species. The example problem below illustrates the use of the Nernst equation in calculations involving concentration cells.

Example 17.8

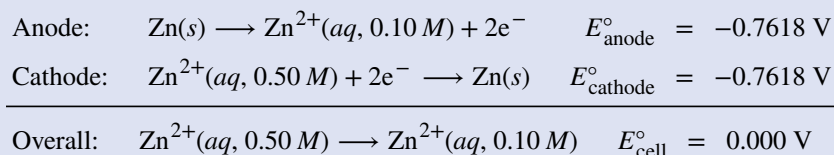
Concentration Cells

What is the cell potential of the concentration cell described by



Solution

From the information given:



Substituting into the Nernst equation,

$$E_{\text{cell}} = 0.000 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{0.10}{0.50} = +0.021 \text{ V}$$

The positive value for cell potential indicates the overall cell reaction (see above) is spontaneous. This spontaneous reaction is one in which the zinc ion concentration in the cathode falls (it is reduced to

elemental zinc) while that in the anode rises (it is produced by oxidation of the zinc anode). A greater driving force for zinc reduction is present in the cathode, where the zinc(II) ion concentration is greater ($E_{\text{cathode}} > E_{\text{anode}}$).

Check Your Learning

The concentration cell above was allowed to operate until the cell reaction reached equilibrium. What are the cell potential and the concentrations of zinc(II) in each half-cell for the cell now?

Answer: $E_{\text{cell}} = 0.000 \text{ V}$; $[\text{Zn}^{2+}]_{\text{cathode}} = [\text{Zn}^{2+}]_{\text{anode}} = 0.30 \text{ M}$

17.5 Batteries and Fuel Cells

By the end of this section, you will be able to:

- Describe the electrochemistry associated with several common batteries
- Distinguish the operation of a fuel cell from that of a battery

There are many technological products associated with the past two centuries of electrochemistry research, none more immediately obvious than the battery. A **battery** is a galvanic cell that has been specially designed and constructed in a way that best suits its intended use as a source of electrical power for specific applications. Among the first successful batteries was the *Daniell cell*, which relied on the spontaneous oxidation of zinc by copper(II) ions (**Figure 17.8**):

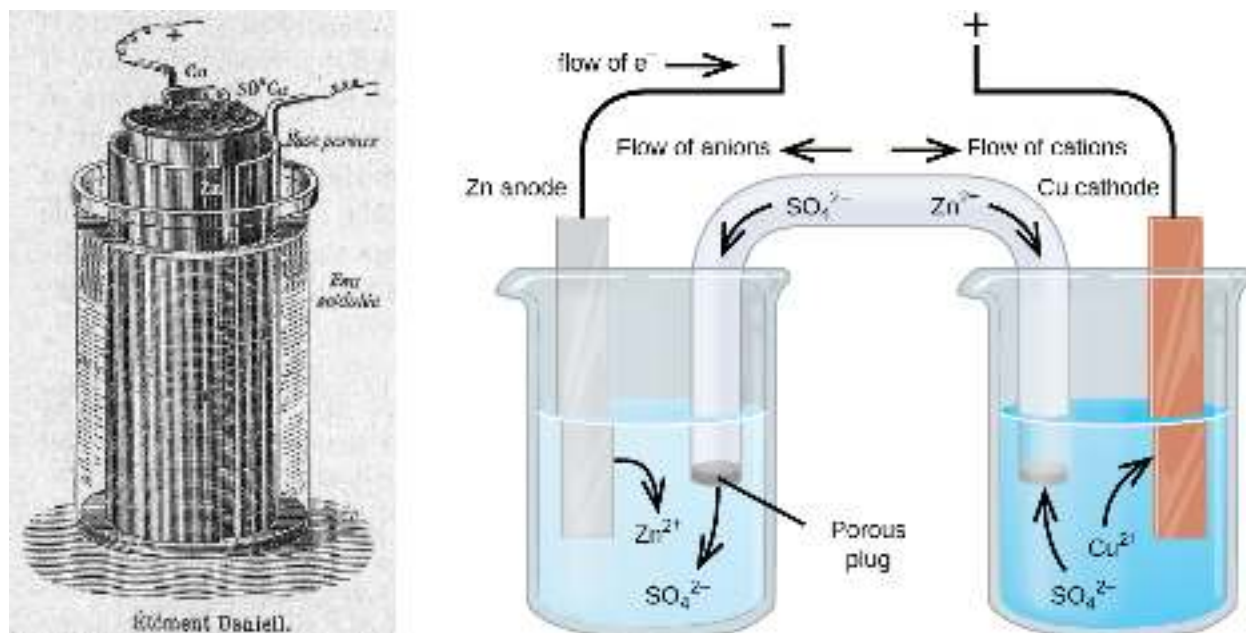
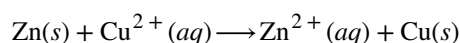


Figure 17.8 Illustration of a Daniell cell taken from a 1904 journal publication (left) along with a simplified illustration depicting the electrochemistry of the cell (right). The 1904 design used a porous clay pot to both contain one of the half-cell's content and to serve as a salt bridge to the other half-cell.

Modern batteries exist in a multitude of forms to accommodate various applications, from tiny button batteries that provide the modest power needs of a wristwatch to the very large batteries used to supply backup energy to municipal power grids. Some batteries are designed for single-use applications and cannot be recharged (**primary cells**), while others are based on conveniently reversible cell reactions that allow recharging by an external power

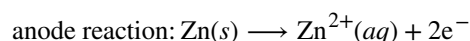
source (**secondary cells**). This section will provide a summary of the basic electrochemical aspects of several batteries familiar to most consumers, and will introduce a related electrochemical device called a *fuel cell* that can offer improved performance in certain applications.

Link to Learning

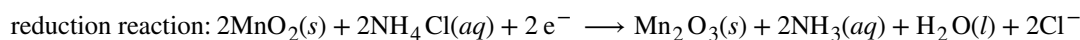
Visit this [site \(http://openstaxcollege.org/l/16batteries\)](http://openstaxcollege.org/l/16batteries) to learn more about batteries.

Single-Use Batteries

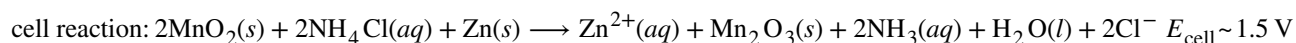
A common primary battery is the **dry cell**, which uses a zinc can as both container and anode (“−” terminal) and a graphite rod as the cathode (“+” terminal). The Zn can is filled with an electrolyte paste containing manganese(IV) oxide, zinc(II) chloride, ammonium chloride, and water. A graphite rod is immersed in the electrolyte paste to complete the cell. The spontaneous cell reaction involves the oxidation of zinc:



and the reduction of manganese(IV)



which together yield the cell reaction:



The voltage (*cell potential*) of a dry cell is approximately 1.5 V. Dry cells are available in various sizes (e.g., D, C, AA, AAA). All sizes of dry cells comprise the same components, and so they exhibit the same voltage, but larger cells contain greater amounts of the redox reactants and therefore are capable of transferring correspondingly greater amounts of charge. Like other galvanic cells, dry cells may be connected in series to yield batteries with greater voltage outputs, if needed.

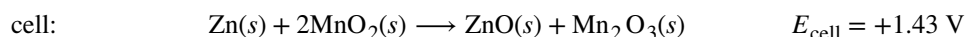
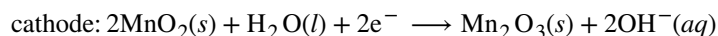
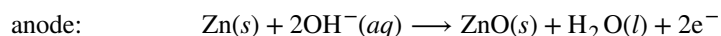


Figure 17.9 A schematic diagram shows a typical dry cell.

Link to Learning

Visit this [site \(http://openstaxcollege.org//16zinccarbon\)](http://openstaxcollege.org//16zinccarbon) to learn more about zinc-carbon batteries.

Alkaline batteries (Figure 17.10) were developed in the 1950s to improve on the performance of the dry cell, and they were designed around the same redox couples. As their name suggests, these types of batteries use alkaline electrolytes, often potassium hydroxide. The reactions are



An alkaline battery can deliver about three to five times the energy of a zinc-carbon dry cell of similar size. Alkaline batteries are prone to leaking potassium hydroxide, so they should be removed from devices for long-term storage. While some alkaline batteries are rechargeable, most are not. Attempts to recharge an alkaline battery that is not rechargeable often leads to rupture of the battery and leakage of the potassium hydroxide electrolyte.

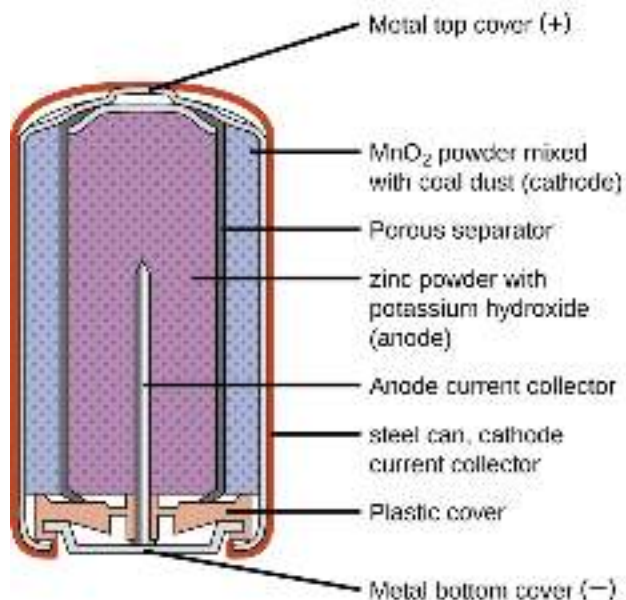


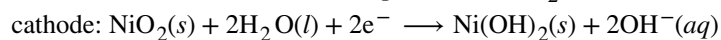
Figure 17.10 Alkaline batteries were designed as improved replacements for zinc-carbon (dry cell) batteries.

Link to Learning

Visit this [site \(http://openstaxcollege.org/l/16alkaline\)](http://openstaxcollege.org/l/16alkaline) to learn more about alkaline batteries.

Rechargeable (Secondary) Batteries

Nickel-cadmium, or NiCd, batteries (**Figure 17.11**) consist of a nickel-plated cathode, cadmium-plated anode, and a potassium hydroxide electrode. The positive and negative plates, which are prevented from shorting by the separator, are rolled together and put into the case. This is a “jelly-roll” design and allows the NiCd cell to deliver much more current than a similar-sized alkaline battery. The reactions are



When properly treated, a NiCd battery can be recharged about 1000 times. Cadmium is a toxic heavy metal so NiCd batteries should never be ruptured or incinerated, and they should be disposed of in accordance with relevant toxic waste guidelines.

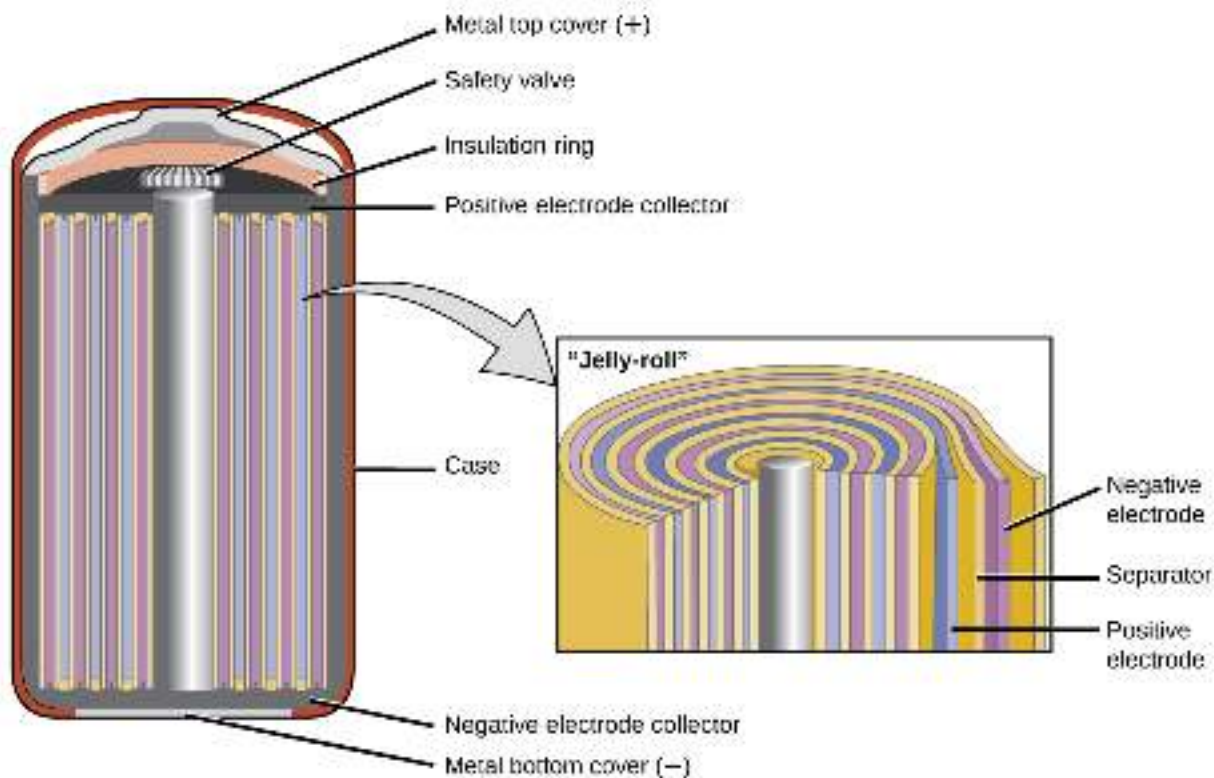
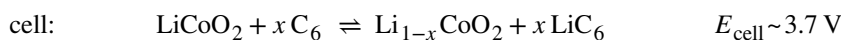
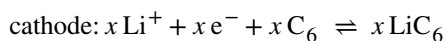
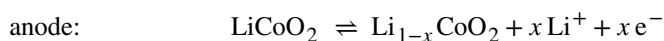


Figure 17.11 NiCd batteries use a “jelly-roll” design that significantly increases the amount of current the battery can deliver as compared to a similar-sized alkaline battery.

Link to Learning

Visit this [site \(http://openstaxcollege.org//16NiCdrecharge\)](http://openstaxcollege.org//16NiCdrecharge) for more information about nickel cadmium rechargeable batteries.

Lithium ion batteries (Figure 17.12) are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are



The variable stoichiometry of the cell reaction leads to variation in cell voltages, but for typical conditions, x is usually no more than 0.5 and the cell voltage is approximately 3.7 V. Lithium batteries are popular because they can provide a large amount of current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored.

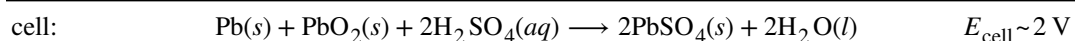
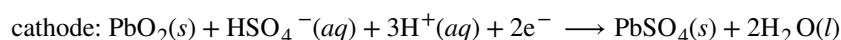


Figure 17.12 In a lithium ion battery, charge flows as the lithium ions are transferred between the anode and cathode.

Link to Learning

Visit this [site \(http://openstaxcollege.org/l/16lithiumion\)](http://openstaxcollege.org/l/16lithiumion) for more information about lithium ion batteries.

The **lead acid battery** (**Figure 17.13**) is the type of secondary battery commonly used in automobiles. It is inexpensive and capable of producing the high current required by automobile starter motors. The reactions for a lead acid battery are



Each cell produces 2 V, so six cells are connected in series to produce a 12-V car battery. Lead acid batteries are heavy and contain a caustic liquid electrolyte, $\text{H}_2\text{SO}_4(aq)$, but are often still the battery of choice because of their high current density. Since these batteries contain a significant amount of lead, they must always be disposed of properly.

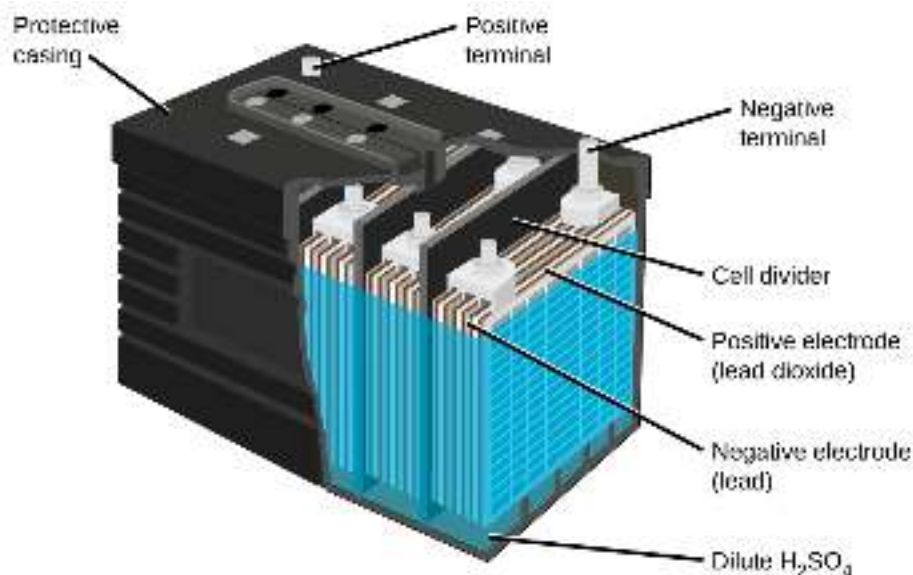


Figure 17.13 The lead acid battery in your automobile consists of six cells connected in series to give 12 V.

Link to Learning

Visit this [site \(http://openstaxcollege.org//16leadacid\)](http://openstaxcollege.org//16leadacid) for more information about lead acid batteries.

Fuel Cells

A **fuel cell** is a galvanic cell that uses traditional combustible fuels, most often hydrogen or methane, that are continuously fed into the cell along with an oxidant. (An alternative, but not very popular, name for a fuel cell is a *flow battery*.) Within the cell, fuel and oxidant undergo the same redox chemistry as when they are combusted, but via a catalyzed electrochemical that is significantly more efficient. For example, a typical hydrogen fuel cell uses graphite electrodes embedded with platinum-based catalysts to accelerate the two half-cell reactions:

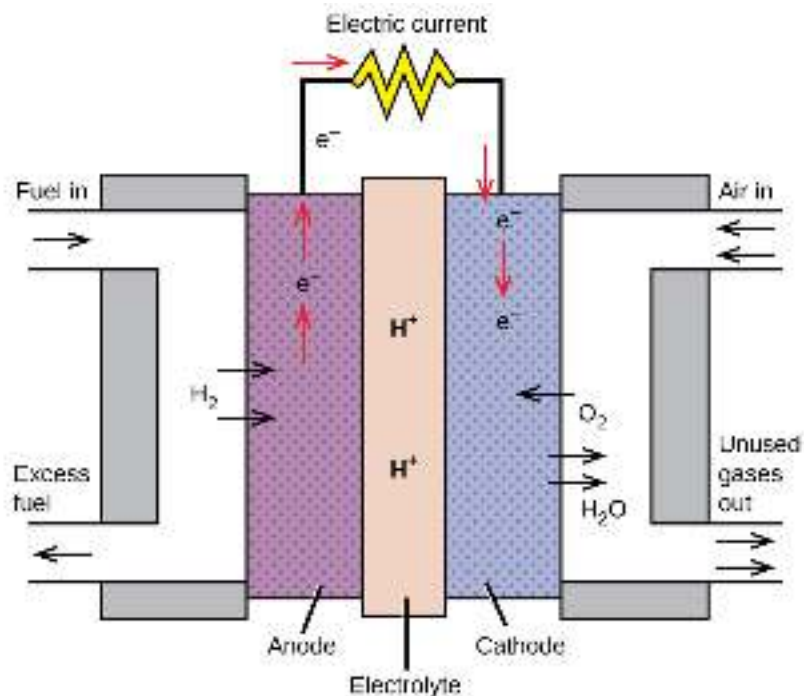
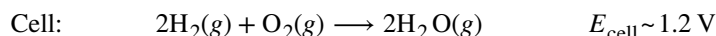
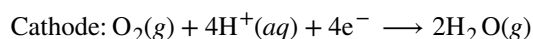
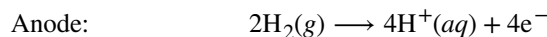


Figure 17.14 In this hydrogen fuel cell, oxygen from the air reacts with hydrogen, producing water and electricity.



These types of fuel cells generally produce voltages of approximately 1.2 V. Compared to an internal combustion engine, the energy efficiency of a fuel cell using the same redox reaction is typically more than double (~20%–25% for an engine versus ~50%–75% for a fuel cell). Hydrogen fuel cells are commonly used on extended space missions, and prototypes for personal vehicles have been developed, though the technology remains relatively immature.

Link to Learning

Check out this [link \(http://openstaxcollege.org/l/16fuelcells\)](http://openstaxcollege.org/l/16fuelcells) to learn more about fuel cells.

17.6 Corrosion

By the end of this section, you will be able to:

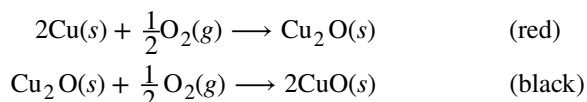
- Define corrosion
- List some of the methods used to prevent or slow corrosion

Corrosion is usually defined as the degradation of metals by a naturally occurring electrochemical process. The formation of rust on iron, tarnish on silver, and the blue-green patina that develops on copper are all examples of corrosion. The total cost of corrosion remediation in the United States is significant, with estimates in excess of half a trillion dollars a year.

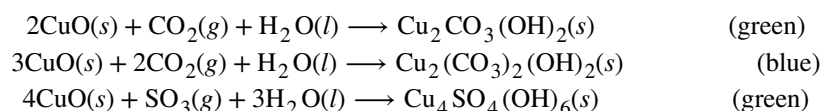
Chemistry in Everyday Life

Statue of Liberty: Changing Colors

The Statue of Liberty is a landmark every American recognizes. The Statue of Liberty is easily identified by its height, stance, and unique blue-green color (**Figure 17.15**). When this statue was first delivered from France, its appearance was not green. It was brown, the color of its copper “skin.” So how did the Statue of Liberty change colors? The change in appearance was a direct result of corrosion. The copper that is the primary component of the statue slowly underwent oxidation from the air. The oxidation-reduction reactions of copper metal in the environment occur in several steps. Copper metal is oxidized to copper(I) oxide (Cu_2O), which is red, and then to copper(II) oxide, which is black



Coal, which was often high in sulfur, was burned extensively in the early part of the last century. As a result, atmospheric sulfur trioxide, carbon dioxide, and water all reacted with the CuO



These three compounds are responsible for the characteristic blue-green patina seen on the Statue of Liberty (and other outdoor copper structures). Fortunately, formation of patina creates a protective layer on the copper surface, preventing further corrosion of the underlying copper. The formation of the protective layer is called *passivation*, a phenomenon discussed further in another chapter of this text.



(a)

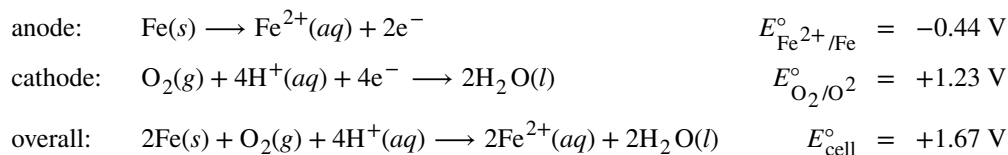


(b)

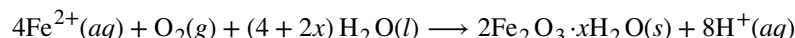
Figure 17.15 (a) The Statue of Liberty is covered with a copper skin, and was originally brown, as shown in this painting. (b) Exposure to the elements has resulted in the formation of the blue-green patina seen today.

Perhaps the most familiar example of corrosion is the formation of rust on iron. Iron will rust when it is exposed to oxygen and water. Rust formation involves the creation of a galvanic cell at an iron surface, as illustrated in **Figure**

17.15. The relevant redox reactions are described by the following equations:



Further reaction of the iron(II) product in humid air results in the production of an iron(III) oxide hydrate known as rust:



The stoichiometry of the hydrate varies, as indicated by the use of x in the compound formula. Unlike the patina on copper, the formation of rust does not create a protective layer and so corrosion of the iron continues as the rust flakes off and exposes fresh iron to the atmosphere.

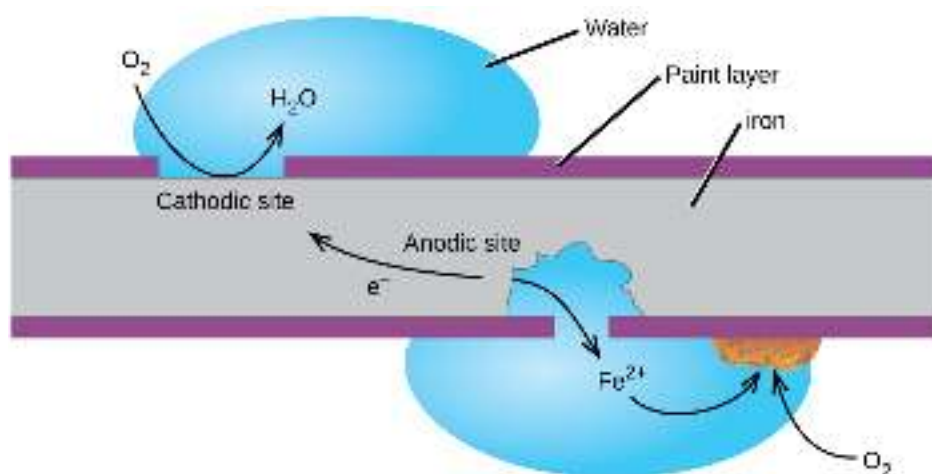


Figure 17.16 Corrosion can occur when a painted iron or steel surface is exposed to the environment by a scratch through the paint. A galvanic cell results that may be approximated by the simplified cell schematic $\text{Fe}(s) | \text{Fe}^{2+}(aq) || \text{O}_2(aq), \text{H}_2\text{O}(l) | \text{Fe}(s)$.

One way to keep iron from corroding is to keep it painted. The layer of paint prevents the water and oxygen necessary for rust formation from coming into contact with the iron. As long as the paint remains intact, the iron is protected from corrosion.

Other strategies include alloying the iron with other metals. For example, stainless steel is an alloy of iron containing a small amount of chromium. The chromium tends to collect near the surface, where it corrodes and forms a passivating an oxide layer that protects the iron.

Iron and other metals may also be protected from corrosion by **galvanization**, a process in which the metal to be protected is coated with a layer of a more readily oxidized metal, usually zinc. When the zinc layer is intact, it prevents air from contacting the underlying iron and thus prevents corrosion. If the zinc layer is breached by either corrosion or mechanical abrasion, the iron may still be protected from corrosion by a *cathodic protection* process, which is described in the next paragraph.

Another important way to protect metal is to make it the cathode in a galvanic cell. This is **cathodic protection** and can be used for metals other than just iron. For example, the rusting of underground iron storage tanks and pipes can be prevented or greatly reduced by connecting them to a more active metal such as zinc or magnesium (**Figure 17.17**). This is also used to protect the metal parts in water heaters. The more active metals (lower reduction potential) are called **sacrificial anodes** because as they get used up as they corrode (oxidize) at the anode. The metal being

protected serves as the cathode for the reduction of oxygen in air, and so it simply serves to conduct (not react with) the electrons being transferred. When the anodes are properly monitored and periodically replaced, the useful lifetime of the iron storage tank can be greatly extended.

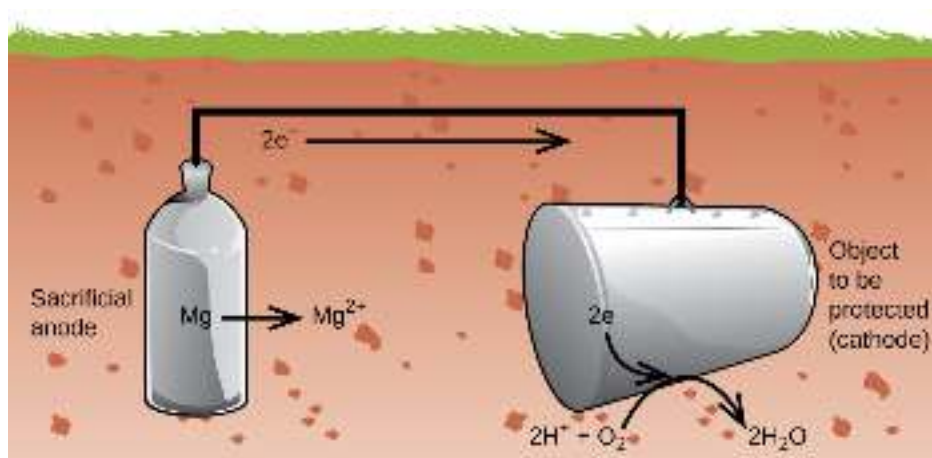


Figure 17.17 Cathodic protection is a useful approach to electrochemically preventing corrosion of underground storage tanks.

17.7 Electrolysis

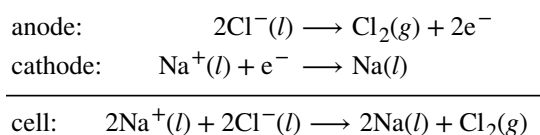
By the end of this section you will be able to:

- Describe the process of electrolysis
- Compare the operation of electrolytic cells with that of galvanic cells
- Perform stoichiometric calculations for electrolytic processes

Electrochemical cells in which spontaneous redox reactions take place (*galvanic cells*) have been the topic of discussion so far in this chapter. In these cells, *electrical work is done by a redox system on its surroundings* as electrons produced by the redox reaction are transferred through an external circuit. This final section of the chapter will address an alternative scenario in which *an external circuit does work on a redox system* by imposing a voltage sufficient to drive an otherwise nonspontaneous reaction, a process known as **electrolysis**. A familiar example of electrolysis is recharging a battery, which involves use of an external power source to drive the spontaneous (discharge) cell reaction in the reverse direction, restoring to some extent the composition of the half-cells and the voltage of the battery. Perhaps less familiar is the use of electrolysis in the refinement of metallic ores, the manufacture of commodity chemicals, and the *electroplating* of metallic coatings on various products (e.g., jewelry, utensils, auto parts). To illustrate the essential concepts of electrolysis, a few specific processes will be considered.

The Electrolysis of Molten Sodium Chloride

Metallic sodium, Na, and chlorine gas, Cl_2 , are used in numerous applications, and their industrial production relies on the large-scale electrolysis of molten sodium chloride, $\text{NaCl}(l)$. The industrial process typically uses a *Downs cell* similar to the simplified illustration shown in **Figure 17.18**. The reactions associated with this process are:



The cell potential for the above process is negative, indicating the reaction as written (decomposition of liquid NaCl) is not spontaneous. To force this reaction, a *positive potential of magnitude greater than the negative cell potential* must be applied to the cell.

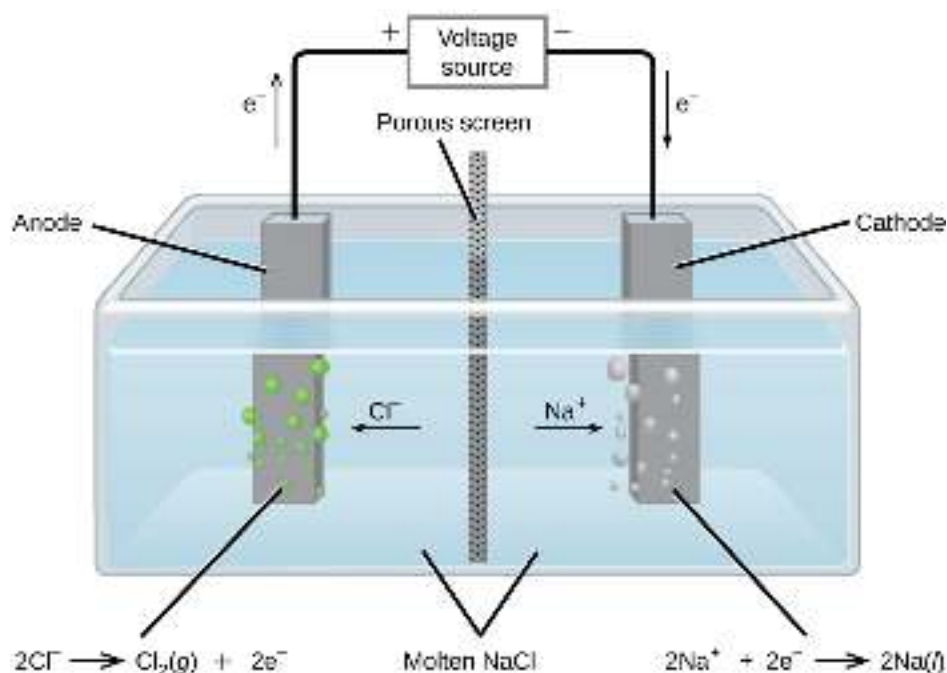
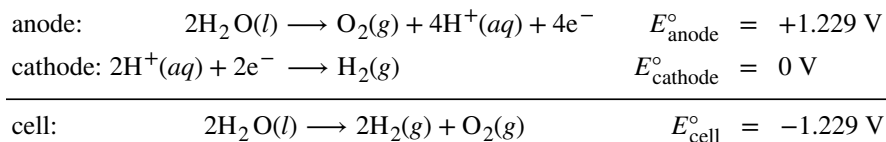


Figure 17.18 Cells of this sort (a cell for the electrolysis of molten sodium chloride) are used in the *Downs process* for production of sodium and chlorine, and they typically use iron cathodes and carbon anodes.

The Electrolysis of Water

Water may be electrolytically decomposed in a cell similar to the one illustrated in **Figure 17.19**. To improve electrical conductivity without introducing a different redox species, the hydrogen ion concentration of the water is typically increased by addition of a strong acid. The redox processes associated with this cell are



Again, the cell potential as written is negative, indicating a nonspontaneous cell reaction that must be driven by imposing a cell voltage greater than +1.229 V. Keep in mind that *standard* electrode potentials are used to inform thermodynamic predictions here, though the cell is *not* operating under standard state conditions. Therefore, at best, calculated cell potentials should be considered ballpark estimates.

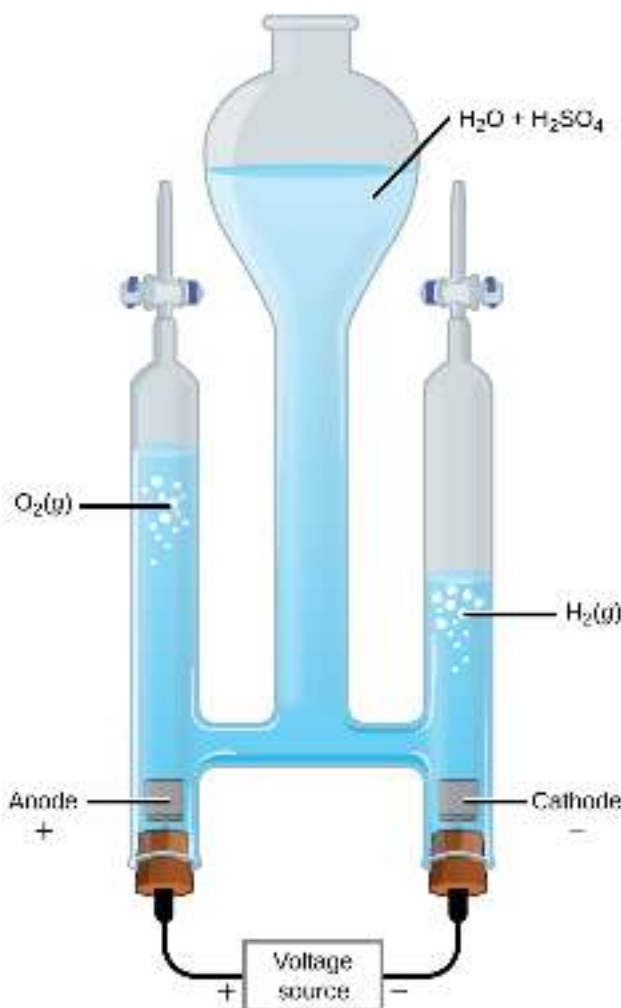
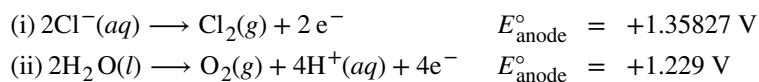


Figure 17.19 The electrolysis of water produces stoichiometric amounts of oxygen gas at the anode and hydrogen at the anode.

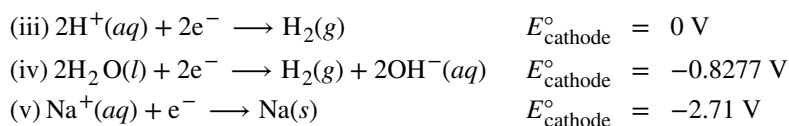
The Electrolysis of Aqueous Sodium Chloride

When aqueous solutions of ionic compounds are electrolyzed, the anode and cathode half-reactions may involve the electrolysis of either water species (H_2O , H^+ , OH^-) or solute species (the cations and anions of the compound). As an example, the electrolysis of aqueous sodium chloride could involve either of these two anode reactions:

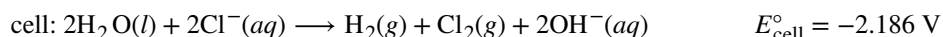


The standard electrode (*reduction*) potentials of these two half-reactions indicate water may be *oxidized* at a less negative/more positive potential (-1.229 V) than chloride ion (-1.358 V). Thermodynamics thus predicts that water would be more readily oxidized, though in practice it is observed that both water and chloride ion are oxidized under typical conditions, producing a mixture of oxygen and chlorine gas.

Turning attention to the cathode, the possibilities for reduction are:



Comparison of these *standard* half-reaction potentials suggests the reduction of hydrogen ion is thermodynamically favored. However, in a neutral aqueous sodium chloride solution, the concentration of hydrogen ion is far below the standard state value of 1 M (approximately 10^{-7} M), and so the observed cathode reaction is actually reduction of water. The net cell reaction in this case is then



This electrolysis reaction is part of the *chlor-alkali process* used by industry to produce chlorine and sodium hydroxide (lye).

Chemistry in Everyday Life

Electroplating

An important use for electrolytic cells is in **electroplating**. Electroplating results in a thin coating of one metal on top of a conducting surface. Reasons for electroplating include making the object more corrosion resistant, strengthening the surface, producing a more attractive finish, or for purifying metal. The metals commonly used in electroplating include cadmium, chromium, copper, gold, nickel, silver, and tin. Common consumer products include silver-plated or gold-plated tableware, chrome-plated automobile parts, and jewelry. The silver plating of eating utensils is used here to illustrate the process. (Figure 17.20).

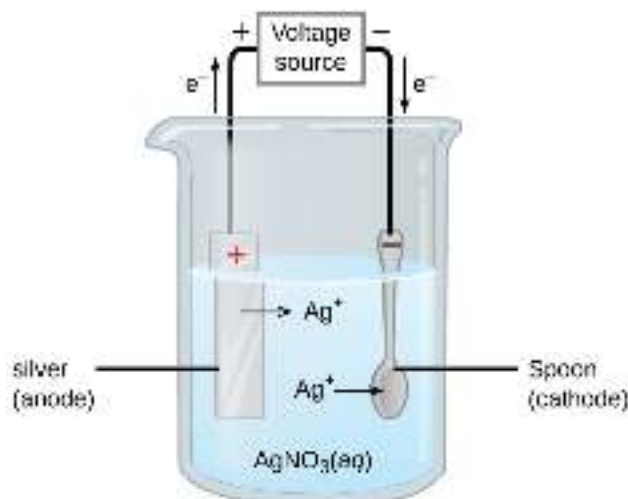
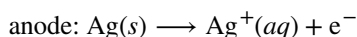
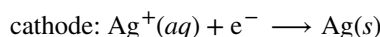


Figure 17.20 This schematic shows an electrolytic cell for silver plating eating utensils.

In the figure, the anode consists of a silver electrode, shown on the left. The cathode is located on the right and is the spoon, which is made from inexpensive metal. Both electrodes are immersed in a solution of silver nitrate. Applying a sufficient potential results in the oxidation of the silver anode



and reduction of silver ion at the (spoon) cathode:



The net result is the transfer of silver metal from the anode to the cathode. Several experimental factors must

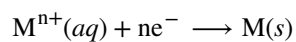
be carefully controlled to obtain high-quality silver coatings, including the exact composition of the electrolyte solution, the cell voltage applied, and the rate of the electrolysis reaction (electrical current).

Quantitative Aspects of Electrolysis

Electrical current is defined as the rate of flow for any charged species. Most relevant to this discussion is the flow of electrons. Current is measured in a composite unit called an ampere, defined as one coulomb per second ($A = 1 \text{ C/s}$). The charge transferred, Q , by passage of a constant current, I , over a specified time interval, t , is then given by the simple mathematical product

$$Q = It$$

When electrons are transferred during a redox process, the stoichiometry of the reaction may be used to derive the total amount of (electronic) charge involved. For example, the generic reduction process



involves the transfer of n mole of electrons. The charge transferred is, therefore,

$$Q = nF$$

where F is Faraday's constant, the charge in coulombs for one mole of electrons. If the reaction takes place in an electrochemical cell, the current flow is conveniently measured, and it may be used to assist in stoichiometric calculations related to the cell reaction.

Example 17.9

Converting Current to Moles of Electrons

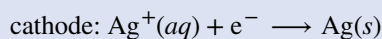
In one process used for electroplating silver, a current of 10.23 A was passed through an electrolytic cell for exactly 1 hour. How many moles of electrons passed through the cell? What mass of silver was deposited at the cathode from the silver nitrate solution?

Solution

Faraday's constant can be used to convert the charge (Q) into moles of electrons (n). The charge is the current (I) multiplied by the time

$$n = \frac{Q}{F} = \frac{\frac{10.23 \text{ C}}{\text{s}} \times 1 \text{ hr} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{60 \text{ s}}{\text{min}}}{96,485 \text{ C/mol e}^-} = \frac{36,830 \text{ C}}{96,485 \text{ C/mol e}^-} = 0.3817 \text{ mol e}^-$$

From the problem, the solution contains AgNO_3 , so the reaction at the cathode involves 1 mole of electrons for each mole of silver



The atomic mass of silver is 107.9 g/mol, so

$$\text{mass Ag} = 0.3817 \text{ mol e}^- \times \frac{1 \text{ mol Ag}}{1 \text{ mol e}^-} \times \frac{107.9 \text{ g Ag}}{1 \text{ mol Ag}} = 41.19 \text{ g Ag}$$

Check Your Learning

Aluminum metal can be made from aluminum(III) ions by electrolysis. What is the half-reaction at the cathode? What mass of aluminum metal would be recovered if a current of 25.0 A passed through the solution for 15.0 minutes?

Answer: $\text{Al}^{3+}(aq) + 3 \text{e}^- \longrightarrow \text{Al}(s)$; 0.0777 mol Al = 2.10 g Al.

Example 17.10

Time Required for Deposition

In one application, a 0.010-mm layer of chromium must be deposited on a part with a total surface area of 3.3 m^2 from a solution of containing chromium(III) ions. How long would it take to deposit the layer of chromium if the current was 33.46 A? The density of chromium (metal) is 7.19 g/cm^3 .

Solution

First, compute the volume of chromium that must be produced (equal to the product of surface area and thickness):

$$\text{volume} = \left(0.010 \text{ mm} \times \frac{1 \text{ cm}}{10 \text{ mm}}\right) \times \left(3.3 \text{ m}^2 \times \left(\frac{10,000 \text{ cm}^2}{1 \text{ m}^2}\right)\right) = 33 \text{ cm}^3$$

Use the computed volume and the provided density to calculate the molar amount of chromium required:

$$\text{mass} = \text{volume} \times \text{density} = 33 \frac{\text{cm}^3}{\text{cm}^3} \times \frac{7.19 \text{ g}}{\text{cm}^3} = 237 \text{ g Cr}$$

$$\text{mol Cr} = 237 \text{ g Cr} \times \frac{1 \text{ mol Cr}}{52.00 \text{ g Cr}} = 4.56 \text{ mol Cr}$$

The stoichiometry of the chromium(III) reduction process requires three moles of electrons for each mole of chromium(0) produced, and so the total charge required is:

$$Q = 4.56 \text{ mol Cr} \times \frac{3 \text{ mol e}^-}{1 \text{ mol Cr}} \times \frac{96485 \text{ C}}{\text{mol e}^-} = 1.32 \times 10^6 \text{ C}$$

Finally, if this charge is passed at a rate of 33.46 C/s, the required time is:

$$t = \frac{Q}{I} = \frac{1.32 \times 10^6 \text{ C}}{33.46 \text{ C/s}} = 3.95 \times 10^4 \text{ s} = 11.0 \text{ hr}$$

Check Your Learning

What mass of zinc is required to galvanize the top of a 3.00 m \times 5.50 m sheet of iron to a thickness of 0.100 mm of zinc? If the zinc comes from a solution of $\text{Zn}(\text{NO}_3)_2$ and the current is 25.5 A, how long will it take to galvanize the top of the iron? The density of zinc is 7.140 g/cm³.

Answer: 11.8 kg Zn requires 382 hours.