

Chapter 17

Electrochemistry



Figure 17.1 Electric vehicles contain batteries that can be recharged, thereby using electric energy to bring about a chemical change and vice versa. (credit: modification of work by Robert Couse-Baker)

Chapter Outline

- 17.1 Balancing Oxidation-Reduction Reactions
- 17.2 Galvanic Cells
- 17.3 Standard Reduction Potentials
- 17.4 The Nernst Equation
- 17.5 Batteries and Fuel Cells
- 17.6 Corrosion
- 17.7 Electrolysis

Introduction

Electrochemistry deals with chemical reactions that produce electricity and the changes associated with the passage of electrical current through matter. The reactions involve electron transfer, and so they are oxidation-reduction (or redox) reactions. Many metals may be purified or electroplated using electrochemical methods. Devices such as automobiles, smartphones, electronic tablets, watches, pacemakers, and many others use batteries for power. Batteries use chemical reactions that produce electricity spontaneously and that can be converted into useful work. All electrochemical systems involve the transfer of electrons in a reacting system. In many systems, the reactions occur in a region known as the cell, where the transfer of electrons occurs at electrodes.

17.1 Balancing Oxidation-Reduction Reactions

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

- Define electrochemistry and a number of important associated terms
- Split oxidation-reduction reactions into their oxidation half-reactions and reduction half-reactions
- Produce balanced oxidation-reduction equations for reactions in acidic or basic solution
- Identify oxidizing agents and reducing agents

Electricity refers to a number of phenomena associated with the presence and flow of electric charge. Electricity includes such diverse things as lightning, static electricity, the current generated by a battery as it discharges, and many other influences on our daily lives. The flow or movement of charge is an electric current (**Figure 17.2**). Electrons or ions may carry the charge. The elementary unit of charge is the charge of a proton, which is equal in magnitude to the charge of an electron. The SI unit of charge is the coulomb (C) and the charge of a proton is 1.602×10^{-19} C. The presence of an electric charge generates an electric field. Electric **current** is the rate of flow of charge. The SI unit for electrical current is the SI base unit called the ampere (A), which is a flow rate of 1 coulomb of charge per second ($1\text{ A} = 1\text{ C/s}$). An electric current flows in a path, called an electric **circuit**. In most chemical systems, it is necessary to maintain a closed path for current to flow. The flow of charge is generated by an electrical potential difference, or potential, between two points in the circuit. **Electrical potential** is the ability of the electric field to do work on the charge. The SI unit of electrical potential is the volt (V). When 1 coulomb of charge moves through a potential difference of 1 volt, it gains or loses 1 joule (J) of energy. **Table 17.1** summarizes some of this information about electricity.

Common Electrical Terms		
Quantity	Definition	Measure or Unit
Electric charge	Charge on a proton	1.602×10^{-19} C
Electric current	The movement of charge	ampere = A = 1 C/s
Electric potential	The force trying to move the charge	volt = V = J/C
Electric field	The force acting upon other charges in the vicinity	

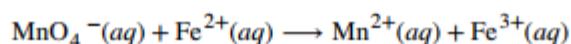
Table 17.1



Figure 17.2 Electricity-related phenomena include lightning, accumulation of static electricity, and current produced by a battery. (credit left: modification of work by Thomas Bresson; credit middle: modification of work by Chris Darling; credit right: modification of work by Windell Oskay)

Electrochemistry studies oxidation-reduction reactions, which were first discussed in an earlier chapter, where we learned that oxidation was the loss of electrons and reduction was the gain of electrons. The reactions discussed tended to be rather simple, and conservation of mass (atom counting by type) and deriving a correctly balanced chemical equation were relatively simple. In this section, we will concentrate on the half-reaction method for balancing oxidation-reduction reactions. The use of half-reactions is important partly for balancing more complicated reactions and partly because many aspects of electrochemistry are easier to discuss in terms of half-reactions. There are alternate methods of balancing these reactions; however, there are no good alternatives to half-reactions for discussing what is occurring in many systems. The **half-reaction method** splits oxidation-reduction reactions into their oxidation "half" and reduction "half" to make finding the overall equation easier.

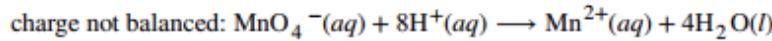
Electrochemical reactions frequently occur in solutions, which could be acidic, basic, or neutral. When balancing oxidation-reduction reactions, the nature of the solution may be important. It helps to see this in an actual problem. Consider the following unbalanced oxidation-reduction reaction in acidic solution:



We can start by collecting the species we have so far into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction. Each of these half-reactions contain the same element in two different oxidation states. The Fe^{2+} has lost an electron to become Fe^{3+} ; therefore, the iron underwent oxidation. The reduction is not as obvious; however, the manganese gained five electrons to change from Mn^{7+} to Mn^{2+} .

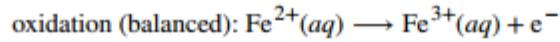


In acidic solution, there are hydrogen ions present, which are often useful in balancing half-reactions. It may be necessary to use the hydrogen ions directly or as a reactant that may react with oxygen to generate water. Hydrogen ions are very important in acidic solutions where the reactants or products contain hydrogen and/or oxygen. In this example, the oxidation half-reaction involves neither hydrogen nor oxygen, so hydrogen ions are not necessary to the balancing. However, the reduction half-reaction does involve oxygen. It is necessary to use hydrogen ions to convert this oxygen to water.



The situation is different in basic solution because the hydrogen ion concentration is lower and the hydroxide ion concentration is higher. After finishing this example, we will examine how basic solutions differ from acidic solutions. A neutral solution may be treated as acidic or basic, though treating it as acidic is usually easier.

The iron atoms in the oxidation half-reaction are balanced (mass balance); however, the charge is unbalanced, since the charges on the ions are not equal. It is necessary to use electrons to balance the charge. The way to balance the charge is by *adding* electrons to one side of the equation. Adding a single electron on the right side gives a balanced oxidation half-reaction:



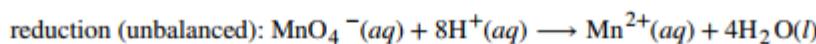
You should check the half-reaction for the number of each atom type and the total charge on each side of the equation. The charges include the actual charges of the ions times the number of ions and the charge on an electron times the number of electrons.

Fe: Does $(1 \times 1) = (1 \times 1)$? Yes.

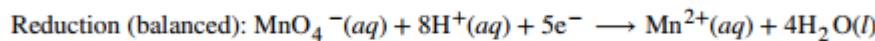
Charge: Does $[1 \times (+2)] = [1 \times (+3) + 1 \times (-1)]$? Yes.

If the atoms and charges balance, the half-reaction is balanced. In oxidation half-reactions, electrons appear as products (on the right). As discussed in the earlier chapter, since iron underwent oxidation, iron is the reducing agent.

Now return to the reduction half-reaction equation:



The atoms are balanced (mass balance), so it is now necessary to check for charge balance. The total charge on the left of the reaction arrow is $[(-1) \times (1) + (8) \times (+1)]$, or +7, while the total charge on the right side is $[(1) \times (+2) + (4) \times (0)]$, or +2. The difference between +7 and +2 is five; therefore, it is necessary to add five electrons to the left side to achieve charge balance.



You should check this half-reaction for each atom type and for the charge, as well:

Mn: Does $(1 \times 1) = (1 \times 1)$? Yes.

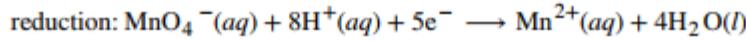
H: Does $(8 \times 1) = (4 \times 2)$? Yes.

O: Does $(1 \times 4) = (4 \times 1)$? Yes.

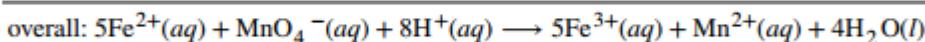
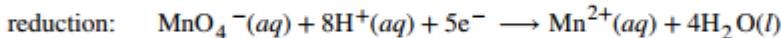
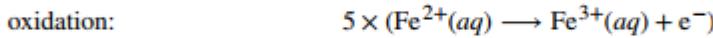
Charge: Does $[1 \times (-1) + 8 \times (+1) + 5 \times (-1)] = [1 \times (+2)]$? Yes.

Now that this half-reaction is balanced, it is easy to see it involves reduction because electrons were gained when MnO_4^- was reduced to Mn^{2+} . In all reduction half-reactions, electrons appear as reactants (on the left side). As discussed in the earlier chapter, the species that was reduced, MnO_4^- in this case, is also called the oxidizing agent.

We now have two balanced half-reactions.



It is now necessary to combine the two halves to produce a whole reaction. The key to combining the half-reactions is the electrons. The electrons lost during oxidation must go somewhere. These electrons go to cause reduction. The number of electrons transferred from the oxidation half-reaction to the reduction half-reaction must be equal. There can be no missing or excess electrons. In this example, the oxidation half-reaction generates one electron, while the reduction half-reaction requires five. The lowest common multiple of one and five is five; therefore, it is necessary to multiply every term in the oxidation half-reaction by five and every term in the reduction half-reaction by one. (In this case, the multiplication of the reduction half-reaction generates no change; however, this will not always be the case.) The multiplication of the two half-reactions by the appropriate factor followed by addition of the two halves gives



The electrons do not appear in the final answer because the oxidation electrons are the same electrons as the reduction electrons and they “cancel.” Carefully check each side of the overall equation to verify everything was combined correctly:

Fe: Does $(5 \times 1) = (5 \times 1)$? Yes.

Mn: Does $(1 \times 1) = (1 \times 1)$? Yes.

H: Does $(8 \times 1) = (4 \times 2)$? Yes.

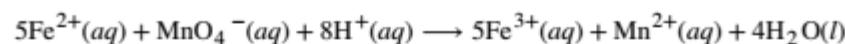
O: Does $(1 \times 4) = (4 \times 1)$? Yes.

Charge: Does $[5 \times (+2) + 1 \times (-1) + 8 \times (+1)] = [5 \times (+3) + 1 \times (+2)]$? Yes.

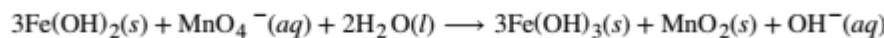
Everything checks, so this is the overall equation in acidic solution. If something does not check, the most common error occurs during the multiplication of the individual half-reactions.

Now suppose we wanted the solution to be basic. Recall that basic solutions have excess hydroxide ions. Some of these hydroxide ions will react with hydrogen ions to produce water. The simplest way to generate the balanced

overall equation in basic solution is to start with the balanced equation in acidic solution, then “convert” it to the equation for basic solution. However, it is necessary to exercise caution when doing this, as many reactants behave differently under basic conditions and many metal ions will precipitate as the metal hydroxide. We just produced the following reaction, which we want to change to a basic reaction:



However, under basic conditions, MnO_4^- normally reduces to MnO_2 and iron will be present as either Fe(OH)_2 or Fe(OH)_3 . For these reasons, under basic conditions, this reaction will be



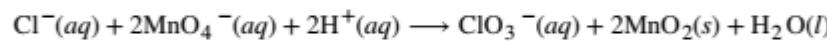
(Under very basic conditions MnO_4^- will reduce to MnO_4^{2-} , instead of MnO_2 .)

It is still possible to balance any oxidation-reduction reaction as an acidic reaction and then, when necessary, convert the equation to a basic reaction. This will work if the acidic and basic reactants and products are the same or if the basic reactants and products are used before the conversion from acidic or basic. There are very few examples in which the acidic and basic reactions will involve the same reactants and products. However, balancing a basic reaction as acidic and then converting to basic will work. To convert to a basic reaction, it is necessary to add the same number of hydroxide ions to each side of the equation so that all the hydrogen ions (H^+) are removed and mass balance is maintained. Hydrogen ion combines with hydroxide ion (OH^-) to produce water.

Let us now try a basic equation. We will start with the following basic reaction:



Balancing this as acid gives



In this case, it is necessary to add two hydroxide ions to each side of the equation to convert the two hydrogen ions on the left into water:



Note that both sides of the equation show water. Simplifying should be done when necessary, and gives the desired equation. In this case, it is necessary to remove one H_2O from each side of the reaction arrows.



Again, check each side of the overall equation to make sure there are no errors:

Cl: Does $(1 \times 1) = (1 \times 1)$? Yes.

Mn: Does $(2 \times 1) = (2 \times 1)$? Yes.

H: Does $(1 \times 2) = (2 \times 1)$? Yes.

O: Does $(2 \times 4 + 1 \times 1) = (3 \times 1 + 2 \times 2 + 2 \times 1)$? Yes.

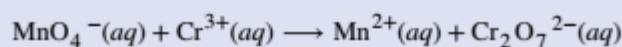
Charge: Does $[1 \times (-1) + 2 \times (-1)] = [1 \times (-1) + 2 \times (-1)]$? Yes.

Everything checks, so this is the overall equation in basic solution.

Example 17.1

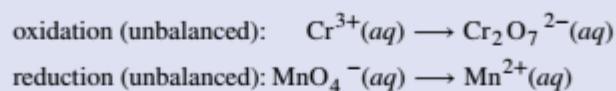
Balancing Acidic Oxidation-Reduction Reactions

Balance the following reaction equation in acidic solution:

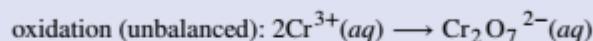


Solution

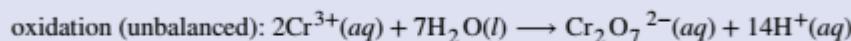
This is an oxidation-reduction reaction, so start by collecting the species given into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction.



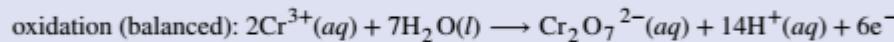
Starting with the oxidation half-reaction, we can balance the chromium



In acidic solution, we can use or generate hydrogen ions (H^+). Adding seven water molecules to the left side provides the necessary oxygen; the “left over” hydrogen appears as 14 H^+ on the right:



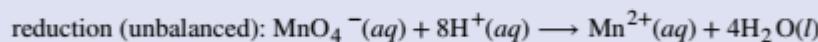
The left side of the equation has a total charge of $[2 \times (+3) = +6]$, and the right side a total charge of $[-2 + 14 \times (+1) = +12]$. The difference is six; adding six electrons to the right side produces a mass- and charge-balanced oxidation half-reaction (in acidic solution):



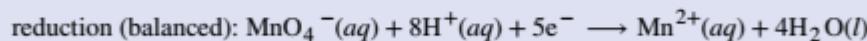
Checking the half-reaction:

- Cr: Does $(2 \times 1) = (1 \times 2)$? Yes.
- H: Does $(7 \times 2) = (14 \times 1)$? Yes.
- O: Does $(7 \times 1) = (1 \times 7)$? Yes.
- Charge: Does $[2 \times (+3)] = [1 \times (-2) + 14 \times (+1) + 6 \times (-1)]$? Yes.

Now work on the reduction. It is necessary to convert the four oxygen atoms in the permanganate into four water molecules. To do this, add eight H^+ to convert the oxygen into four water molecules:



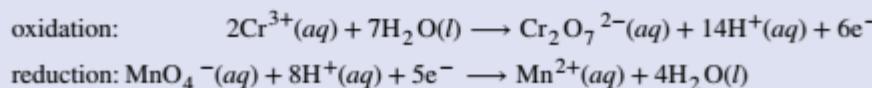
Then add five electrons to the left side to balance the charge:



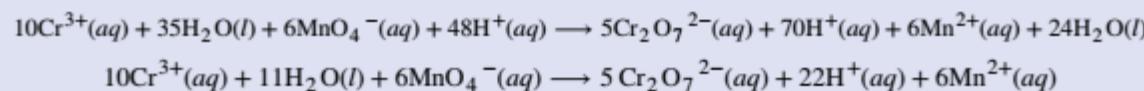
Make sure to check the half-reaction:

- Mn: Does $(1 \times 1) = (1 \times 1)$? Yes.
- H: Does $(8 \times 1) = (4 \times 2)$? Yes.
- O: Does $(1 \times 4) = (4 \times 1)$? Yes.
- Charge: Does $[1 \times (-1) + 8 \times (+1) + 5 \times (-1)] = [1 \times (+2)]$? Yes.

Collecting what we have so far:



The least common multiple for the electrons is 30, so multiply the oxidation half-reaction by five, the reduction half-reaction by six, combine, and simplify:



Checking each side of the equation:

Mn: Does $(6 \times 1) = (6 \times 1)$? Yes.

Cr: Does $(10 \times 1) = (5 \times 2)$? Yes.

H: Does $(11 \times 2) = (22 \times 1)$? Yes.

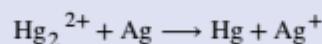
O: Does $(11 \times 1 + 6 \times 4) = (5 \times 7)$? Yes.

Charge: Does $[10 \times (+3) + 6 \times (-1)] = [5 \times (-2) + 22 \times (+1) + 6 \times (+2)]$? Yes.

This is the balanced equation in acidic solution.

Check your learning

Balance the following equation in acidic solution:

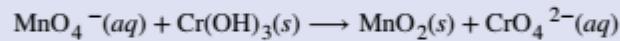


Answer: $\text{Hg}_2^{2+}(aq) + 2\text{Ag}(s) \longrightarrow 2\text{Hg}(l) + 2\text{Ag}^+(aq)$

Example 17.2

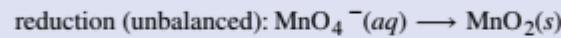
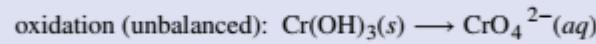
Balancing Basic Oxidation-Reduction Reactions

Balance the following reaction equation in basic solution:

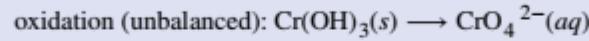


Solution

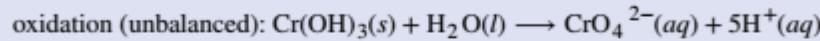
This is an oxidation-reduction reaction, so start by collecting the species given into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction



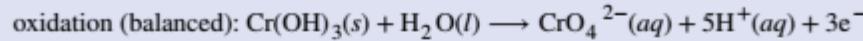
Starting with the oxidation half-reaction, we can balance the chromium



In acidic solution, we can use or generate hydrogen ions (H^+). Adding one water molecule to the left side provides the necessary oxygen; the “left over” hydrogen appears as five H^+ on the right side:



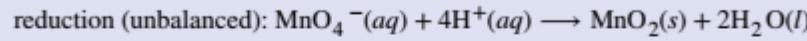
The left side of the equation has a total charge of [0], and the right side a total charge of $[-2 + 5 \times (+1) = +3]$. The difference is three, adding three electrons to the right side produces a mass- and charge-balanced oxidation half-reaction (in acidic solution):



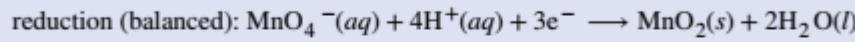
Checking the half-reaction:

Cr: Does $(1 \times 1) = (1 \times 1)$? Yes.
 H: Does $(1 \times 3 + 1 \times 2) = (5 \times 1)$? Yes.
 O: Does $(1 \times 3 + 1 \times 1) = (4 \times 1)$? Yes.
 Charge: Does $[0 = [1 \times (-2) + 5 \times (+1) + 3 \times (-1)]]$? Yes.

Now work on the reduction. It is necessary to convert the four O atoms in the MnO_4^- minus the two O atoms in MnO_2 into two water molecules. To do this, add four H^+ to convert the oxygen into two water molecules:



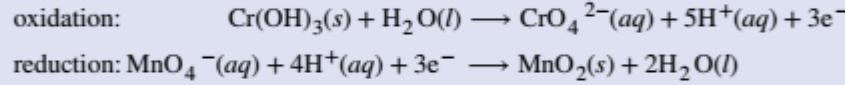
Then add three electrons to the left side to balance the charge:



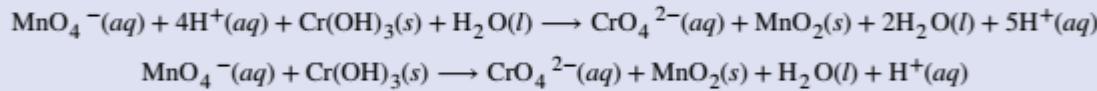
Make sure to check the half-reaction:

Mn: Does $(1 \times 1) = (1 \times 1)$? Yes.
 H: Does $(4 \times 1) = (2 \times 2)$? Yes.
 O: Does $(1 \times 4) = (1 \times 2 + 2 \times 1)$? Yes.
 Charge: Does $[1 \times (-1) + 4 \times (+1) + 3 \times (-1)] = [0]$? Yes.

Collecting what we have so far:



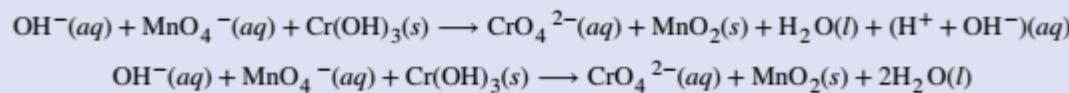
In this case, both half reactions involve the same number of electrons; therefore, simply add the two half-reactions together.



Checking each side of the equation:

Mn: Does $(1 \times 1) = (1 \times 1)$? Yes.
 Cr: Does $(1 \times 1) = (1 \times 1)$? Yes.
 H: Does $(1 \times 3) = (2 \times 1 + 1 \times 1)$? Yes.
 O: Does $(1 \times 4 + 1 \times 3) = (1 \times 4 + 1 \times 2 + 1 \times 1)$? Yes.
 Charge: Does $[1 \times (-1)] = [1 \times (-2) + 1 \times (+1)]$? Yes.

This is the balanced equation in acidic solution. For a basic solution, add one hydroxide ion to each side and simplify:



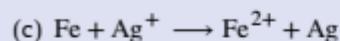
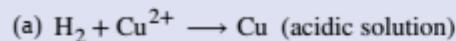
Checking each side of the equation:

Mn: Does $(1 \times 1) = (1 \times 1)$? Yes.
 Cr: Does $(1 \times 1) = (1 \times 1)$? Yes.
 H: Does $(1 \times 1 + 1 \times 3) = (2 \times 2)$? Yes.
 O: Does $(1 \times 1 + 1 \times 4 + 1 \times 3) = (1 \times 4 + 1 \times 2 + 2 \times 1)$? Yes.
 Charge: Does $[1 \times (-1) + 1 \times (-1)] = [1 \times (-2)]$? Yes.

This is the balanced equation in basic solution.

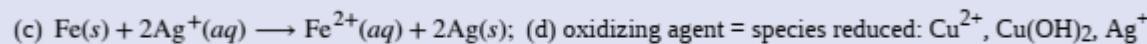
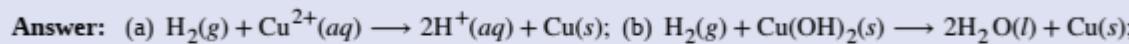
Check Your Learning

Balance the following in the type of solution indicated.



(d) Identify the oxidizing agents in reactions (a), (b), and (c).

(e) Identify the reducing agents in reactions (a), (b), and (c).



(e) reducing agent = species oxidized: H_2 , H_2 , Fe .

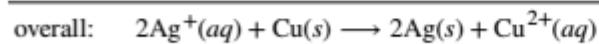
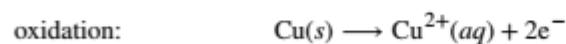
17.2 Galvanic Cells

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

- Use cell notation to describe galvanic cells
- Describe the basic components of galvanic cells

Galvanic cells, also known as **voltaic cells**, are electrochemical cells in which spontaneous oxidation-reduction reactions produce electrical energy. In writing the equations, it is often convenient to separate the oxidation-reduction reactions into half-reactions to facilitate balancing the overall equation and to emphasize the actual chemical transformations.

Consider what happens when a clean piece of copper metal is placed in a solution of silver nitrate (**Figure 17.3**). As soon as the copper metal is added, silver metal begins to form and copper ions pass into the solution. The blue color of the solution on the far right indicates the presence of copper ions. The reaction may be split into its two half-reactions. Half-reactions separate the oxidation from the reduction, so each can be considered individually.



The equation for the reduction half-reaction had to be doubled so the number electrons “gained” in the reduction half-reaction equaled the number of electrons “lost” in the oxidation half-reaction.

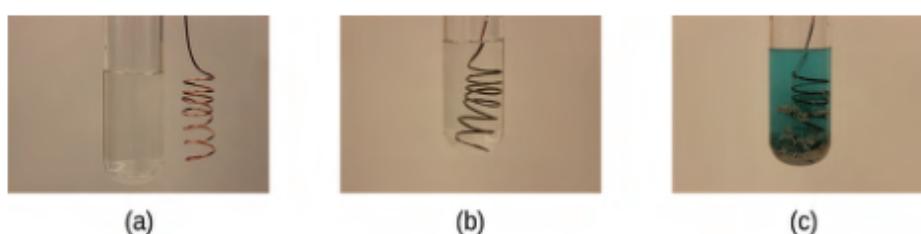


Figure 17.3 When a clean piece of copper metal is placed into a clear solution of silver nitrate (a), an oxidation-reduction reaction occurs that results in the exchange of Cu^{2+} for Ag^+ ions in solution. As the reaction proceeds (b), the solution turns blue (c) because of the copper ions present, and silver metal is deposited on the copper strip as the silver ions are removed from solution. (credit: modification of work by Mark Ott)

Galvanic or voltaic cells involve spontaneous electrochemical reactions in which the half-reactions are separated ([Figure 17.4](#)) so that current can flow through an external wire. The beaker on the left side of the figure is called a half-cell, and contains a 1 M solution of copper(II) nitrate [$\text{Cu}(\text{NO}_3)_2$] with a piece of copper metal partially submerged in the solution. The copper metal is an electrode. The copper is undergoing oxidation; therefore, the copper electrode is the **anode**. The anode is connected to a voltmeter with a wire and the other terminal of the voltmeter is connected to a silver electrode by a wire. The silver is undergoing reduction; therefore, the silver electrode is the **cathode**. The half-cell on the right side of the figure consists of the silver electrode in a 1 M solution of silver nitrate (AgNO_3). At this point, no current flows—that is, no significant movement of electrons through the wire occurs because the circuit is open. The circuit is closed using a salt bridge, which transmits the current with moving ions. The salt bridge consists of a concentrated, nonreactive, electrolyte solution such as the sodium nitrate (NaNO_3) solution used in this example. As electrons flow from left to right through the electrode and wire, nitrate ions (anions) pass through the porous plug on the left into the copper(II) nitrate solution. This keeps the beaker on the left electrically neutral by neutralizing the charge on the copper(II) ions that are produced in the solution as the copper metal is oxidized. At the same time, the nitrate ions are moving to the left, sodium ions (cations) move to the right, through the porous plug, and into the silver nitrate solution on the right. These added cations “replace” the silver ions that are removed from the solution as they were reduced to silver metal, keeping the beaker on the right electrically neutral. Without the salt bridge, the compartments would not remain electrically neutral and no significant current would flow. However, if the two compartments are in direct contact, a salt bridge is not necessary. The instant the circuit is completed, the voltmeter reads +0.46 V, this is called the **cell potential**. The cell potential is created when the two dissimilar metals are connected, and is a measure of the energy per unit charge available from the oxidation-reduction reaction. The volt is the derived SI unit for electrical potential

$$\text{volt} = V = \frac{\text{kg}/\text{m}^2}{\text{A}/\text{s}^3} = \frac{\text{J}}{\text{A}/\text{s}} = \frac{\text{J}}{\text{C}}$$

In this equation, A is the current in amperes and C the charge in coulombs. Note that volts must be multiplied by the charge in coulombs (C) to obtain the energy in joules (J).

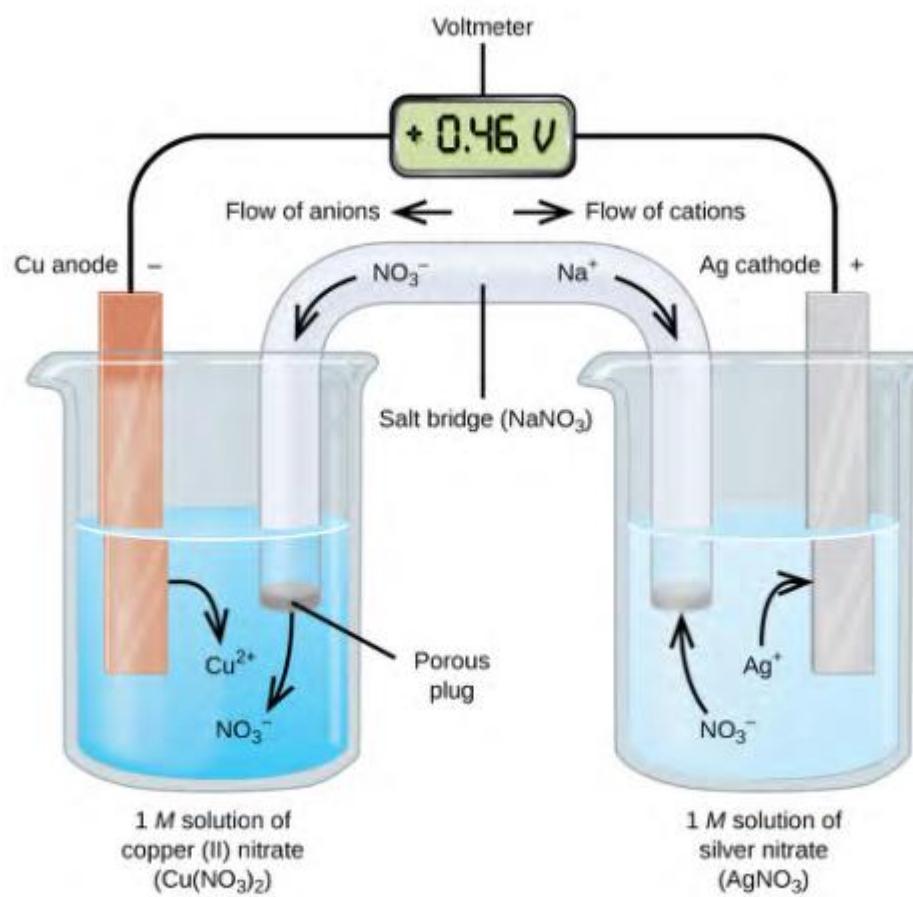


Figure 17.4 In this standard galvanic cell, the half-cells are separated; electrons can flow through an external wire and become available to do electrical work.

When the electrochemical cell is constructed in this fashion, a positive cell potential indicates a spontaneous reaction and that the electrons are flowing from the left to the right. There is a lot going on in **Figure 17.4**, so it is useful to summarize things for this system:

- Electrons flow from the anode to the cathode: left to right in the standard galvanic cell in the figure.
- The electrode in the left half-cell is the anode because oxidation occurs here. The name refers to the flow of anions in the salt bridge toward it.
- The electrode in the right half-cell is the cathode because reduction occurs here. The name refers to the flow of cations in the salt bridge toward it.
- Oxidation occurs at the anode (the left half-cell in the figure).
- Reduction occurs at the cathode (the right half-cell in the figure).
- The cell potential, +0.46 V, in this case, results from the inherent differences in the nature of the materials used to make the two half-cells.
- The salt bridge must be present to close (complete) the circuit and both an oxidation and reduction must occur for current to flow.

There are many possible galvanic cells, so a shorthand notation is usually used to describe them. The **cell notation** (sometimes called a cell diagram) provides information about the various species involved in the reaction. This

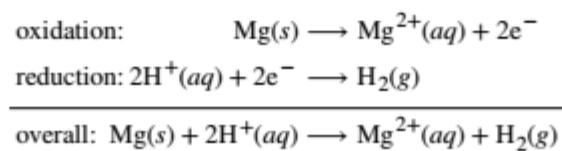
notation also works for other types of cells. A vertical line, |, denotes a phase boundary and a double line, ||, the salt bridge. Information about the anode is written to the left, followed by the anode solution, then the salt bridge (when present), then the cathode solution, and, finally, information about the cathode to the right. The cell notation for the galvanic cell in [Figure 17.4](#) is then



Note that spectator ions are not included and that the simplest form of each half-reaction was used. When known, the initial concentrations of the various ions are usually included.

One of the simplest cells is the Daniell cell. It is possible to construct this battery by placing a copper electrode at the bottom of a jar and covering the metal with a copper sulfate solution. A zinc sulfate solution is floated on top of the copper sulfate solution; then a zinc electrode is placed in the zinc sulfate solution. Connecting the copper electrode to the zinc electrode allows an electric current to flow. This is an example of a cell without a salt bridge, and ions may flow across the interface between the two solutions.

Some oxidation-reduction reactions involve species that are poor conductors of electricity, and so an electrode is used that does not participate in the reactions. Frequently, the electrode is platinum, gold, or graphite, all of which are inert to many chemical reactions. One such system is shown in [Figure 17.5](#). Magnesium undergoes oxidation at the anode on the left in the figure and hydrogen ions undergo reduction at the cathode on the right. The reaction may be summarized as



The cell used an inert platinum wire for the cathode, so the cell notation is

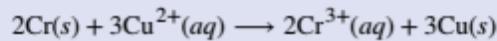


The magnesium electrode is an **active electrode** because it participates in the oxidation-reduction reaction. **Inert electrodes**, like the platinum electrode in [Figure 17.5](#), do not participate in the oxidation-reduction reaction and are present so that current can flow through the cell. Platinum or gold generally make good inert electrodes because they are chemically unreactive.

Example 17.3

Using Cell Notation

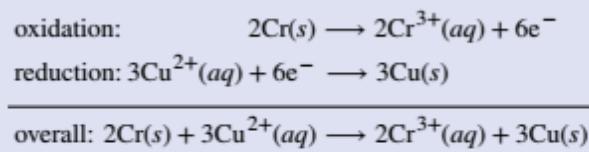
Consider a galvanic cell consisting of



Write the oxidation and reduction half-reactions and write the reaction using cell notation. Which reaction occurs at the anode? The cathode?

Solution

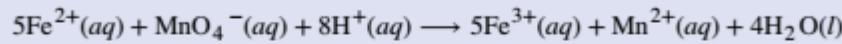
By inspection, Cr is oxidized when three electrons are lost to form Cr^{3+} , and Cu^{2+} is reduced as it gains two electrons to form Cu. Balancing the charge gives



Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. No concentrations were specified so: $\text{Cr}(s) \mid \text{Cr}^{3+}(aq) \parallel \text{Cu}^{2+}(aq) \mid \text{Cu}(s)$. Oxidation occurs at the anode and reduction at the cathode.

Using Cell Notation

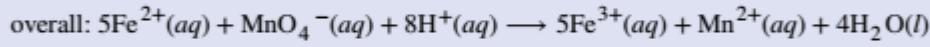
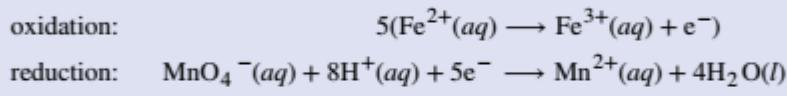
Consider a galvanic cell consisting of



Write the oxidation and reduction half-reactions and write the reaction using cell notation. Which reaction occurs at the anode? The cathode?

Solution

By inspection, Fe^{2+} undergoes oxidation when one electron is lost to form Fe^{3+} , and MnO_4^- is reduced as it gains five electrons to form Mn^{2+} . Balancing the charge gives

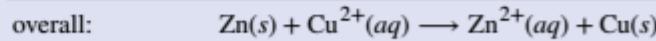
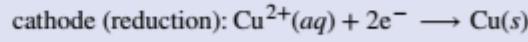


Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. It is necessary to use an inert electrode, such as platinum, because there is no metal present to conduct the electrons from the anode to the cathode. No concentrations were specified so: $\text{Pt}(s) \mid \text{Fe}^{2+}(aq), \text{Fe}^{3+}(aq) \parallel \text{MnO}_4^-(aq), \text{H}^+(aq), \text{Mn}^{2+}(aq) \mid \text{Pt}(s)$. Oxidation occurs at the anode and reduction at the cathode.

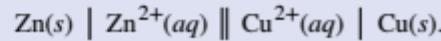
Check Your Learning

Use cell notation to describe the galvanic cell where copper(II) ions are reduced to copper metal and zinc metal is oxidized to zinc ions.

Answer: From the information given in the problem:



Using cell notation:



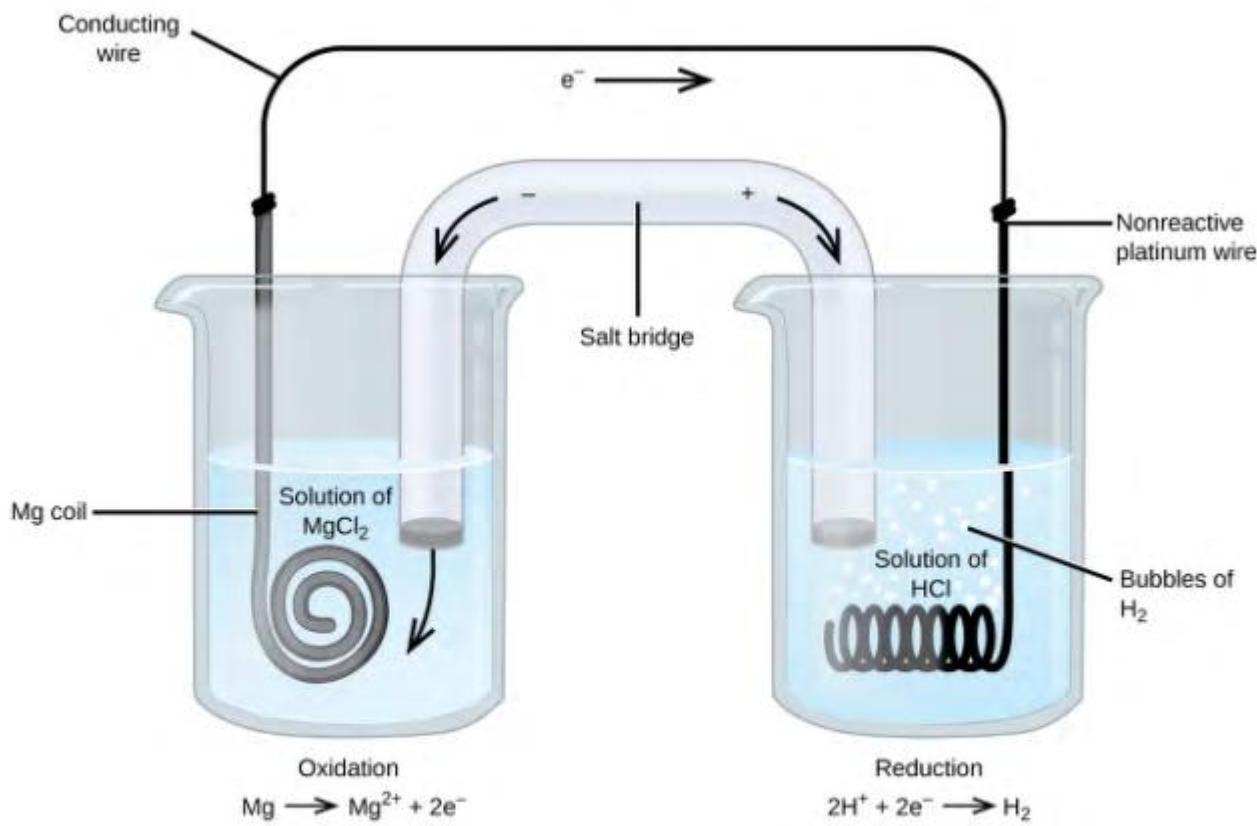


Figure 17.5 The oxidation of magnesium to magnesium ion occurs in the beaker on the left side in this apparatus; the reduction of hydrogen ions to hydrogen occurs in the beaker on the right. A nonreactive, or inert, platinum wire allows electrons from the left beaker to move into the right beaker. The overall reaction is:

$\text{Mg} + 2\text{H}^+ \rightarrow \text{Mg}^{2+} + \text{H}_2$, which is represented in cell notation as:

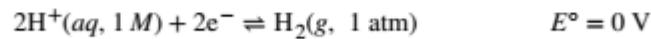
$\text{Mg}(s) \mid \text{Mg}^{2+}(aq) \parallel \text{H}^+(aq) \mid \text{H}_2(g) \mid \text{Pt}(s)$.

17.3 Standard Reduction Potentials

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

- Determine standard cell potentials for oxidation-reduction reactions
- Use standard reduction potentials to determine the better oxidizing or reducing agent from among several possible choices

The cell potential in **Figure 17.4** (+0.46 V) results from the difference in the electrical potentials for each electrode. While it is impossible to determine the electrical potential of a single electrode, we can assign an electrode the value of zero and then use it as a reference. The electrode chosen as the zero is shown in **Figure 17.6** and is called the **standard hydrogen electrode (SHE)**. The SHE consists of 1 atm of hydrogen gas bubbled through a 1 M HCl solution, usually at room temperature. Platinum, which is chemically inert, is used as the electrode. The reduction half-reaction chosen as the reference is



E° is the standard reduction potential. The superscript “°” on the E denotes standard conditions (1 bar or 1 atm for gases, 1 M for solutes). The voltage is defined as zero for all temperatures.

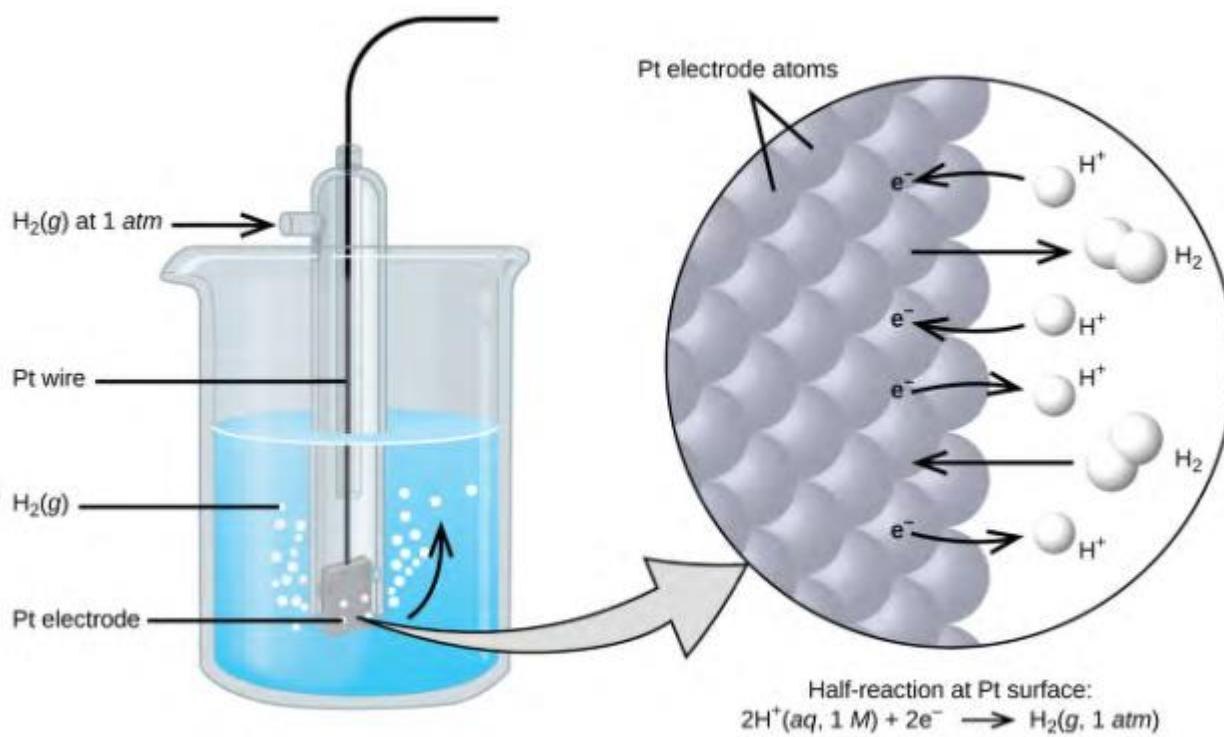
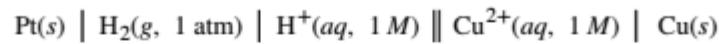
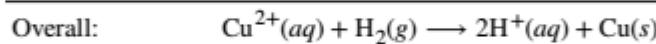
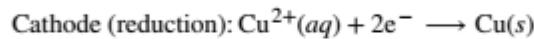


Figure 17.6 Hydrogen gas at 1 atm is bubbled through 1 M HCl solution. Platinum, which is inert to the action of the 1 M HCl, is used as the electrode. Electrons on the surface of the electrode combine with H^+ in solution to produce hydrogen gas.

A galvanic cell consisting of a SHE and Cu^{2+}/Cu half-cell can be used to determine the standard reduction potential for Cu^{2+} (Figure 17.7). In cell notation, the reaction is



Electrons flow from the anode to the cathode. The reactions, which are reversible, are



The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is necessary because oxidation is the reverse of reduction.

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \\ +0.34 \text{ V} &= E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{H}^{+}/\text{H}_2}^{\circ} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - 0 = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} \end{aligned}$$

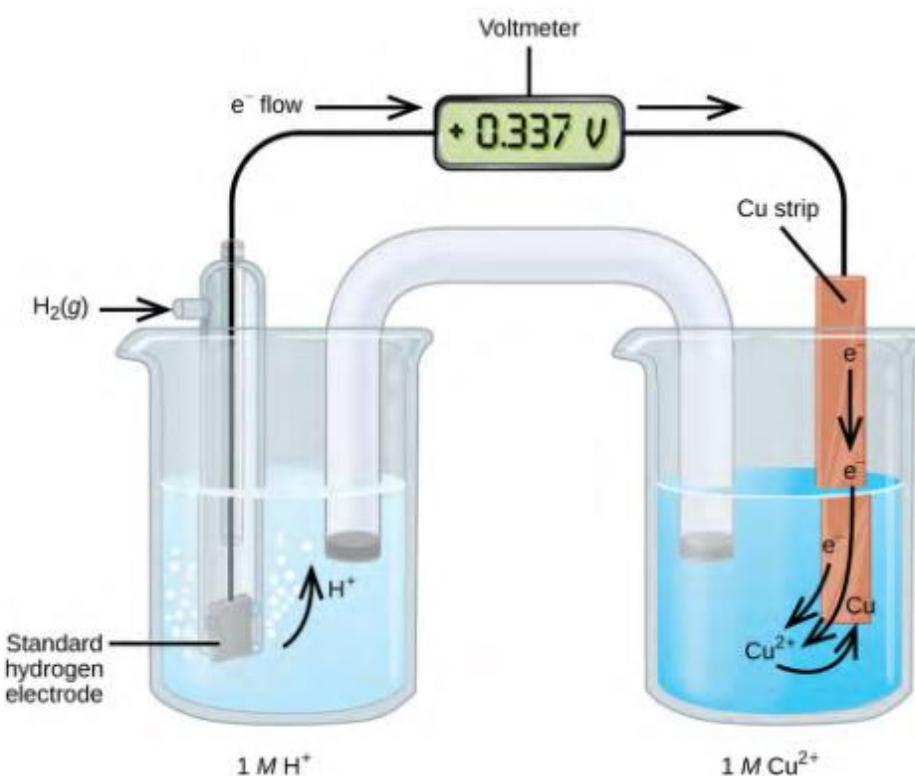
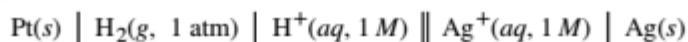
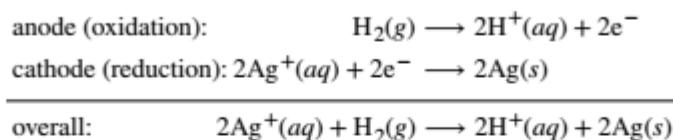


Figure 17.7 A galvanic cell can be used to determine the standard reduction potential of Cu^{2+} .

Using the SHE as a reference, other standard reduction potentials can be determined. Consider the cell shown in **Figure 17.8**, where



Electrons flow from left to right, and the reactions are

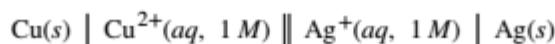


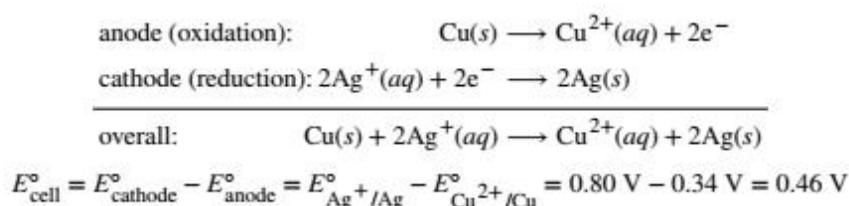
The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is needed because oxidation is the reverse of reduction.

$$\begin{aligned} E_{\text{cell}}^\circ &= E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ \\ +0.80 \text{ V} &= E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{H}^+/\text{H}_2}^\circ = E_{\text{Ag}^+/\text{Ag}}^\circ - 0 = E_{\text{Ag}^+/\text{Ag}}^\circ \end{aligned}$$

It is important to note that the potential is *not* doubled for the cathode reaction.

The SHE is rather dangerous and rarely used in the laboratory. Its main significance is that it established the zero for standard reduction potentials. Once determined, standard reduction potentials can be used to determine the **standard cell potential**, E_{cell}° , for any cell. For example, for the cell shown in **Figure 17.4**,





Again, note that when calculating E_{cell}° , standard reduction potentials always remain the same even when a half-reaction is multiplied by a factor. Standard reduction potentials for selected reduction reactions are shown in **Table 17.2**. A more complete list is provided in **Appendix L**.

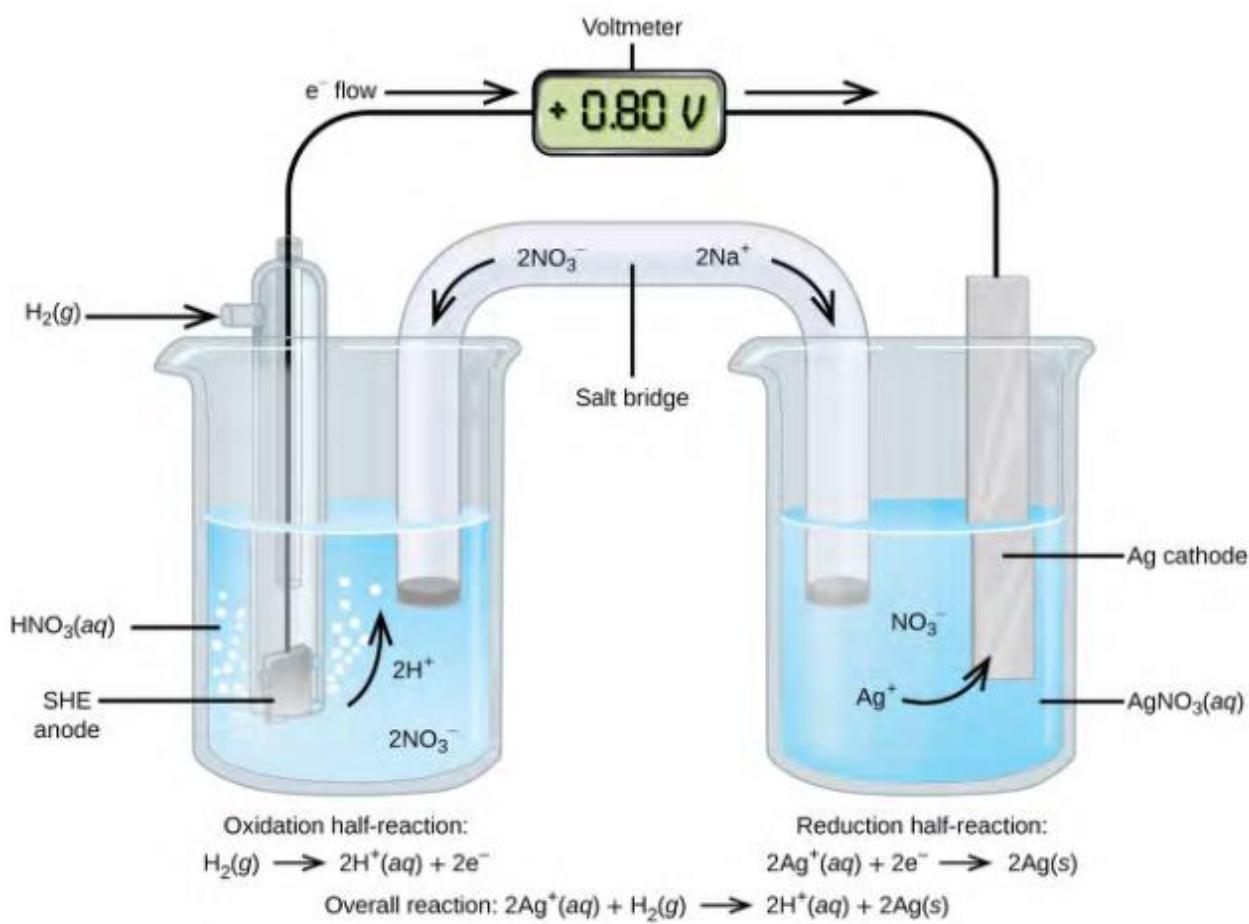


Figure 17.8 A galvanic cell can be used to determine the standard reduction potential of Ag^+ . The SHE on the left is the anode and assigned a standard reduction potential of zero.

Selected Standard Reduction Potentials at 25 °C

Half-Reaction	E° (V)
$\text{F}_2(g) + 2e^- \longrightarrow 2\text{F}^-(aq)$	+2.866
$\text{PbO}_2(s) + \text{SO}_4^{2-}(aq) + 4\text{H}^+(aq) + 2e^- \longrightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}(l)$	+1.69

Table 17.2

Selected Standard Reduction Potentials at 25 °C

Half-Reaction	E° (V)
$\text{MnO}_4^-(aq) + 8\text{H}^+(aq) + 5\text{e}^- \longrightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l)$	+1.507
$\text{Au}^{3+}(aq) + 3\text{e}^- \longrightarrow \text{Au}(s)$	+1.498
$\text{Cl}_2(g) + 2\text{e}^- \longrightarrow 2\text{Cl}^-(aq)$	+1.35827
$\text{O}_2(g) + 4\text{H}^+(aq) + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}(l)$	+1.229
$\text{Pt}^{2+}(aq) + 2\text{e}^- \longrightarrow \text{Pt}(s)$	+1.20
$\text{Br}_2(aq) + 2\text{e}^- \longrightarrow 2\text{Br}^-(aq)$	+1.0873
$\text{Ag}^+(aq) + \text{e}^- \longrightarrow \text{Ag}(s)$	+0.7996
$\text{Hg}_2^{2+}(aq) + 2\text{e}^- \longrightarrow 2\text{Hg}(l)$	+0.7973
$\text{Fe}^{3+}(aq) + \text{e}^- \longrightarrow \text{Fe}^{2+}(aq)$	+0.771
$\text{MnO}_4^-(aq) + 2\text{H}_2\text{O}(l) + 3\text{e}^- \longrightarrow \text{MnO}_2(s) + 4\text{OH}^-(aq)$	+0.558
$\text{I}_2(s) + 2\text{e}^- \longrightarrow 2\text{I}^-(aq)$	+0.5355
$\text{NiO}_2(s) + 2\text{H}_2\text{O}(l) + 2\text{e}^- \longrightarrow \text{Ni(OH)}_2(s) + 2\text{OH}^-(aq)$	+0.49
$\text{Cu}^{2+}(aq) + 2\text{e}^- \longrightarrow \text{Cu}(s)$	+0.337
$\text{Hg}_2\text{Cl}_2(s) + 2\text{e}^- \longrightarrow 2\text{Hg}(l) + 2\text{Cl}^-(aq)$	+0.26808
$\text{AgCl}(s) + 2\text{e}^- \longrightarrow \text{Ag}(s) + \text{Cl}^-(aq)$	+0.22233
$\text{Sn}^{4+}(aq) + 2\text{e}^- \longrightarrow \text{Sn}^{2+}(aq)$	+0.151
$2\text{H}^+(aq) + 2\text{e}^- \longrightarrow \text{H}_2(g)$	0.00
$\text{Pb}^{2+}(aq) + 2\text{e}^- \longrightarrow \text{Pb}(s)$	-0.126
$\text{Sn}^{2+}(aq) + 2\text{e}^- \longrightarrow \text{Sn}(s)$	-0.1262
$\text{Ni}^{2+}(aq) + 2\text{e}^- \longrightarrow \text{Ni}(s)$	-0.257
$\text{Co}^{2+}(aq) + 2\text{e}^- \longrightarrow \text{Co}(s)$	-0.28

Table 17.2

Selected Standard Reduction Potentials at 25 °C

Half-Reaction	E° (V)
$\text{PbSO}_4(s) + 2\text{e}^- \longrightarrow \text{Pb}(s) + \text{SO}_4^{2-}(aq)$	-0.3505
$\text{Cd}^{2+}(aq) + 2\text{e}^- \longrightarrow \text{Cd}(s)$	-0.4030
$\text{Fe}^{2+}(aq) + 2\text{e}^- \longrightarrow \text{Fe}(s)$	-0.447
$\text{Cr}^{3+}(aq) + 3\text{e}^- \longrightarrow \text{Cr}(s)$	-0.744
$\text{Mn}^{2+}(aq) + 2\text{e}^- \longrightarrow \text{Mn}(s)$	-1.185
$\text{Zn(OH)}_2(s) + 2\text{e}^- \longrightarrow \text{Zn}(s) + 2\text{OH}^-(aq)$	-1.245
$\text{Zn}^{2+}(aq) + 2\text{e}^- \longrightarrow \text{Zn}(s)$	-0.7618
$\text{Al}^{3+}(aq) + 3\text{e}^- \longrightarrow \text{Al}(s)$	-1.662
$\text{Mg}^{2+}(aq) + 2\text{e}^- \longrightarrow \text{Mg}(s)$	-2.372
$\text{Na}^+(aq) + \text{e}^- \longrightarrow \text{Na}(s)$	-2.71
$\text{Ca}^{2+}(aq) + 2\text{e}^- \longrightarrow \text{Ca}(s)$	-2.868
$\text{Ba}^{2+}(aq) + 2\text{e}^- \longrightarrow \text{Ba}(s)$	-2.912
$\text{K}^+(aq) + \text{e}^- \longrightarrow \text{K}(s)$	-2.931
$\text{Li}^+(aq) + \text{e}^- \longrightarrow \text{Li}(s)$	-3.04

Table 17.2

Tables like this make it possible to determine the standard cell potential for many oxidation-reduction reactions.

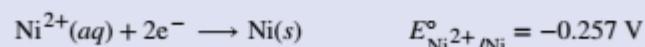
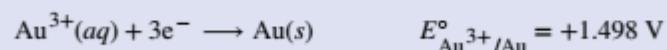
Example 17.4

Cell Potentials from Standard Reduction Potentials

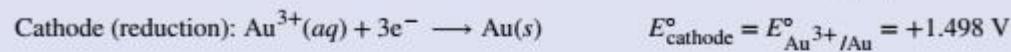
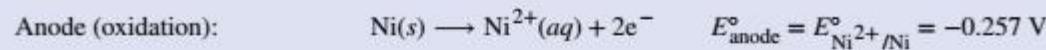
What is the standard cell potential for a galvanic cell that consists of Au^{3+}/Au and Ni^{2+}/Ni half-cells? Identify the oxidizing and reducing agents.

Solution

Using **Table 17.2**, the reactions involved in the galvanic cell, both written as reductions, are



Galvanic cells have positive cell potentials, and all the reduction reactions are reversible. The reaction at the anode will be the half-reaction with the smaller or more negative standard reduction potential. Reversing the reaction at the anode (to show the oxidation) but *not* its standard reduction potential gives:



The least common factor is six, so the overall reaction is



The reduction potentials are *not* scaled by the stoichiometric coefficients when calculating the cell potential, and the unmodified standard reduction potentials must be used.

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 1.498 \text{ V} - (-0.257 \text{ V}) = 1.755 \text{ V}$$

From the half-reactions, Ni is oxidized, so it is the reducing agent, and Au³⁺ is reduced, so it is the oxidizing agent.

Check Your Learning

A galvanic cell consists of a Mg electrode in 1 M Mg(NO₃)₂ solution and a Ag electrode in 1 M AgNO₃ solution. Calculate the standard cell potential at 25 °C.

Answer:

$$\text{Mg}(s) + 2\text{Ag}^{+}(aq) \longrightarrow \text{Mg}^{2+}(aq) + 2\text{Ag}(s) \quad E_{\text{cell}}^{\circ} = 0.7996 \text{ V} - (-2.372 \text{ V}) = 3.172 \text{ V}$$

17.4 The Nernst Equation

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

- Relate cell potentials to free energy changes
- Use the Nernst equation to determine cell potentials at nonstandard conditions
- Perform calculations that involve converting between cell potentials, free energy changes, and equilibrium constants

We will now extend electrochemistry by determining the relationship between E_{cell}° and the thermodynamics quantities such as ΔG° (Gibbs free energy) and K (the equilibrium constant). In galvanic cells, chemical energy is converted into electrical energy, which can do work. The electrical work is the product of the charge transferred multiplied by the potential difference (voltage):

$$\text{electrical work} = \text{volts} \times (\text{charge in coulombs}) = J$$

The charge on 1 mole of electrons is given by **Faraday's constant (F)**

$$F = \frac{6.022 \times 10^{23} e^-}{\text{mol}} \times \frac{1.602 \times 10^{-19} \text{ C}}{e^-} = 9.648 \times 10^4 \frac{\text{C}}{\text{mol}} = 9.684 \times 10^4 \frac{\text{J}}{\text{V}\cdot\text{mol}}$$

$$\text{total charge} = (\text{number of moles of } e^-) \times F = nF$$

In this equation, n is the number of moles of electrons for the *balanced* oxidation-reduction reaction. The measured cell potential is the maximum potential the cell can produce and is related to the **electrical work (w_{ele})** by

$$E_{\text{cell}} = \frac{-w_{\text{ele}}}{nF} \quad \text{or} \quad w_{\text{ele}} = -nFE_{\text{cell}}$$

The negative sign for the work indicates that the electrical work is done by the system (the galvanic cell) on the surroundings. In an earlier chapter, the free energy was defined as the energy that was available to do work. In particular, the change in free energy was defined in terms of the maximum work (w_{max}), which, for electrochemical systems, is w_{ele} .

$$\Delta G = w_{\text{max}} = w_{\text{ele}}$$

$$\Delta G = -nFE_{\text{cell}}$$

We can verify the signs are correct when we realize that n and F are positive constants and that galvanic cells, which have positive cell potentials, involve spontaneous reactions. Thus, spontaneous reactions, which have $\Delta G < 0$, must have $E_{\text{cell}} > 0$. If all the reactants and products are in their standard states, this becomes

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ$$

This provides a way to relate standard cell potentials to equilibrium constants, since

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

$$-nFE_{\text{cell}}^\circ = -RT \ln K \quad \text{or} \quad E_{\text{cell}}^\circ = \frac{RT}{nF} \ln K$$

Most of the time, the electrochemical reactions are run at standard temperature (298.15 K). Collecting terms at this temperature yields

$$E_{\text{cell}}^\circ = \frac{RT}{nF} \ln K = \frac{(8.314 \frac{\text{J}}{\text{K}\cdot\text{mol}})(298.15\text{K})}{n \times 96,485 \frac{\text{C/V}\cdot\text{mol}}{\text{V}\cdot\text{mol}}} \ln K = \frac{0.0257 \text{ V}}{n} \ln K$$

where n is the number of moles of electrons. For historical reasons, the logarithm in equations involving cell potentials is often expressed using base 10 logarithms (log), which changes the constant by a factor of 2.303:

$$E_{\text{cell}}^\circ = \frac{0.0592 \text{ V}}{n} \log K$$

Thus, if ΔG° , K , or E_{cell}° is known or can be calculated, the other two quantities can be readily determined. The relationships are shown graphically in **Figure 17.9**.

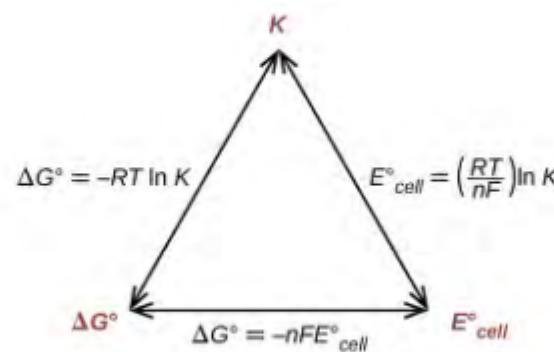


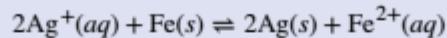
Figure 17.9 The relationships between ΔG° , K , and E_{cell}° . Given any one of the three quantities, the other two can be calculated, so any of the quantities could be used to determine whether a process was spontaneous.

Given any one of the quantities, the other two can be calculated.

Example 17.5

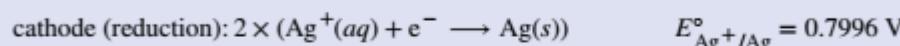
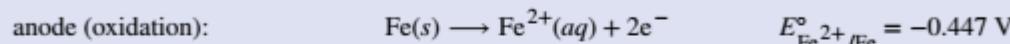
Equilibrium Constants, Standard Cell Potentials, and Standard Free Energy Changes

What is the standard free energy change and equilibrium constant for the following reaction at 25 °C?



Solution

The reaction involves an oxidation-reduction reaction, so the standard cell potential can be calculated using the data in [Appendix L](#).



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{Fe}^{2+}/\text{Fe}}^\circ = +1.247 \text{ V}$$

Remember that the cell potential for the cathode is not multiplied by two when determining the standard cell potential. With $n = 2$, the equilibrium constant is then

$$E_{\text{cell}}^\circ = \frac{0.0592 \text{ V}}{n} \log K$$

$$K = 10^{\frac{n \times E_{\text{cell}}^\circ}{0.0592 \text{ V}}}$$

$$K = 10^{\frac{2 \times 1.247 \text{ V}}{0.0592 \text{ V}}}$$

$$K = 10^{42.128}$$

$$K = 1.3 \times 10^{42}$$

The two equilibrium constants differ slightly due to rounding in the constants 0.0257 V and 0.0592 V. The standard free energy is then

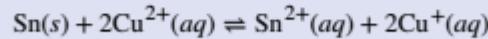
$$\Delta G^\circ = -nFE_{\text{cell}}^\circ$$

$$\Delta G^\circ = -2 \times 96,485 \frac{\text{J}}{\text{V}\cdot\text{mol}} \times 1.247 \text{ V} = -240.6 \frac{\text{kJ}}{\text{mol}}$$

Check your answer: A positive standard cell potential means a spontaneous reaction, so the standard free energy change should be negative, and an equilibrium constant should be >1.

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

Now that the connection has been made between the free energy and cell potentials, nonstandard concentrations follow. Recall that

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

where Q is the reaction quotient (see the chapter on equilibrium fundamentals). Converting to cell potentials:

$$-nFE_{\text{cell}} = -nFE_{\text{cell}}^\circ + RT \ln Q \quad \text{or} \quad E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q$$

This is the **Nernst equation**. At standard temperature (298.15 K), it is possible to write the above equations as

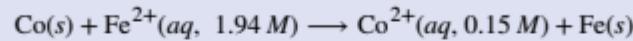
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0257 \text{ V}}{n} \ln Q \quad \text{or} \quad E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q$$

If the temperature is not 273.15 K, it is necessary to recalculate the value of the constant. With the Nernst equation, it is possible to calculate the cell potential at nonstandard conditions. This adjustment is necessary because potentials determined under different conditions will have different values.

Example 17.6

Cell Potentials at Nonstandard Conditions

Consider the following reaction at room temperature:



Is the process spontaneous?

Solution

There are two ways to solve the problem. If the thermodynamic information in **Appendix G** were available, you could calculate the free energy change. If the free energy change is negative, the process is spontaneous. The other approach, which we will use, requires information like that given in **Appendix L**. Using those data, the cell potential can be determined. If the cell potential is positive, the process is spontaneous. Collecting information from **Appendix L** and the problem,

$$\begin{aligned} \text{Anode (oxidation): } & \text{Co}(s) \longrightarrow \text{Co}^{2+}(aq) + 2e^- \quad E_{\text{Co}^{2+}/\text{Co}}^{\circ} = -0.28 \text{ V} \\ \text{Cathode (reduction): } & \text{Fe}^{2+}(aq) + 2e^- \longrightarrow \text{Fe}(s) \quad E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.447 \text{ V} \\ E_{\text{cell}}^{\circ} &= E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = -0.447 \text{ V} - (-0.28 \text{ V}) = -0.17 \text{ V} \end{aligned}$$

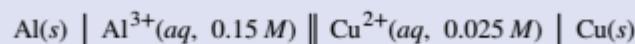
The process is not spontaneous under standard conditions. Using the Nernst equation and the concentrations stated in the problem and $n = 2$,

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

The process is (still) nonspontaneous.

Check Your Learning

What is the cell potential for the following reaction at room temperature?



What are the values of n and Q for the overall reaction? Is the reaction spontaneous under these conditions?

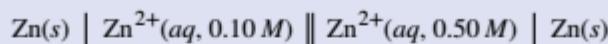
Answer: $n = 6$; $Q = 1440$; $E_{\text{cell}} = +1.97 \text{ V}$, spontaneous.

Finally, we will take a brief look at a special type of cell called a **concentration cell**. In a concentration cell, the electrodes are the same material and the half-cells differ only in concentration. Since one or both compartments is not standard, the cell potentials will be unequal; therefore, there will be a potential difference, which can be determined with the aid of the Nernst equation.

Example 17.7

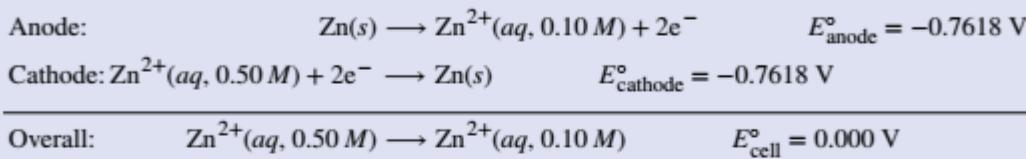
Concentration Cells

What is the cell potential of the concentration cell described by



Solution

From the information given:



The standard cell potential is zero because the anode and cathode involve the same reaction; only the concentration of Zn^{2+} changes. Substituting into the Nernst equation,

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

and the process is spontaneous at these conditions.

Check your answer: In a concentration cell, the standard cell potential will always be zero. To get a positive cell potential (spontaneous process) the reaction quotient Q must be < 1 . $Q < 1$ in this case, so the process is spontaneous.

Check Your Learning

What value of Q for the previous concentration cell would result in a voltage of 0.10 V? If the concentration of zinc ion at the cathode was 0.50 M, what was the concentration at the anode?

Answer: $Q = 0.00042$; $[\text{Zn}^{2+}]_{\text{cat}} = 2.1 \times 10^{-4}\text{ M}$.

17.5 Batteries and Fuel Cells

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

- Classify batteries as primary or secondary
- List some of the characteristics and limitations of batteries
- Provide a general description of a fuel cell

A **battery** is an electrochemical cell or series of cells that produces an electric current. In principle, any galvanic cell could be used as a battery. An ideal battery would never run down, produce an unchanging voltage, and be capable of withstanding environmental extremes of heat and humidity. Real batteries strike a balance between ideal characteristics and practical limitations. For example, the mass of a car battery is about 18 kg or about 1% of the mass of an average car or light-duty truck. This type of battery would supply nearly unlimited energy if used in a smartphone, but would be rejected for this application because of its mass. Thus, no single battery is “best” and batteries are selected for a particular application, keeping things like the mass of the battery, its cost, reliability, and current capacity in mind. There are two basic types of batteries: primary and secondary. A few batteries of each type are described next.

Primary Batteries

Primary batteries are single-use batteries because they cannot be recharged. A common primary battery is the **dry cell** (Figure 17.10). The dry cell is a zinc–carbon battery. The zinc can serves as both a container and the negative electrode. The positive electrode is a rod made of carbon that is surrounded by a paste of manganese(IV) oxide, zinc chloride, ammonium chloride, carbon powder, and a small amount of water. The reaction at the anode can be represented as the ordinary oxidation of zinc:



The reaction at the cathode is more complicated, in part because more than one reaction occurs. The series of reactions that occurs at the cathode is approximately

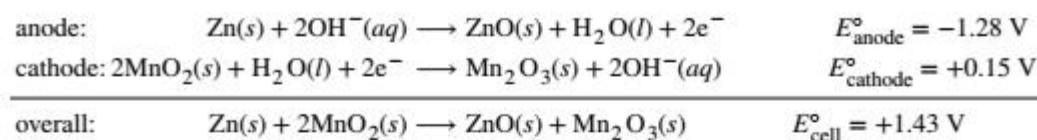


The overall reaction for the zinc–carbon battery can be represented as $2\text{MnO}_2(s) + 2\text{NH}_4\text{Cl}(aq) + \text{Zn}(s) \longrightarrow \text{Zn}^{2+}(aq) + \text{Mn}_2\text{O}_3(s) + 2\text{NH}_3(aq) + \text{H}_2\text{O}(l) + 2\text{Cl}^-$ with an overall cell potential which is initially about 1.5 V, but decreases as the battery is used. It is important to remember that the voltage delivered by a battery is the same regardless of the size of a battery. For this reason, D, C, A, AA, and AAA batteries all have the same voltage rating. However, larger batteries can deliver more moles of electrons. As the zinc container oxidizes, its contents eventually leak out, so this type of battery should not be left in any electrical device for extended periods.



Figure 17.10 The diagram shows a cross section of a flashlight battery, a zinc–carbon dry cell.

Alkaline batteries (Figure 17.11) were developed in the 1950s partly to address some of the performance issues with zinc–carbon dry cells. They are manufactured to be exact replacements for zinc–carbon dry cells. 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 these should also 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.

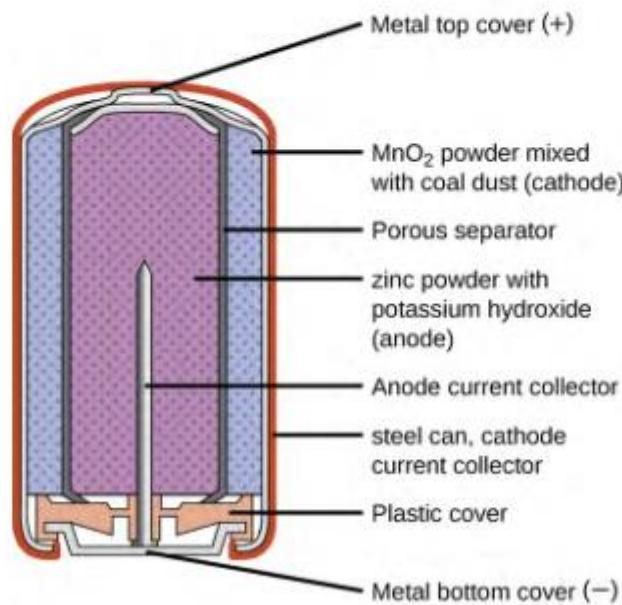
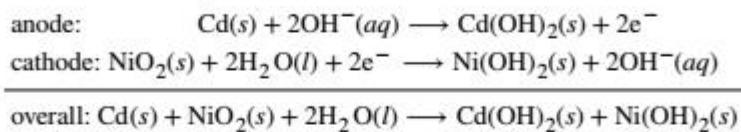


Figure 17.11 Alkaline batteries were designed as direct replacements for zinc–carbon (dry cell) batteries.

Secondary Batteries

Secondary batteries are rechargeable. These are the types of batteries found in devices such as smartphones, electronic tablets, and automobiles.

Nickel-cadmium, or NiCd, batteries (Figure 17.12) 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



The voltage is about 1.2 V to 1.25 V as the battery discharges. When properly treated, a NiCd battery can be recharged about 1000 times. Cadmium is a toxic heavy metal so NiCd batteries should never be opened or put into the regular trash.

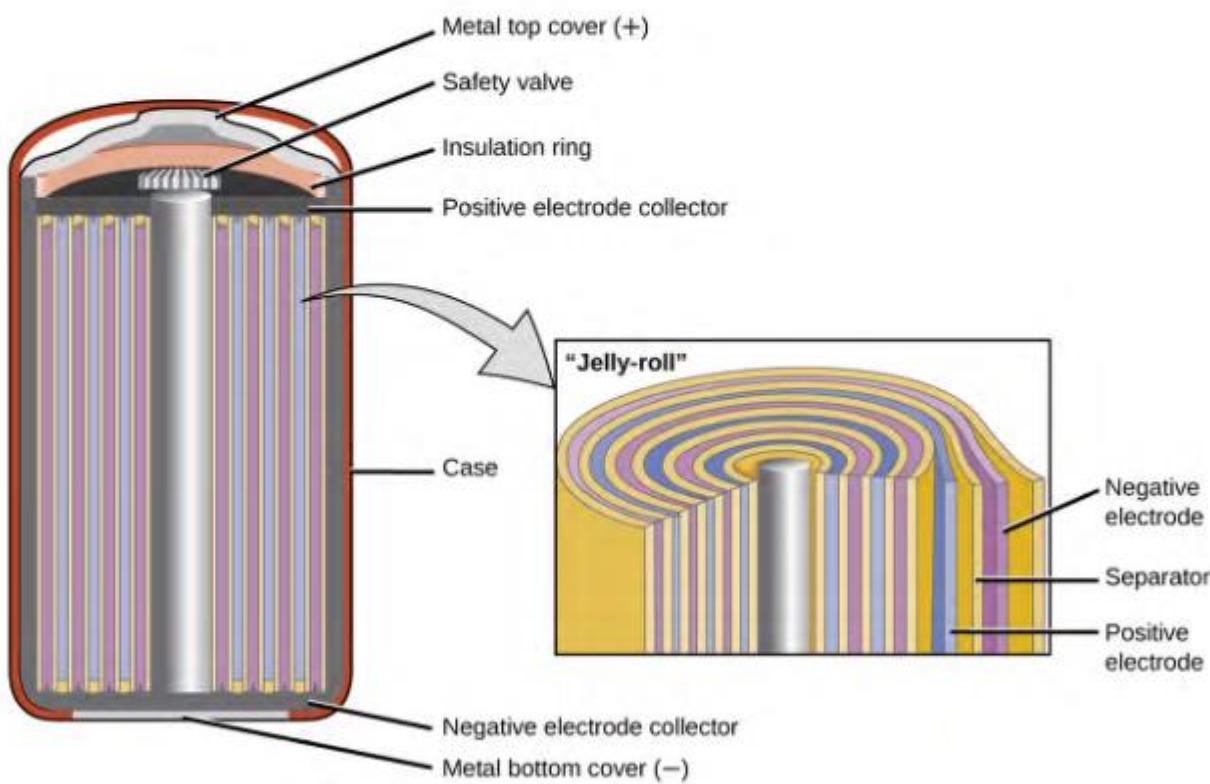
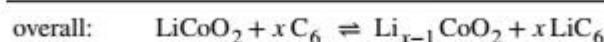
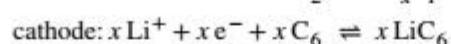
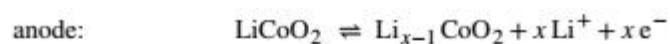


Figure 17.12 NiCd batteries use a “jelly-roll” design that significantly increases the amount of current the battery can deliver as compared to a similar-sized alkaline battery.

Lithium ion batteries (Figure 17.13) are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are



With the coefficients representing moles, x is no more than about 0.5 moles. The battery voltage is about 3.7 V. Lithium batteries are popular because they can provide a large amount 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.

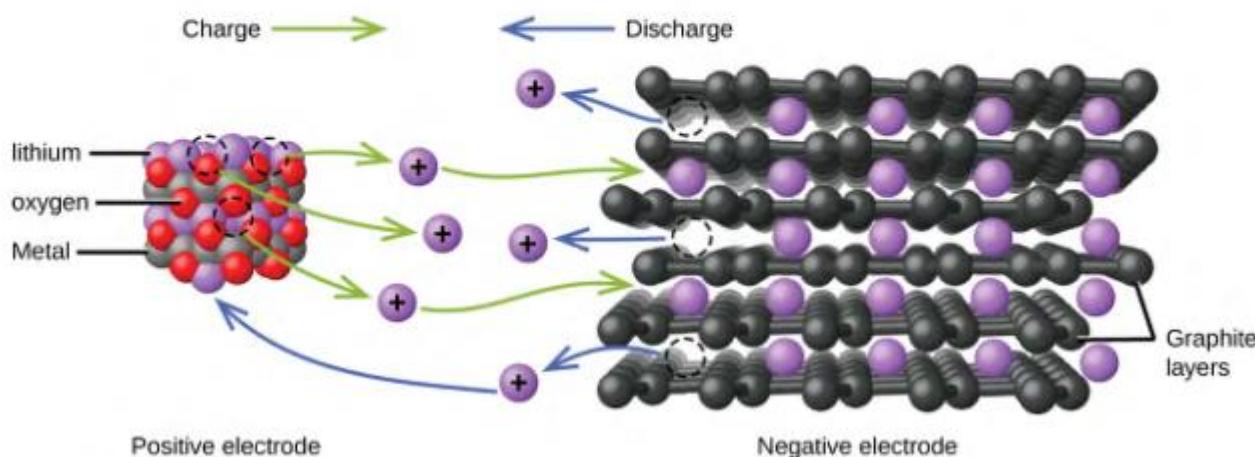
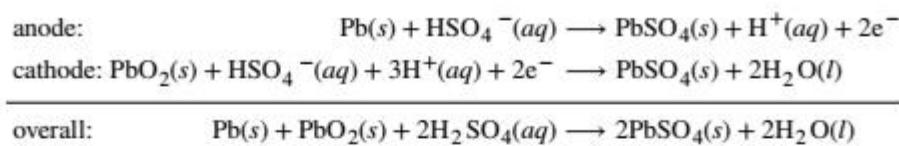


Figure 17.13 In a lithium ion battery, charge flows between the electrodes as the lithium ions move between the anode and cathode.

The **lead acid battery** (Figure 17.14) is the type of secondary battery used in your automobile. 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, 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.

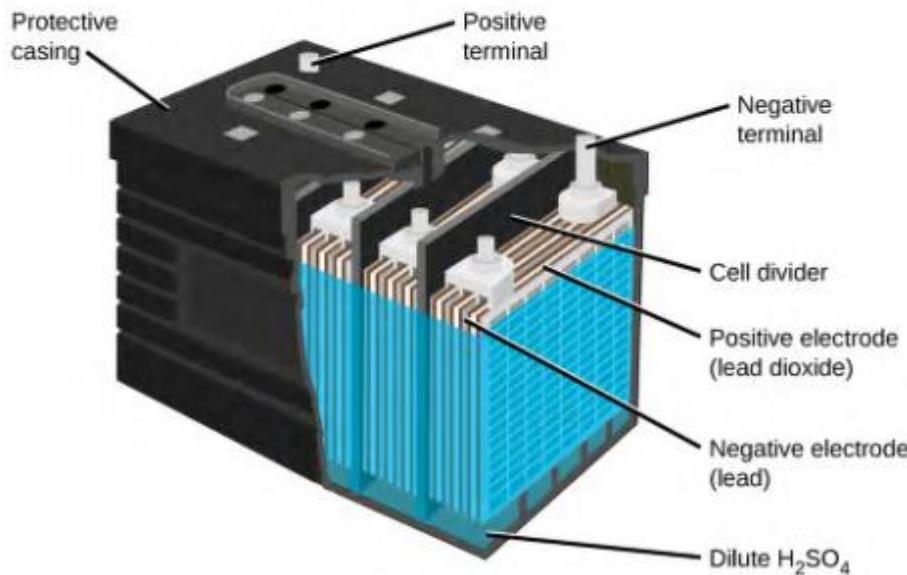


Figure 17.14 The lead acid battery in your automobile consists of six cells connected in series to give 12 V. Their low cost and high current output makes these excellent candidates for providing power for automobile starter motors.

Fuel Cells

A **fuel cell** is a device that converts chemical energy into electrical energy. Fuel cells are similar to batteries but require a continuous source of fuel, often hydrogen. They will continue to produce electricity as long as fuel is available. Hydrogen fuel cells have been used to supply power for satellites, space capsules, automobiles, boats, and submarines (**Figure 17.15**).

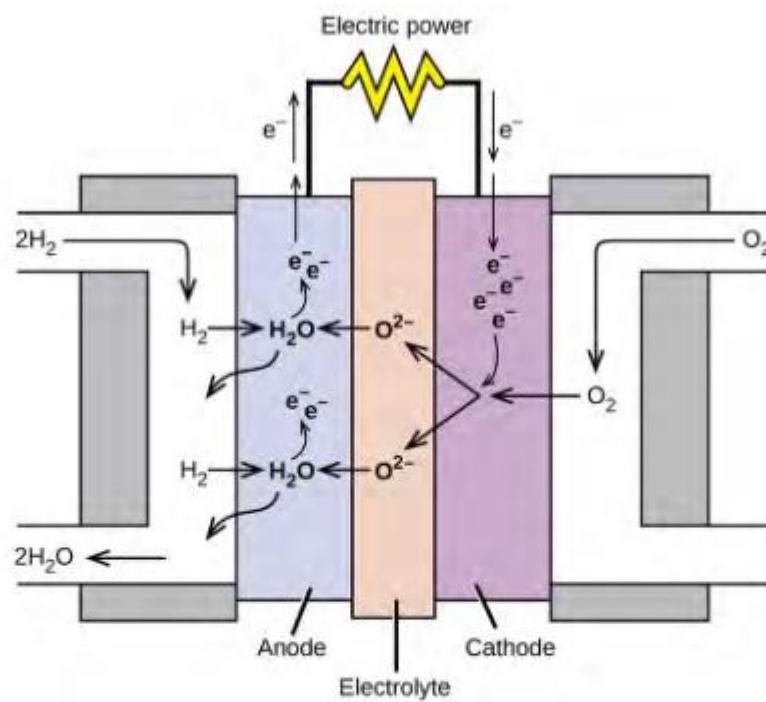
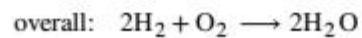
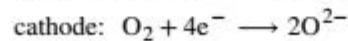
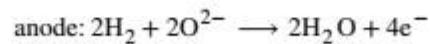


Figure 17.15 In this hydrogen fuel-cell schematic, oxygen from the air reacts with hydrogen, producing water and electricity.

In a hydrogen fuel cell, the reactions are



The voltage is about 0.9 V. The efficiency of fuel cells is typically about 40% to 60%, which is higher than the typical internal combustion engine (25% to 35%) and, in the case of the hydrogen fuel cell, produces only water as exhaust. Currently, fuel cells are rather expensive and contain features that cause them to fail after a relatively short time.

17.6 Corrosion

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

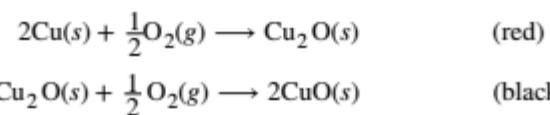
- Define corrosion
- List some of the methods used to prevent or slow corrosion

Corrosion is usually defined as the degradation of metals due to an 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 in the United States is significant, with estimates in excess of half a trillion dollars a year.

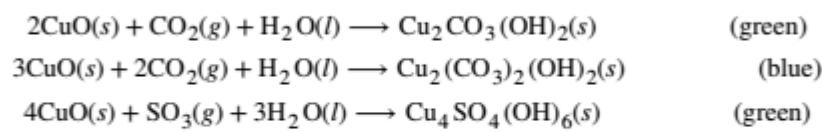
Chemistry in Everyday Life

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 17.16). 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, sulfur trioxide, carbon dioxide, and water all reacted with the CuO

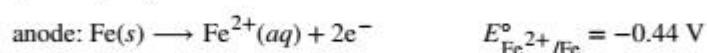


These three compounds are responsible for the characteristic blue-green patina seen today. Fortunately, formation of the patina created a protective layer on the surface, preventing further corrosion of the copper skin. The formation of the protective layer is a form of passivation, which is discussed further in a later chapter.

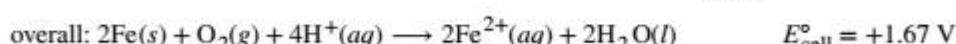
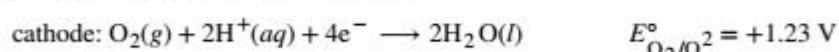


Figure 17.16 (a) The Statue of Liberty is covered with a copper skin, and was originally brown, as shown in this painting. (b) Exposure to the elements has resulted in the formation of the blue-green patina seen today.

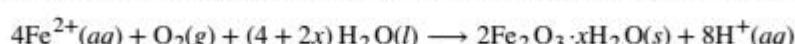
Perhaps the most familiar example of corrosion is the formation of rust on iron. Iron will rust when it is exposed to oxygen and water. The main steps in the rusting of iron appear to involve the following (**Figure 17.17**). Once exposed to the atmosphere, iron rapidly oxidizes.



The electrons reduce oxygen in the air in acidic solutions.



What we call rust is hydrated iron(III) oxide, which forms when iron(II) ions react further with oxygen.



The number of water molecules is variable, so it is represented by x . 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.

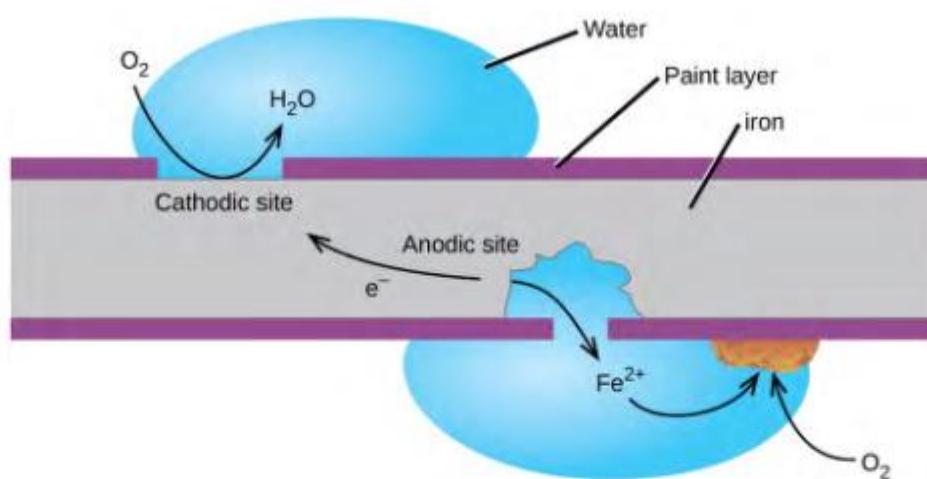


Figure 17.17 Once the paint is scratched on a painted iron surface, corrosion occurs and rust begins to form. The speed of the spontaneous reaction is increased in the presence of electrolytes, such as the sodium chloride used on roads to melt ice and snow or in salt water.

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 mostly iron with a bit of chromium. The chromium tends to collect near the surface, where it forms an oxide layer that protects the iron.

Zinc-plated or **galvanized iron** uses a different strategy. Zinc is more easily oxidized than iron because zinc has a lower reduction potential. Since zinc has a lower reduction potential, it is a more active metal. Thus, even if the zinc coating is scratched, the zinc will still oxidize before the iron. This suggests that this approach should work with other active metals.

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 17.18**). 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, and so does not oxidize (corrode). When the anodes are properly monitored and periodically replaced, the useful lifetime of the iron storage tank can be greatly extended.

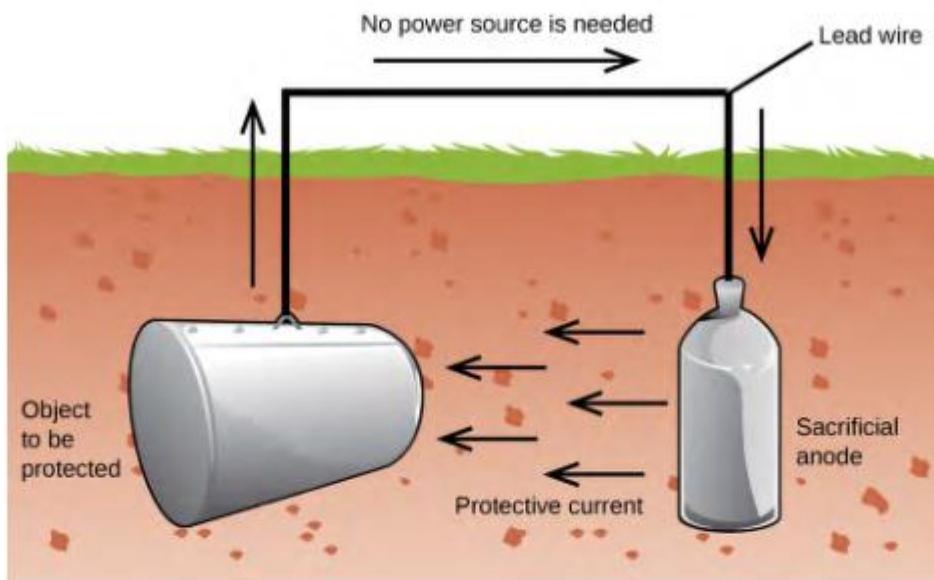


Figure 17.18 One way to protect an underground iron storage tank is through cathodic protection. Using an active metal like zinc or magnesium for the anode effectively makes the storage tank the cathode, preventing it from corroding (oxidizing).

17.7 Electrolysis

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

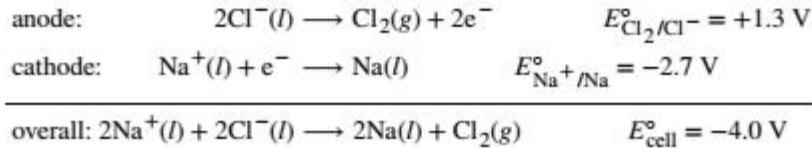
- Describe electrolytic cells and their relationship to galvanic cells
- Perform various calculations related to electrolysis

In galvanic cells, chemical energy is converted into electrical energy. The opposite is true for electrolytic cells. In **electrolytic cells**, electrical energy causes nonspontaneous reactions to occur in a process known as **electrolysis**. The charging electric car pictured in **Figure 17.1** at the beginning of this chapter shows one such process. Electrical energy is converted into the chemical energy in the battery as it is charged. Once charged, the battery can be used to power the automobile.

The same principles are involved in electrolytic cells as in galvanic cells. We will look at three electrolytic cells and the quantitative aspects of electrolysis.

The Electrolysis of Molten Sodium Chloride

In molten sodium chloride, the ions are free to migrate to the electrodes of an electrolytic cell. A simplified diagram of the cell commercially used to produce sodium metal and chlorine gas is shown in **Figure 17.19**. Sodium is a strong reducing agent and chlorine is used to purify water, and is used in antiseptics and in paper production. The reactions are



The power supply (battery) must supply a minimum of 4 V, but, in practice, the applied voltages are typically higher because of inefficiencies in the process itself.

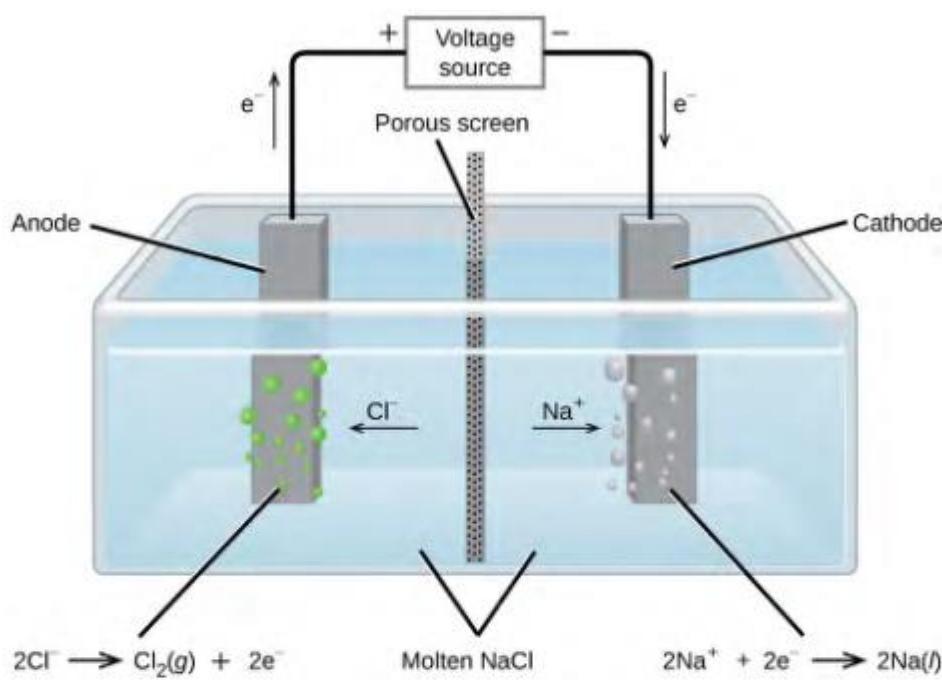
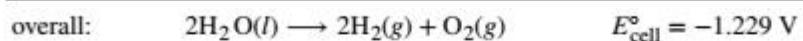
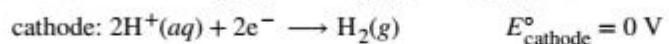
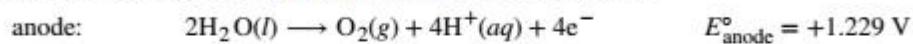


Figure 17.19 Passing an electric current through molten sodium chloride decomposes the material into sodium metal and chlorine gas. Care must be taken to keep the products separated to prevent the spontaneous formation of sodium chloride.

The Electrolysis of Water

It is possible to split water into hydrogen and oxygen gas by electrolysis. Acids are typically added to increase the concentration of hydrogen ion in solution (Figure 17.20). The reactions are



Note that the sulfuric acid is not consumed and that the volume of hydrogen gas produced is twice the volume of oxygen gas produced. The minimum applied voltage is 1.229 V.

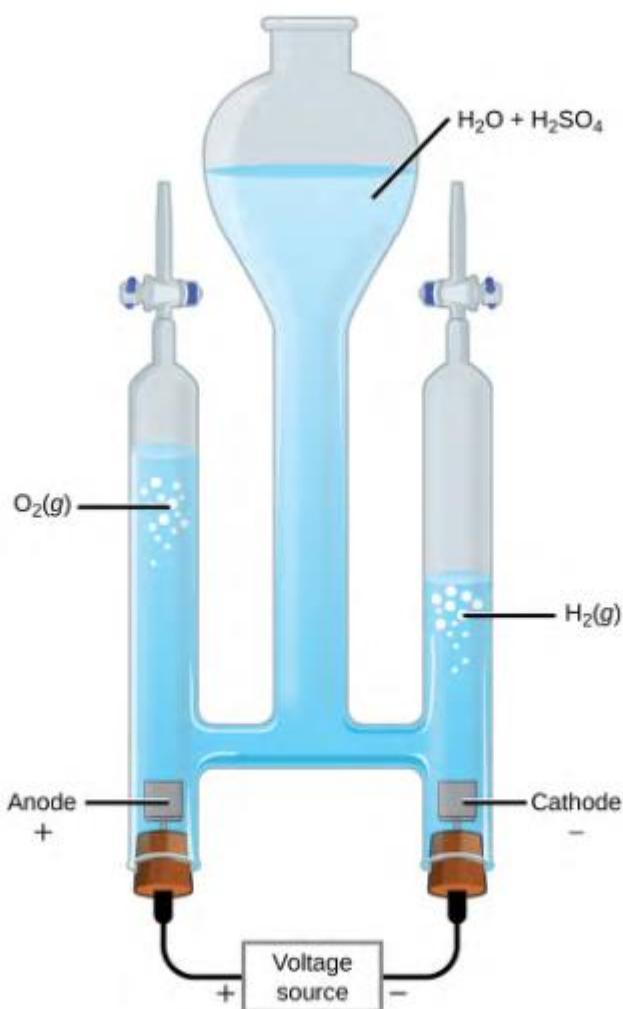
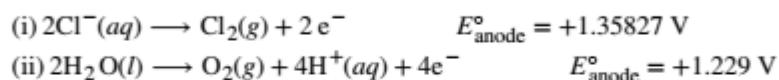


Figure 17.20 Water decomposes into oxygen and hydrogen gas during electrolysis. Sulfuric acid was added to increase the concentration of hydrogen ions and the total number of ions in solution, but does not take part in the reaction. The volume of hydrogen gas collected is twice the volume of oxygen gas collected, due to the stoichiometry of the reaction.

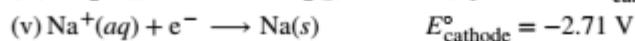
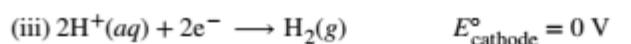
The Electrolysis of Aqueous Sodium Chloride

The electrolysis of aqueous sodium chloride is the more common example of electrolysis because more than one species can be oxidized and reduced. Considering the anode first, the possible reactions are

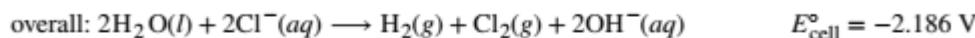


These values suggest that water should be oxidized at the anode because a smaller potential would be needed—using reaction (ii) for the oxidation would give a less-negative cell potential. When the experiment is run, it turns out chlorine, not oxygen, is produced at the anode. The unexpected process is so common in electrochemistry that it has been given the name overpotential. The **overpotential** is the difference between the theoretical cell voltage and the actual voltage that is necessary to cause electrolysis. It turns out that the overpotential for oxygen is rather high and effectively makes the reduction potential more positive. As a result, under normal conditions, chlorine gas is what actually forms at the anode.

Now consider the cathode. Three reductions could occur:



Reaction (v) is ruled out because it has such a negative reduction potential. Under standard state conditions, reaction (iii) would be preferred to reaction (iv). However, the pH of a sodium chloride solution is 7, so the concentration of hydrogen ions is only $1 \times 10^{-7} \text{ M}$. At such low concentrations, reaction (iii) is unlikely and reaction (iv) occurs. The overall reaction is then



As the reaction proceeds, hydroxide ions replace chloride ions in solution. Thus, sodium hydroxide can be obtained by evaporating the water after the electrolysis is complete. Sodium hydroxide is valuable in its own right and is used for things like oven cleaner, drain opener, and in the production of paper, fabrics, and soap.

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. We can get an idea of how this works by investigating how silver-plated tableware is produced (Figure 17.21).

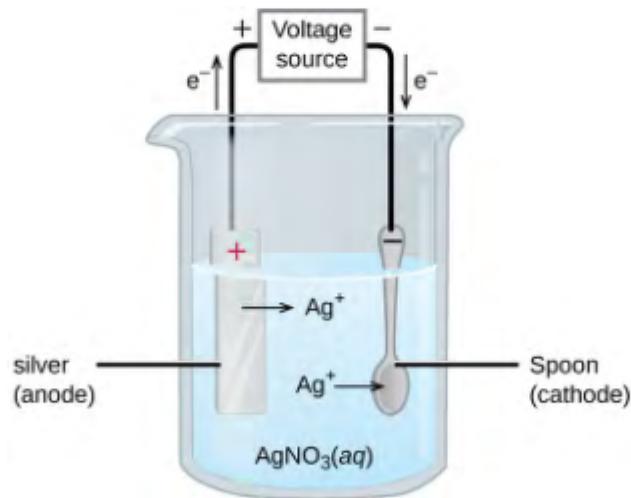
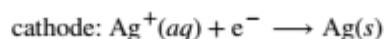


Figure 17.21 The spoon, which is made of an inexpensive metal, is connected to the negative terminal of the voltage source and acts as the cathode. The anode is a silver electrode. Both electrodes are immersed in a silver nitrate solution. When a steady current is passed through the solution, the net result is that silver metal is removed from the anode and deposited on the cathode.

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. As the potential is increased, current flows. Silver metal is lost at the anode as it goes into solution.



The mass of the cathode increases as silver ions from the solution are deposited onto the spoon



The net result is the transfer of silver metal from the anode to the cathode. The quality of the object is usually determined by the thickness of the deposited silver and the rate of deposition.

Quantitative Aspects of Electrolysis

The amount of current that is allowed to flow in an electrolytic cell is related to the number of moles of electrons. The number of moles of electrons can be related to the reactants and products using stoichiometry. Recall that the SI unit for current (I) is the ampere (A), which is the equivalent of 1 coulomb per second ($1 \text{ A} = 1 \frac{\text{C}}{\text{s}}$). The total charge (Q , in coulombs) is given by

$$Q = I \times t = n \times F$$

Where t is the time in seconds, n the number of moles of electrons, and F is the Faraday constant.

Moles of electrons can be used in stoichiometry problems. The time required to deposit a specified amount of metal might also be requested, as in the second of the following examples.

Example 17.8

Converting Current to Moles of Electrons

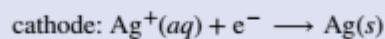
In one process used for electroplating silver, a current of 10.23 A was passed through an electrolytic cell for exactly 1 hour. How many moles of electrons passed through the cell? What mass of silver was deposited at the cathode from the silver nitrate solution?

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

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

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 answer: From the stoichiometry, 1 mole of electrons would produce 1 mole of silver. Less than one-half a mole of electrons was involved and less than one-half a mole of silver was produced.

Check Your Learning

Aluminum metal can be made from aluminum ions by electrolysis. What is the half-reaction at the cathode?

What mass of aluminum metal would be recovered if a current of $2.50 \times 10^3 \text{ A}$ passed through the solution for 15.0 minutes? Assume the yield is 100%.

Answer: $\text{Al}^{3+}(aq) + 3 e^- \longrightarrow \text{Al}(s)$; $7.77 \text{ mol Al} = 210.0 \text{ g Al}$.

Example 17.9

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 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

This problem brings in a number of topics covered earlier. An outline of what needs to be done is:

- If the total charge can be determined, the time required is just the charge divided by the current
- The total charge can be obtained from the amount of Cr needed and the stoichiometry
- The amount of Cr can be obtained using the density and the volume Cr required
- The volume Cr required is the thickness times the area

Solving in steps, and taking care with the units, the volume of Cr required is

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

Cubic centimeters were used because they match the volume unit used for the density. The amount of Cr is then

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

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

Since the solution contains chromium(III) ions, 3 moles of electrons are required per mole of Cr. The total charge is then

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

The time required is then

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

Check your answer: In a long problem like this, a single check is probably not enough. Each of the steps gives a reasonable number, so things are probably correct. Pay careful attention to unit conversions and the stoichiometry.

Check Your Learning

What mass of zinc is required to galvanize the top of a $3.00 \text{ m} \times 5.50 \text{ m}$ 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/cm^3 .

Answer: 231 g Zn required 446 minutes.

Key Terms

active electrode electrode that participates in the oxidation-reduction reaction of an electrochemical cell; the mass of an active electrode changes during the oxidation-reduction reaction

alkaline battery primary battery that uses an alkaline (often potassium hydroxide) electrolyte; designed to be an exact replacement for the dry cell, but with more energy storage and less electrolyte leakage than typical dry cell

anode electrode in an electrochemical cell at which oxidation occurs; information about the anode is recorded on the left side of the salt bridge in cell notation

battery galvanic cell or series of cells that produces a current; in theory, any galvanic cell

cathode electrode in an electrochemical cell at which reduction occurs; information about the cathode is recorded on the right side of the salt bridge in cell notation

cathodic protection method of protecting metal by using a sacrificial anode and effectively making the metal that needs protecting the cathode, thus preventing its oxidation

cell notation shorthand way to represent the reactions in an electrochemical cell

cell potential difference in electrical potential that arises when dissimilar metals are connected; the driving force for the flow of charge (current) in oxidation-reduction reactions

circuit path taken by a current as it flows because of an electrical potential difference

concentration cell galvanic cell in which the two half-cells are the same except for the concentration of the solutes; spontaneous when the overall reaction is the dilution of the solute

corrosion degradation of metal through an electrochemical process

current flow of electrical charge; the SI unit of charge is the coulomb (C) and current is measured in amperes
 $(1 \text{ A} = 1 \frac{\text{C}}{\text{s}})$

dry cell primary battery, also called a zinc-carbon battery; can be used in any orientation because it uses a paste as the electrolyte; tends to leak electrolyte when stored

electrical potential energy per charge; in electrochemical systems, it depends on the way the charges are distributed within the system; the SI unit of electrical potential is the volt $(1 \text{ V} = 1 \frac{\text{J}}{\text{C}})$

electrical work (w_{ele}) negative of total charge times the cell potential; equal to w_{max} for the system, and so equals the free energy change (ΔG)

electrolysis process using electrical energy to cause a nonspontaneous process to occur

electrolytic cell electrochemical cell in which electrolysis is used; electrochemical cell with negative cell potentials

electroplating depositing a thin layer of one metal on top of a conducting surface

Faraday's constant (F) charge on 1 mol of electrons; $F = 96,485 \text{ C/mol e}^-$

fuel cell devices that produce an electrical current as long as fuel and oxidizer are continuously added; more efficient than internal combustion engines

galvanic cell electrochemical cell that involves a spontaneous oxidation-reduction reaction; electrochemical cells with positive cell potentials; also called a voltaic cell

galvanized iron method for protecting iron by covering it with zinc, which will oxidize before the iron; zinc-plated iron

half-reaction method method that produces a balanced overall oxidation-reduction reaction by splitting the reaction into an oxidation “half” and reduction “half,” balancing the two half-reactions, and then combining the oxidation half-reaction and reduction half-reaction in such a way that the number of electrons generated by the oxidation is exactly canceled by the number of electrons required by the reduction

inert electrode electrode that allows current to flow, but that does not otherwise participate in the oxidation-reduction reaction in an electrochemical cell; the mass of an inert electrode does not change during the oxidation-reduction reaction; inert electrodes are often made of platinum or gold because these metals are chemically unreactive.

lead acid battery secondary battery that consists of multiple cells; the lead acid battery found in automobiles has six cells and a voltage of 12 V

lithium ion battery very popular secondary battery; uses lithium ions to conduct current and is light, rechargeable, and produces a nearly constant potential as it discharges

Nernst equation equation that relates the logarithm of the reaction quotient (Q) to nonstandard cell potentials; can be used to relate equilibrium constants to standard cell potentials

nickel-cadmium battery (NiCd battery) secondary battery that uses cadmium, which is a toxic heavy metal; heavier than lithium ion batteries, but with similar performance characteristics

overpotential difference between the theoretical potential and actual potential in an electrolytic cell; the “extra” voltage required to make some nonspontaneous electrochemical reaction to occur

oxidation half-reaction the “half” of an oxidation-reduction reaction involving oxidation; the half-reaction in which electrons appear as products; balanced when each atom type, as well as the charge, is balanced

primary battery single-use nonrechargeable battery

reduction half-reaction the “half” of an oxidation-reduction reaction involving reduction; the half-reaction in which electrons appear as reactants; balanced when each atom type, as well as the charge, is balanced

sacrificial anode more active, inexpensive metal used as the anode in cathodic protection; frequently made from magnesium or zinc

secondary battery battery that can be recharged

standard cell potential (E_{cell}°) the cell potential when all reactants and products are in their standard states (1 bar or 1 atm or gases; 1 M for solutes), usually at 298.15 K; can be calculated by subtracting the standard reduction potential for the half-reaction at the anode from the standard reduction potential for the half-reaction occurring at the cathode

standard hydrogen electrode (SHE) the electrode consists of hydrogen gas bubbling through hydrochloric acid over an inert platinum electrode whose reduction at standard conditions is assigned a value of 0 V; the reference point for standard reduction potentials

standard reduction potential (E°) the value of the reduction under standard conditions (1 bar or 1 atm for gases; 1 M for solutes) usually at 298.15 K; tabulated values used to calculate standard cell potentials

voltaic cell another name for a galvanic cell

Key Equations

- $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$
- $E_{\text{cell}}^{\circ} = \frac{RT}{nF} \ln K$
- $E_{\text{cell}}^{\circ} = \frac{0.0257 \text{ V}}{n} \ln K = \frac{0.0592 \text{ V}}{n} \log K$ (at 298.15 K)
- $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q$ (Nernst equation)
- $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0257 \text{ V}}{n} \ln Q = E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q$ (at 298.15 K)
- $\Delta G = -nFE_{\text{cell}}$
- $\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$
- $w_{\text{ele}} = w_{\text{max}} = -nFE_{\text{cell}}$
- $Q = I \times t = n \times F$

Summary

17.1 Balancing Oxidation-Reduction Reactions

An electric current consists of moving charge. The charge may be in the form of electrons or ions. Current flows through an unbroken or closed circular path called a circuit. The current flows through a conducting medium as a result of a difference in electrical potential between two points in a circuit. Electrical potential has the units of energy per charge. In SI units, charge is measured in coulombs (C), current in amperes ($A = \frac{C}{s}$), and electrical potential in volts ($V = \frac{J}{C}$).

Oxidation is the loss of electrons, and the species that is oxidized is also called the reducing agent. Reduction is the gain of electrons, and the species that is reduced is also called the oxidizing agent. Oxidation-reduction reactions can be balanced using the half-reaction method. In this method, the oxidation-reduction reaction is split into an oxidation half-reaction and a reduction half-reaction. The oxidation half-reaction and reduction half-reaction are then balanced separately. Each of the half-reactions must have the same number of each type of atom on both sides of the equation and show the same total charge on each side of the equation. Charge is balanced in oxidation half-reactions by adding electrons as products; in reduction half-reactions, charge is balanced by adding electrons as reactants. The total number of electrons gained by reduction must exactly equal the number of electrons lost by oxidation when combining the two half-reactions to give the overall balanced equation. Balancing oxidation-reduction reaction equations in aqueous solutions frequently requires that oxygen or hydrogen be added or removed from a reactant. In acidic solution, hydrogen is added by adding hydrogen ion (H^+) and removed by producing hydrogen ion; oxygen is removed by adding hydrogen ion and producing water, and added by adding water and producing hydrogen ion. A balanced equation in basic solution can be obtained by first balancing the equation in acidic solution, and then adding hydroxide ion to each side of the balanced equation in such numbers that all the hydrogen ions are converted to water.

17.2 Galvanic Cells

Electrochemical cells typically consist of two half-cells. The half-cells separate the oxidation half-reaction from the reduction half-reaction and make it possible for current to flow through an external wire. One half-cell, normally depicted on the left side in a figure, contains the anode. Oxidation occurs at the anode. The anode is connected to the cathode in the other half-cell, often shown on the right side in a figure. Reduction occurs at the cathode. Adding a

salt bridge completes the circuit allowing current to flow. Anions in the salt bridge flow toward the anode and cations in the salt bridge flow toward the cathode. The movement of these ions completes the circuit and keeps each half-cell electrically neutral. Electrochemical cells can be described using cell notation. In this notation, information about the reaction at the anode appears on the left and information about the reaction at the cathode on the right. The salt bridge is represented by a double line, \parallel . The solid, liquid, or aqueous phases within a half-cell are separated by a single line, $|$. The phase and concentration of the various species is included after the species name. Electrodes that participate in the oxidation-reduction reaction are called active electrodes. Electrodes that do not participate in the oxidation-reduction reaction but are there to allow current to flow are inert electrodes. Inert electrodes are often made from platinum or gold, which are unchanged by many chemical reactions.

17.3 Standard Reduction Potentials

Assigning the potential of the standard hydrogen electrode (SHE) as zero volts allows the determination of standard reduction potentials, E° , for half-reactions in electrochemical cells. As the name implies, standard reduction potentials use standard states (1 bar or 1 atm for gases; 1 M for solutes, often at 298.15 K) and are written as reductions (where electrons appear on the left side of the equation). The reduction reactions are reversible, so standard cell potentials can be calculated by subtracting the standard reduction potential for the reaction at the anode from the standard reduction for the reaction at the cathode. When calculating the standard cell potential, the standard reduction potentials are *not* scaled by the stoichiometric coefficients in the balanced overall equation.

17.4 The Nernst Equation

Electrical work (w_{ele}) is the negative of the product of the total charge (Q) and the cell potential (E_{cell}). The total charge can be calculated as the number of moles of electrons (n) times the Faraday constant ($F = 96,485 \text{ C/mol e}^-$). Electrical work is the maximum work that the system can produce and so is equal to the change in free energy. Thus, anything that can be done with or to a free energy change can also be done to or with a cell potential. The Nernst equation relates the cell potential at nonstandard conditions to the logarithm of the reaction quotient. Concentration cells exploit this relationship and produce a positive cell potential using half-cells that differ only in the concentration of their solutes.

17.5 Batteries and Fuel Cells

Batteries are galvanic cells, or a series of cells, that produce an electric current. When cells are combined into batteries, the potential of the battery is an integer multiple of the potential of a single cell. There are two basic types of batteries: primary and secondary. Primary batteries are “single use” and cannot be recharged. Dry cells and (most) alkaline batteries are examples of primary batteries. The second type is rechargeable and is called a secondary battery. Examples of secondary batteries include nickel-cadmium (NiCd), lead acid, and lithium ion batteries. Fuel cells are similar to batteries in that they generate an electrical current, but require continuous addition of fuel and oxidizer. The hydrogen fuel cell uses hydrogen and oxygen from the air to produce water, and is generally more efficient than internal combustion engines.

17.6 Corrosion

Corrosion is the degradation of a metal caused by an electrochemical process. Large sums of money are spent each year repairing the effects of, or preventing, corrosion. Some metals, such as aluminum and copper, produce a protective layer when they corrode in air. The thin layer that forms on the surface of the metal prevents oxygen from coming into contact with more of the metal atoms and thus “protects” the remaining metal from further corrosion. Iron corrodes (forms rust) when exposed to water and oxygen. The rust that forms on iron metal flakes off, exposing fresh metal, which also corrodes. One way to prevent, or slow, corrosion is by coating the metal. Coating prevents water and oxygen from contacting the metal. Paint or other coatings will slow corrosion, but they are not effective once scratched. Zinc-plated or galvanized iron exploits the fact that zinc is more likely to oxidize than iron. As long as the coating remains, even if scratched, the zinc will oxidize before the iron. Another method for protecting metals is cathodic protection. In this method, an easily oxidized and inexpensive metal, often zinc or magnesium (the sacrificial anode), is electrically connected to the metal that must be protected. The more active metal is the sacrificial anode,

and is the anode in a galvanic cell. The “protected” metal is the cathode, and remains unoxidized. One advantage of cathodic protection is that the sacrificial anode can be monitored and replaced if needed.

17.7 Electrolysis

Using electricity to force a nonspontaneous process to occur is electrolysis. Electrolytic cells are electrochemical cells with negative cell potentials (meaning a positive Gibbs free energy), and so are nonspontaneous. Electrolysis can occur in electrolytic cells by introducing a power supply, which supplies the energy to force the electrons to flow in the nonspontaneous direction. Electrolysis is done in solutions, which contain enough ions so current can flow. If the solution contains only one material, like the electrolysis of molten sodium chloride, it is a simple matter to determine what is oxidized and what is reduced. In more complicated systems, like the electrolysis of aqueous sodium chloride, more than one species can be oxidized or reduced and the standard reduction potentials are used to determine the most likely oxidation (the half-reaction with the largest [most positive] standard reduction potential) and reduction (the half-reaction with the smallest [least positive] standard reduction potential). Sometimes unexpected half-reactions occur because of overpotential. Overpotential is the difference between the theoretical half-reaction reduction potential and the actual voltage required. When present, the applied potential must be increased, making it possible for a different reaction to occur in the electrolytic cell. The total charge, Q , that passes through an electrolytic cell can be expressed as the current (I) multiplied by time ($Q = It$) or as the moles of electrons (n) multiplied by Faraday’s constant ($Q = nF$). These relationships can be used to determine things like the amount of material used or generated during electrolysis, how long the reaction must proceed, or what value of the current is required.

Exercises

17.1 Balancing Oxidation-Reduction Reactions

- If a 2.5 A current is run through a circuit for 35 minutes, how many coulombs of charge moved through the circuit?
- For the scenario in the previous question, how many electrons moved through the circuit?
- For each of the following balanced half-reactions, determine whether an oxidation or reduction is occurring.
 - $\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$
 - $\text{Cr} \rightarrow \text{Cr}^{3+} + 3\text{e}^-$
 - $\text{MnO}_4^{2-} \rightarrow \text{MnO}_4^- + \text{e}^-$
 - $\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$
- For each of the following unbalanced half-reactions, determine whether an oxidation or reduction is occurring.
 - $\text{Cl}^- \rightarrow \text{Cl}_2$
 - $\text{Mn}^{2+} \rightarrow \text{MnO}_2$
 - $\text{H}_2 \rightarrow \text{H}^+$
 - $\text{NO}_3^- \rightarrow \text{NO}$
- Given the following pairs of balanced half-reactions, determine the balanced reaction for each pair of half-reactions in an acidic solution.
 - $\text{Ca} \rightarrow \text{Ca}^{2+} + 2\text{e}^-$, $\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$
 - $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$, $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$
 - $\text{Fe} \rightarrow \text{Fe}^{3+} + 3\text{e}^-$, $\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$