ELECTROCHEMISTRY

The content in this topic is the basis for mastering Learning Objectives 3.8, 3.9, 3.12, and 3.13 as found in the Curriculum Framework.

When you finish reviewing this topic, be sure you are able to:

- Recognize redox reactions by the electrons transferred from the oxidized reactant to the reduced reactant
- Assign an oxidation number to each atom in a chemical formula
- Balance a redox reaction using the half-reaction method
- Calculate quantities involved in a redox titration
- Identify important redox reactions related to energy production such as the combustion of fossil fuels and the metabolism of food
- Interpret diagrams of voltaic and electrolytic cells
- Know that oxidation occurs at the anode of an electrochemical cell and reduction happens at the cathode.
- Calculate cell potential (voltage, EMF) under standard conditions using a table of standard reduction potentials
- Compare qualitatively, using Le Châtelier's principle, the voltage and electron flow in a cell at nonstandard conditions to that of a cell at standard conditions
- Relate cell potential to spontaneity (thermodynamic favorability) of a redox reaction and its standard free energy, $\Delta G°$
- Calculate quantities such as mass, current, time, charge, and number of moles of electrons using Faraday's constant and the stoichiometry of a redox reaction

Oxidation States and Oxidation–Reduction Reactions

Section 20.1

Electrochemistry refers to the interchange of electrical and chemical energy. In electrochemical processes, chemical energy is transformed to electrical energy or electricity is used to cause chemical change.

An **oxidation number**, also called **oxidation state**, is a positive or negative number assigned to an element in a molecule or ion according to a set of rules.

Common misconception: Oxidation state or oxidation number is often incorrectly confused with charge. Oxidation number is not charge. Oxidation number and charge are equivalent only when considering a monatomic ion.

Oxidation numbers are a way to keep track of electrons in redox reactions. Table 20.1 lists a set of simplified rules for determining oxidation numbers. For a more complete list of rules, see Section 4.4 of *Chemistry: The Central Science*.

Table 20.1   Simplified rules for determining oxidation numbers.

1. The oxidation number of combined oxygen is usually $2-$, except in the peroxide ion, O_2^{2-}, where the oxidation number of oxygen is $1-$.   Examples: In H_2O_2 and BaO_2, O is $1-$.
2. The oxidation number of combined hydrogen is usually $1+$, except in the hydride ion, H^-, where it is $1-$.   Examples: In NaH and CaH_2, H is $1-$.
3. The oxidation numbers of all individual atoms of a formula add to the charge on that formula. When in doubt, separate ionic compounds into common cation–anion pairs.   Examples: Na K^+ O_2 Ca^{2+} H_2SO_4 NO_3^- $Mg_3(PO_4)_2 =$ Mg^{2+} PO_4^{3-} 0 $1+$ 0 $2+$ $1+6+2-$ $5+2-$ $2+$ $5+2-$ $2+$ $5+2-$

Your Turn 20.1

What is the oxidation number of sulfur in each of the following atoms, molecules, and ions: sulfate, thiosulfate, sulfide, sulfite, thiocyanate, sulfur, sulfur dioxide, sulfur trioxide? In which case(s) is(are) oxidation number equal to charge?

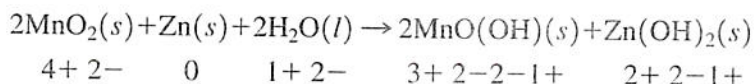*Write your answer in the space provided.*

An **oxidation–reduction reaction**, also called a **redox reaction**, is a reaction where electrons are transferred between reactants. The oxidation numbers of some of the elements change as they become products.

Oxidation is the loss of electrons. Substances that lose electrons are said to be oxidized.

Reduction is the gain of electrons. Substances that gain electrons are reduced. Both an oxidation and a reduction occur in all redox reactions.

In a redox reaction, one substance loses electrons and another gains electrons. For example, the chemical reaction in a common alkaline flashlight cell is complex, but it can be approximately represented by the equation below. The oxidation numbers of each element are assigned according to the rules given in Table 20.1.

$$2MnO_2(s) + Zn(s) + 2H_2O(l) \rightarrow 2MnO(OH)(s) + Zn(OH)_2(s)$$
$$4+ \ 2- \quad 0 \quad \ 1+ \ 2- \quad \ 3+ \ 2- \ 2- \ 1+ \quad 2+ \ 2- \ 1+$$

Notice that Mn changes oxidation numbers from 4+ to 3+ as it goes from MnO_2 to $MnO(OH)$. Also Zn changes from 0 to 2+. MnO_2 is reduced because it has gained electrons. (The oxidation number of Mn has been reduced.) Zn is oxidized because it has lost electrons. (The oxidation number of Zn has increased.)

In the alkaline cell reaction, there is a transfer of electrons from Zn to MnO_2. The cell is designed to take advantage of this transfer of electrons by allowing the electrons to flow as electricity through an external circuit.

Common misconception: Although you will see the terms *reducing agent* and *oxidizing agent* in many texts, these terms are not used on the AP exam. *In the reaction above, Zn is called the reducing agent because it is the agent that provides electrons for MnO_2 to be reduced. MnO_2 is the oxidizing agent because it is the agent that takes electrons away from Zn, causing Zn to be oxidized. The substance oxidized is the reducing agent and the substance reduced is the oxidizing agent.*

Your Turn 20.2

How can you tell that the following reaction is a redox reaction? Explain your reasoning. Assign oxidation numbers and identify the reactant that is oxidized and the reduced reactant.

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$. *Write your answers in the space provided.*

Section 20.2

Balancing Redox Equations

A **half-reaction** is an equation that shows either a reduction or an oxidation. Aqueous redox equations are conveniently balanced by the method of half-reactions. For example, we can represent the alkaline cell reaction shown above as separate oxidation and reduction half-reactions.

The **reduction half-reaction** shows electrons as reactants. The **oxidation half-reaction** shows electrons as products. The sum of the half-reactions yields the complete equation.

Table 20.2 illustrates some simplified rules for balancing half-reactions. For a detailed set of rules, see Section 20.2 of *Chemistry: The Central Science*.

Table 20.2   Simplified rules for balancing half-reactions.

If the reaction is in acidic solution, stop at Step 4:
1. Balance all elements other than H or O.
2. Balance O by adding H_2O as required.
3. Balance H by adding H^+ as required.
4. Balance charge by adding e^- to the more positive side.
If the reaction is in basic solution, continue through Step 7:
5. Count H^+ and add equal numbers of OH^- to both sides.
6. Combine each H^+ and OH^- on one side to yield water. $(H^+ + OH^- \rightarrow H_2O)$.
7. Combine or cancel water molecules as needed.

Example:

Balance the following equation in acidic solution.

$$HOCl(aq) + NO(g) \rightarrow Cl_2(g) + NO_3^-(aq)$$
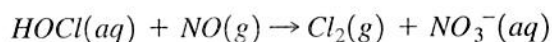
Solution:

First, separate the reactants and products into two half-reactions. HOCl and Cl_2 go together because they both contain Cl. Also, NO and NO_3^- are a pair because they both have N. Once the reactants and products are separated, just follow the rules.
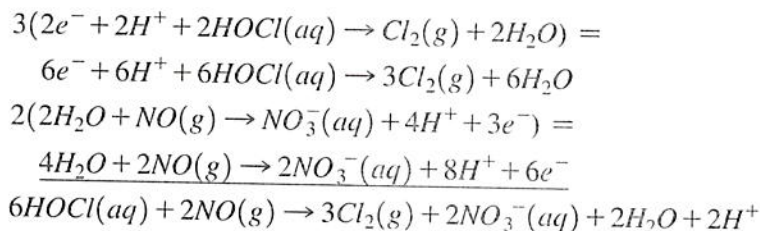
$$HOCl(aq) \rightarrow Cl_2(g) \qquad NO(g) \rightarrow NO_3^-(aq)$$

1. $2HOCl(aq) \rightarrow Cl_2(g)$

2. $2HOCl(aq) \rightarrow Cl_2(g) + 2H_2O$

3. $2H^+ + 2HOCl(aq) \rightarrow Cl_2(g) + 2H_2O$

4. $2e^- + 2H^+ + 2HOCl(aq) \rightarrow Cl_2(g) + 2H_2O$

$NO(g) \rightarrow NO_3^-(aq)$

1. $NO(g) \rightarrow NO_3^-(aq)$

2. $2H_2O + NO(g) \rightarrow NO_3^-(aq)$

3. $2H_2O + NO(g) \rightarrow NO_3^-(aq) + 4H^+$

4. $2H_2O + NO(g) \rightarrow NO_3^-(aq) + 4H^+ + 3e^-$

Now, equalize the number of electrons transferred in the half-reactions by multiplying the Cl reaction by 3 and the N reaction by 2 and add the half-reactions. The goal is to cancel all the electrons in the final balanced equation.

$3(2e^- + 2H^+ + 2HOCl(aq) \rightarrow Cl_2(g) + 2H_2O) =$
$\quad 6e^- + 6H^+ + 6HOCl(aq) \rightarrow 3Cl_2(g) + 6H_2O$
$2(2H_2O + NO(g) \rightarrow NO_3^-(aq) + 4H^+ + 3e^-) =$
$\quad \underline{4H_2O + 2NO(g) \rightarrow 2NO_3^-(aq) + 8H^+ + 6e^-}$
$6HOCl(aq) + 2NO(g) \rightarrow 3Cl_2(g) + 2NO_3^-(aq) + 2H_2O + 2H^+$

Example:

*Balance the above reaction assuming it also happens in basic solution.*

Solution:

First, apply Rules 1–4 as if the reaction were in acidic solution. Then, continue with Rules 5–7 to balance it in basic solution:

$6HOCl(aq) + 2NO(g) \rightarrow 3Cl_2(g) + 2NO_3^-(aq) + 2H_2O + 2H^+$

5. $2OH^- + 6HOCl(aq) + 2NO(g) \rightarrow 3Cl_2(g) + 2NO_3^-(aq) + 2H_2O +$
$\quad 2H^+ + 2OH^-$

6. $2OH^- + 6HOCl(aq) + 2NO(g) \rightarrow 3Cl_2(g) + 2NO_3^-(aq) + 2H_2O + 2H_2O$

7. $2OH^- + 6HOCl(aq) + 2NO(g) \rightarrow 3Cl_2(g) + 2NO_3^-(aq) + 4H_2O$
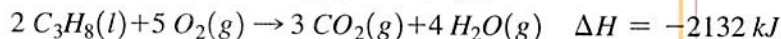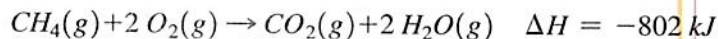
Your Turn 20.3

The percentage of hydrogen peroxide can be determined by a redox titration of the unknown solution into a standard solution of potassium permanganate. The endpoint of the titration is visualized by the abrupt disappearance of the deep purple permanganate ion to yield a colorless solution. The standard solution is prepared by dissolving 20.65 g of $KMnO_4$ in enough water to make 500 mL of solution. Exactly 25.00 mL of this solution is titrated with an unknown solution of hydrogen peroxide. The endpoint is reached upon addition of 34.05 mL of H_2O_2. The density of the H_2O_2 solution is 1.05 g/mL. The half-reactions are given:

$$H_2O_2 \rightarrow 2H^+ + O_2 + 2e^-$$
$$5\,e^- + 8H^+ + MnO_4^- \rightarrow 4H_2O + Mn^{2+}$$
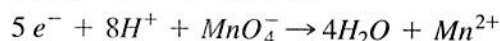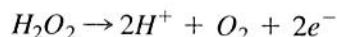
a. *Calculate the molar concentration of the standard $KMnO_4$ solution.*
b. *Write a balanced chemical equation for the reaction.*
c. *Determine the molar concentration of the H_2O_2 solution.*
d. *Calculate the grams of H_2O_2 used in the experiment.*
e. *Determine the percent of hydrogen peroxide in the solution.*

Write your answers in the space provided.

The production of energy by burning fossil fuels or metabolizing food is a practical application of redox reactions. For example, methane in natural gas and propane in a barbecue grill burn exothermically in air to produce carbon dioxide, water, and significant amounts of heat:

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g) \quad \Delta H = -802\ kJ$$
$$2\,C_3H_8(l) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(g) \quad \Delta H = -2132\ kJ$$

Glucose, $C_6H_{12}O_6$, is a typical carbohydrate that has a heat of combustion of
−2803 kJ/mol. The fat tristearin, $C_{57}H_{110}O_6$, has a food value of about 9.00 Cal/g.

    a. Write and balance thermochemical equations for the combustion of each of
       these foods.
    b. Calculate the food value in Calories per gram for glucose.
   *c. Calculate the molar heat of combustion of tristearin.*

Write your answers in the space provided.

Voltaic Cells   Section 20.3

A **voltaic cell** (also called a galvanic cell) is a device that spontaneously transforms chemical energy into electrical energy. The transfer of electrons of a redox reaction takes place through an external pathway.

Figure 20.1 illustrates a typical voltaic cell. Two compartments, called half-cells, physically separate the reactants. Each half-cell consists of a metal electrode immersed in an aqueous solution.
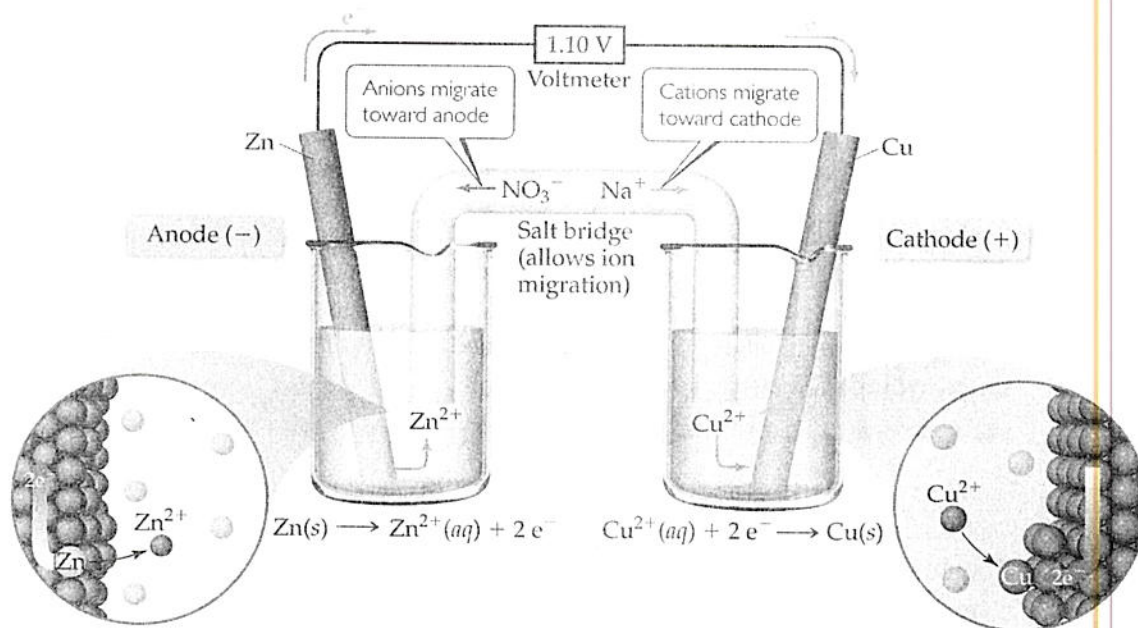
Figure 20.1 A voltaic cell uses a redox reaction to spontaneously generate an electric current. Electrons flow from the anode to the cathode. Anions migrate toward the anode and cations migrate toward the cathode.

The **anode** compartment is where **oxidation,** the loss of electrons, takes place. In Figure 20.1, the anode compartment contains a zinc metal anode and a zinc nitrate solution.

In the **cathode** compartment, **reduction,** the gain of electrons, takes place. The cathode compartment in Figure 20.1 contains a copper metal cathode and a copper(II) nitrate solution.

Because the reactants are separated, the reaction can occur only when the transfer of electrons takes place through an external circuit. Electrons always flow spontaneously from the anode to the cathode.

The voltaic cell uses a **salt bridge** to complete the electrical circuit. As oxidation and reduction take place, ions from the half-cell compartments migrate through the salt bridge to maintain the electrical neutrality of the respective solutions. Cations always move toward the cathode and anions move toward the anode.

Anode compartment oxidation half-reaction: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Cathode compartment reduction half-reaction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Overall reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

## Section 20.4   Cell Potentials under Standard Conditions

Cell potential, E_{cell} (also called electromotive force, EMF), is the potential difference that exists between the anode and the cathode of a voltaic cell. As a redox reaction takes place in a voltaic cell, the cell potential pushes electrons through the external circuit. Cell potential is measured in volts.

One **volt** is the potential difference required to impart one joule of energy to one coulomb of charge (1 volt $=$ 1 joule per coulomb, 1 V $=$ 1 J/C).

Cell voltage, E_{cell}, is positive for a spontaneous (thermodynamically favored) reaction.

A **standard reduction potential,** $E°_{cell}$, for a given half-reaction is the electric potential when that half-cell is coupled with a reference half-cell. The standard conditions are 25 °C, 1 atm pressure, and 1 M solutions. The reference half-cell is the standard hydrogen electrode whose potential is assigned 0.000 V. The reduction half-reaction of the hydrogen electrode is:

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad E°_{red} = 0.000 \text{ V}$$
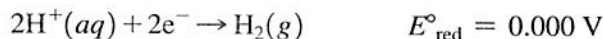
Common misconception: Do not confuse E_{cell} with $E°_{cell}$. E_{cell} refers to a cell potential under any nonstandard conditions. $E°_{cell}$ denotes a cell voltage under the standard conditions of 25 °C, 1 atm pressure, and 1 M solutions.

Table 20.3 lists the standard reduction potentials of several half-cells. (Appendix E of *Chemistry: The Central Science* has a more detailed list of standard reduction potentials.) For convenience, all half-reactions are written as reductions. The reverse reactions (oxidations) have the same cell voltage but with the opposite sign.

Table 20.3 Selected standard reduction potentials.

Oxidized/Reduced Substances	Half-Reaction	$E°_{red}$(volts) Forward Reaction	$E°_{ox}$ (volts) Reverse Reaction
F_2/F^-	$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+2.87	−2.87
Cl_2/Cl^-	$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.359	−1.359
Ag^+/Ag	$Ag^+(aq) + 1e^- \rightarrow Ag(s)$	+0.799	−0.799
Cu^{2+}/Cu	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.337	−0.337
H^+/H_2	$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.000	0.000
Zn^{2+}/Zn	$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.762	+0.762
Al^{3+}/Al	$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	−1.66	+1.66

Reactants that lose electrons are oxidized. A table of standard reduction potentials lists the relative tendency for a substance to be reduced. Easily reduced reactants have relatively high positive values of $E°_{red}$. The more positive the $E°_{red}$ value for a substance, the more easily the species is reduced. For example, $F_2(g)$ is the most easily reduced substance listed in Table 20.3. Al^{3+} is the least easily reduced substance in Table 20.3 because it has the most negative $E°_{red}$.

Reactants that are oxidized lose electrons. If all the half-reactions in a table of standard reduction potentials are reversed, the signs of the accompanying $E°$ values are reversed as well. Such a "reverse table" is a table of oxidation potentials. The more positive the $E°_{ox}$ value, the more readily the substance is oxidized. For example, $Al(s)$ is the most easily oxidized substance listed in Table 20.3.

A table of standard reduction potentials is useful in determining the thermodynamically favored reaction that will take place in a voltaic cell and what its voltage will be. When comparing two reduction potentials, a more positive voltage signifies a greater tendency for reduction. Therefore, when coupling two half-reactions, the one with the more positive voltage will be the reduction and it will force the other half-reaction to occur in reverse and become the oxidation.

All modern references employ tables of standard reduction potentials only. An oxidation potential has the same value as a corresponding reduction potential with an opposite sign.

To determine the thermodynamically favored reaction for any cell made up of two half-cells, reverse the half-reaction with the less positive $E°_{red}$, and add it to the half-reaction with the more positive voltage.

To determine the cell potential of any two coupled half-reactions, use the equation:

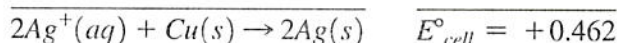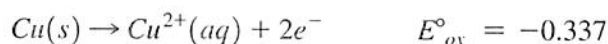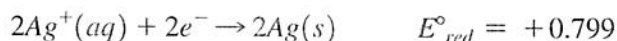$$E°_{cell} = E°_{red} + E°_{ox}$$

Example:

What is the reaction that occurs when a Ag half-cell is coupled with a Cu half-cell? Calculate the cell potential.

Solution:

From Table 20.3, the half-reactions are:

	Half-reaction	$E^°_{red}(V)$	$E^°_{ox}(V)$
Ag^+/Ag	$Ag^+(aq) + 1e^- \rightarrow Ag(s)$	$+0.799$	-0.799
Cu^{2+}/Cu	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$+0.337$	-0.337

The Ag half-reaction has the more positive voltage. Reverse the Cu half-reaction and add it to the Ag half-reaction. (Notice that to cancel the electrons, the Ag half-reaction is multiplied by a factor of 2! This factor does not change the value of $E^°_{red}$!)

$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s) \qquad E^°_{red} = +0.799$$

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^- \qquad E^°_{ox} = -0.337$$

$$\overline{2Ag^+(aq) + Cu(s) \rightarrow 2Ag(s) \qquad E^°_{cell} = +0.462}$$

To determine the voltage, $E^°_{cell}$, for the cell, add the voltages of the half-reactions. (Remember to change the sign of the reduction potential for the oxidation half-reaction.)

$$E^°_{cell} = E^°_{red} + E^°_{ox} = 0.799 + (-0.337) = +0.462 \text{ V}$$

Common misconception: Changing the coefficient in a balanced half-reaction does not affect the value of the standard reduction potential. Although, in the example, the Ag half-reaction is multiplied by a factor of 2 to make the electrons balance, the value of $E^°$ is not proportional to the balanced equation and should not be multiplied by 2!

Table 20.4 summarizes how to determine a cell potential from a table of standard reduction potentials.

Table 20.4 Simplified rules for using a table of standard reduction potentials to determine the overall reaction and the voltage, $E^°_{cell}$, for a cell consisting of any two half-cells.

1. Select the half-reaction with the more positive voltage as the reduction.
2. Reverse the half-reaction with the less positive voltage and add it to the reduction half-reaction.
3. Calculate the cell voltage, $E^°_{cell}$, by adding $E^°_{red}$ for the reduction half-reaction to $-E^°_{red}$ for the oxidation half-reaction.
$E^°_{cell} = E^°_{red} + E^°_{ox}$ ($E^°_{ox} = -E^°_{red}$ for the reversed reaction.)

Using the data in Table 20.3, choose the half-cells that, when coupled, will give the most positive voltage. Write the balanced equation for the reaction and calculate the voltage. Explain your answer. Write your answer in the space provided.

Free Energy and Redox Reactions   Section 20.5

A **thermodynamically favored (spontaneous) process** is one that happens on its own without any outside assistance. A thermodynamically favored reaction has a negative value for free energy, ΔG, and a positive value for cell potential, E_{cell}.

Free energy and cell potential are related by the following equation:

$$\Delta G° = -nFE°$$

where ΔG is free energy in kJ/mol

n is the number of moles of electrons transferred

F is Faraday's constant. One Faraday is the electrical charge carried by one mole of electrons. $1\ F = 96{,}485$ coulombs/mol $e^- = 96{,}485$ J/V-mol e^-.

$E°$ is the cell potential

Example:

Assume that aluminum and zinc half-cells are suitably connected at 298 K and that both aqueous solutions are 1.00 M concentrations (standard conditions).
a. *Write the half-reaction for the cathode.*
b. *Write the half-reaction for the anode.*
c. *Write the overall cell reaction.*
d. *Calculate the $E°$ for the voltaic cell.*
e. *Calculate the free energy change for the cell. Is the reaction thermodynamically favored? Explain.*
f. *Calculate the equilibrium constant for this reaction.*

Solution:

a. From Table 20.3, the reduction half-reactions and their corresponding $E°$ values are:

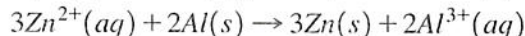Zn^{2+}/Zn $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ -0.762

Al^{3+}/Al $Al^{3+}(aq) + 3e^- \rightarrow Al(s)$ -1.66
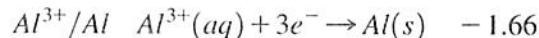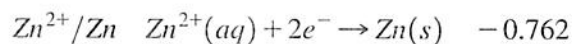
The reduction half-reaction is the Zn^{2+}/Zn half-reaction because it has the more positive $E°_{red}$.

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $E°_{red} = -0.762$ V
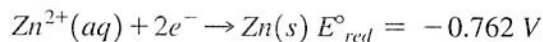
b. The oxidation half-reaction is the reverse of the listed Al^{3+}/Al half-reaction:

$Al(s) \rightarrow Al^{3+}(aq) + 3e^-$ $E°_{ox} = +1.66$ V
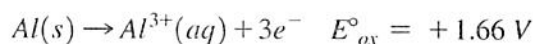
c. Multiply each half-reaction by coefficients that balance the electrons and add the half-reactions.

$3(Zn^{2+}(aq) + 2e^- \rightarrow Zn(s))$ $= 3Zn^{2+}(aq) + 6e^- \rightarrow 3Zn(s)$

$2(Al(s) \rightarrow Al^{3+}(aq) + 3e^-)$ $= 2Al(s) \rightarrow 2Al^{3+}(aq) + 6e^-$

$3Zn^{2+}(aq) + 2Al(s) \rightarrow 3Zn(s) + 2Al^{3+}(aq)$

d. Add the cell potentials of the two half-reactions. Do not multiply the cell voltages by the coefficients that balance the equation.

$E°_{cell} = E°_{red} + E°_{ox} = -0.762$ V $+ 1.66$ V $= +0.90$ V

e. In the equation, $\Delta G° = -nFE°$, the number of moles of electrons transferred is 6, as evidenced by the balanced half-reactions.

$\Delta G° = -nFE°$

$\Delta G° = -(6 \ mol \ e^-)(96,485 \ J/V\text{-}mol \ e^-)(+0.90 \ V) = -520,000 \ J$
$= -520 \ kJ$

The positive value of $E°$ and the corresponding negative value of $\Delta G°$ both indicate that the reaction is thermodynamically favored, which we would expect in a voltaic cell.

f. From Topic 19, $\Delta G = -RT \ln K$

where $R = 8.314$ J/K mol

$T = $ absolute temperature

$K = $ the equilibrium constant

$\Delta G° = -RT \ln K$

$-520,000 \ J/mol = -(8.314 \ J/K \ mol)(298 \ K) \ln K$

$\ln K = 210$

$K = e^{210} = 1.6 \times 10^{91}$

The equilibrium constant is very large, which means that the reaction goes nearly to completion. This is consistent with the very large negative free energy, indicating a thermodynamically favored reaction.

Cell Potentials under Nonstandard Conditions

As a voltaic cell discharges, reactants are consumed and products are generated. The concentrations of reactants decrease while those of products increase. As the cell operates, the conditions become nonstandard and the voltage drops. Some useful predictions can be made by considering the value of Q in the thermodynamic equation, $\Delta G = \Delta G° + RT \ln Q$.

Consider the cell reaction in the previous example.

$$3Zn^{2+}(aq) + 2Al(s) \rightarrow 3Zn(s) + 2Al^{3+}(aq) \quad E°_{cell} = +0.90 \text{ V}$$
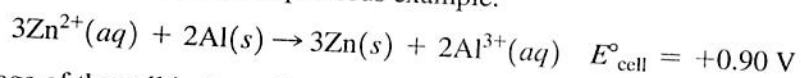
The voltage of the cell is dependent on the concentrations of reactants and products. As the cell operates, $[Zn^{2+}]$ decreases and $[Al^{3+}]$ increases. As the value of Q becomes greater, the value of ΔG becomes more positive and the reaction is less thermodynamically favored in the forward direction. A less thermodynamically favored reaction will experience a drop in voltage from the standard 0.90 V. As time goes on, the reaction eventually reaches equilibrium and the cell voltage becomes zero.

Under what conditions might the reaction in the above example have a cell voltage that is greater than 0.90 V? Justify your answer by considering the value of Q. Write your answer in the space provided.

Common misconception: Remember that E_{cell} is the voltage of a cell at nonstandard conditions and that $E°_{cell}$ is the voltage at standard conditions.

Electrolysis

Electrolysis is the application of an electric current to a chemical system.

An **electrolytic cell** is a device that uses electrical energy to cause a non-thermodynamically favored (nonspontaneous) chemical reaction to occur. An electrolytic cell converts electrical energy into chemical energy. Figure 20.2 illustrates an electrolytic cell.
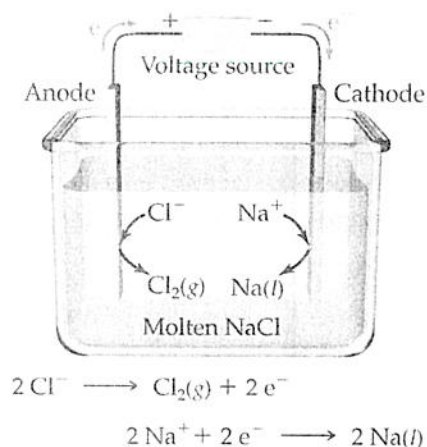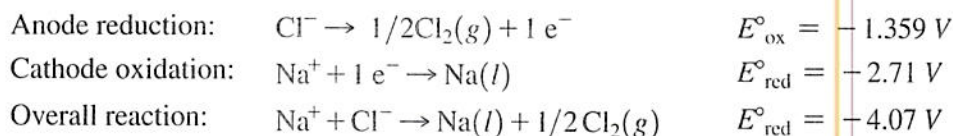
Figure 20.2 Diagram of an electrolytic cell for the electrolysis of molten NaCl.

Solid sodium chloride does not conduct electricity and cannot be electrolyzed because the ions are locked in place in a strong three-dimensional ionic lattice.

However, molten sodium chloride does conduct electricity. The energy required to melt the solid overcomes the attractive forces that hold the ions in the lattice. The ions are free to migrate to the electrodes. Negative chloride ions migrate to the anode and give up their electrons to become chlorine gas. Positive sodium ions move to the cathode, collect electrons, and become liquid sodium. The half-reactions, the overall equation, and the corresponding voltages of the electrolytic cell are:

Anode reduction: $Cl^- \rightarrow 1/2 Cl_2(g) + 1\ e^-$ $E°_{ox} = -1.359\ V$

Cathode oxidation: $Na^+ + 1\ e^- \rightarrow Na(l)$ $E°_{red} = -2.71\ V$

Overall reaction: $Na^+ + Cl^- \rightarrow Na(l) + 1/2\ Cl_2(g)$ $E°_{red} = -4.07\ V$

Notice that the overall reaction has a negative voltage, so it is not thermodynamically favored. It required just over 4 V to electrolyze molten sodium chloride. All electrolysis reactions are not thermodynamically favored.

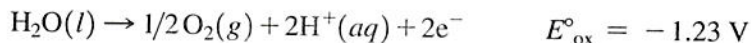### The Electrolysis of Water Using an Inert Electrolyte

Water, in the presence of an inert electrolyte such as sodium sulfate, will undergo electrolysis. While pure water does not conduct electricity, inert ions in water can migrate toward the electrodes and carry an electric current sufficient to electrolyze water. Because water is a polar molecule, the partially positive hydrogen end of a molecule will migrate toward the negative cathode and pick up electrons to become hydrogen gas. The oxygen end of a water molecule will migrate toward the anode and give up electrons to become oxygen gas. The half-reactions and the overall reaction are:
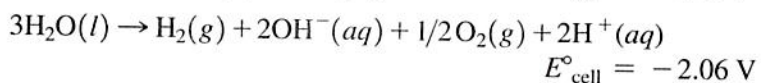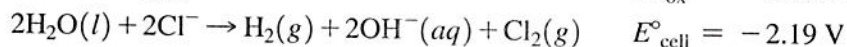
Cathode reduction:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E^\circ_{red} = -0.83 \text{ V}$$

Anode oxidation:

$$H_2O(l) \rightarrow 1/2\,O_2(g) + 2H^+(aq) + 2e^- \qquad E^\circ_{ox} = -1.23 \text{ V}$$

Overall reaction:

$$3H_2O(l) \rightarrow H_2(g) + 2OH^-(aq) + 1/2\,O_2(g) + 2H^+(aq)$$
$$E^\circ_{cell} = -2.06 \text{ V}$$

Or

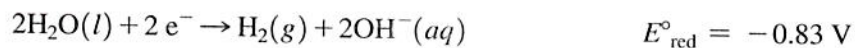$$H_2O(l) \rightarrow H_2(g) + 1/2\,O_2(g) \qquad E^\circ_{cell} = -2.06 \text{ V}$$

The electrolysis of water with an inert electrolyte requires just over 2 V.

The Electrolysis of an Aqueous Sodium Chloride Solution

Electrolysis of an aqueous solution of sodium chloride produces hydrogen gas at the cathode and chlorine gas at the anode. The half-reactions and the overall process are given below.

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E^\circ_{red} = -0.83 \text{ V}$$
$$2Cl^- \rightarrow Cl_2(g) + 2e^- \qquad E^\circ_{ox} = -1.359 \text{ V}$$
$$2H_2O(l) + 2Cl^- \rightarrow H_2(g) + 2OH^-(aq) + Cl_2(g) \qquad E^\circ_{cell} = -2.19 \text{ V}$$

In the case of the electrolysis of aqueous sodium chloride, there are two possible reductions that can take place at the cathode. Either water will gain electrons and produce hydrogen gas or sodium ions pick up electrons to become sodium metal.

Possible cathode reductions:

$$Na^+(aq) + 1\,e^- \rightarrow Na(l) \qquad E^\circ_{red} = -2.71 \text{ V}$$
$$2H_2O(l) + 2\,e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E^\circ_{red} = -0.83 \text{ V}$$
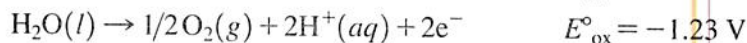
It is usually possible to predict which of the possible half-reactions will occur when solutions are electrolyzed on the basis of their relative E°_{red} values. The reduction potential for water is more favorable than the reduction potential for sodium ion, because water has the more positive value for E°_{red}. Therefore, the water reduction, not the sodium ion reduction, will occur at the cathode.

The same analysis can be made for the possible oxidation reactions. Generally, the oxidation with the more positive E°_{ox} value will predominate.

The Chloride Ion Is an Uncommon Exception

The oxidation potential for chloride ion is less positive than the oxidation potential for water, so from a thermodynamic argument, water should oxidize in the presence of aqueous chloride ion. And, indeed, it does. However, the oxidation of water is kinetically very slow. By comparison, the oxidation of chloride ion is rapid. Additionally, both half-reactions require similar voltages to carry out. Usually, in most electrolytic cells, there is sufficient voltage to drive both reactions. Because of the relative rates of reaction, chlorine gas, not oxygen gas, is produced at the anode.
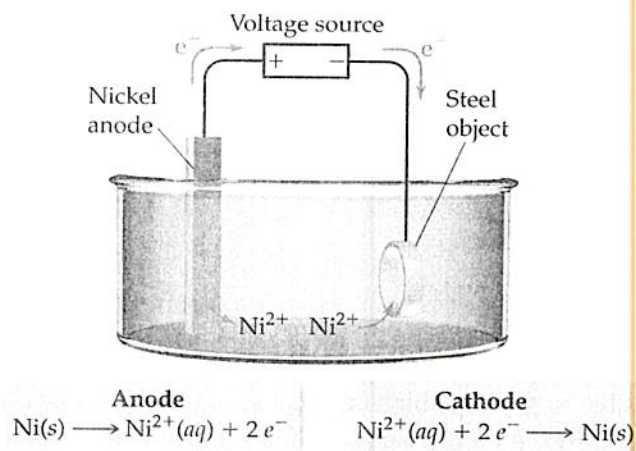
Possible anode oxidations:

$$Cl^-(aq) \rightarrow 1/2\,Cl_2(g) + 1\,e^- \qquad\qquad E^\circ_{ox} = -1.359\ V$$
$$H_2O(l) \rightarrow 1/2\,O_2(g) + 2H^+(aq) + 2e^- \qquad E^\circ_{ox} = -1.23\ V$$
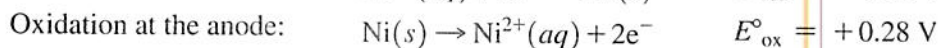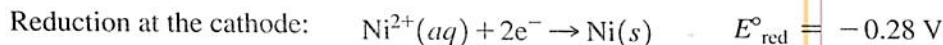
Electroplating

Electrolysis is commonly used in electroplating, the process of depositing a thin coating of one metal onto another metal for ornamental purposes or for corrosion resistance. For example, steel is commonly plated with nickel or chromium and eating utensils are often plated with silver or gold.

To plate nickel on a steel surface, for example, an electrolysis apparatus illustrated in Figure 20.3 consisting of a nickel anode and a steel cathode is used. Both electrodes are immersed in an aqueous solution of nickel nitrate. Voltage applied to the cell forces electrons from the anode to the cathode. Reduction of Ni^{2+} ions occurs at the cathode where nickel metal plates the steel. The nickel anode oxidizes to nickel ions that replace the ions in solution.
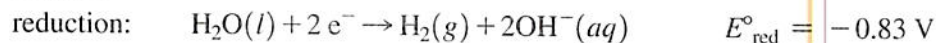

Figure 20.3 Electrolysis device for plating nickel onto a piece of steel.

The half-reactions are:

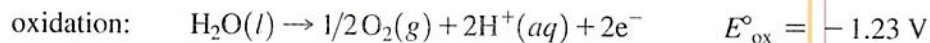|		
Reduction at the cathode:	$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	$E^\circ_{red} = -0.28\ V$
Oxidation at the anode:	$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$	$E^\circ_{ox} = +0.28\ V$

The other possible anode and cathode reactions are the oxidation and reduction of water, both of which have less favorable potentials than do the nickel reactions.

|		
Cathode reduction:	$H_2O(l) + 2\,e^- \rightarrow H_2(g) + 2OH^-(aq)$	$E^\circ_{red} = -0.83\ V$
Anode oxidation:	$H_2O(l) \rightarrow 1/2\,O_2(g) + 2H^+(aq) + 2e^-$	$E^\circ_{ox} = -1.23\ V$

The nickel reactions predominate and the net effect is to move nickel atoms from the anode to the surface of the steel cathode.

Quantitative Aspects of Electrolysis

A balanced half-reaction tells how many moles of electrons are involved in a redox reaction. For example, when silver ion is reduced to silver metal, one mole of electrons is transferred. When water is reduced to hydrogen gas and hydroxide ion, two moles of electrons are involved.

$$Ag^+(aq) + 1\,e^- \rightarrow Ag(s)$$
$$2H_2O(l) + 2\,e^- \rightarrow H_2(g) + 2OH^-(aq)$$
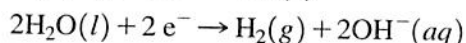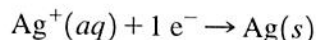
The amount of a substance that is oxidized or reduced in an electrolytic cell is directly proportional to the number of electrons passed through the cell. The balanced half-reaction is a way to convert electrical quantities into moles of chemical quantities and vice versa.
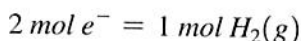
Example:

How many liters of dry hydrogen gas at 30 °C and 720 torr can be obtained by the electrolysis of water for 1 h at 2.50 A?

Solution:

The key ideas in this quantitative electrolysis problem are:

The balanced half-reaction relates moles of electrons transferred to moles of chemical reactants or products:

$2\ mol\ e^- = 1\ mol\ H_2(g)$

The ampere is the measure of electric current. One ampere is one coulomb of electric charge passing a point in an electrical circuit in 1 s:

$2.50\ A = 2.50\ Coulombs\ per\ second = 2.50\ C/s$

Faraday's constant tells the quantity of electric charge carried by a mole of electrons:

$1\ mol\ e^- = 96,485\ C\ (Faraday's\ constant)$

The ideal-gas equation calculates volume in liters from number of moles, n, absolute temperature, T, pressure in atmospheres, P, and the universal gas constant, R. R = 0.0821 L-atm/mol-K.

$V = nRT/P$

$x\ mol\ H_2(g) = 1\ h(60\ min/h)(60\ s/min)(2.50\ C/s)(1\ mole\ e^-/96,485\ C)$
$(1\ mol\ H_2/(2\ mol\ e^-) = 0.0466\ mol\ H_2$

$V = nRT/P = (0.0466\ mol)(0.0821\ L\text{-}atm/mol\text{-}K)(303\ K)/$
$(720/760)\ atm = 1.22\ L$

Multiple Choice Questions

1. When the following species are listed in order of increasing oxidation number of the sulfur atoms (most negative to most positive oxidation number), the correct order is

   A) $CuS, K_2S_2O_3, SO_2, Na_2SO_4$.

   B) $CuS, SO_2, K_2S_2O_3, Na_2SO_4$.

   C) $CuS, SO_2, Na_2SO_4, K_2S_2O_3$.

   D) $Na_2SO_4, CuS, K_2S_2O_3, SO_2$.

   E) $K_2S_2O_3, SO_2, Na_2SO_4, CuS$.

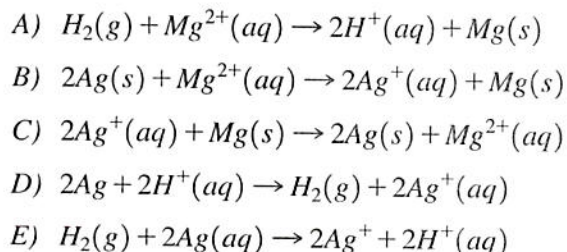2. Use the reduction potentials to determine which one of the reactions below is thermodynamically favored.

   Reduction potentials, E^o

   1) $Cd^{2+} + 2e^- \rightarrow Cd \quad -0.403$ V

   2) $Mn^{2+} + 2e^- \rightarrow Mn \quad -1.18$ V

   3) $Cu^+ + 1e^- \rightarrow Cu \quad +0.521$ V

   4) $Fe^{3+} + 1e^- \rightarrow Fe^{2+} \quad +0.771$ V

   A) $Cd^{2+} + 2Cu \rightarrow Cd + 2Cu^+$

   B) $Mn^{2+} + 2Cu \rightarrow Mn + 2Cu^+$

   C) $Cd^{2+} + Mn \rightarrow Cd + Mn^{2+}$

   D) $Cu^+ + Fe^{2+} \rightarrow Cu + Fe^{3+}$

   E) $Cd^{2+} + 2Fe^{2+} \rightarrow Cd + 2Fe^{3+}$

3. What is the coefficient for MnO_4^- when the following redox equation is balanced in acidic solution using the smallest whole-number coefficients?
   $H^+ + Cr_2O_7^{2-} + Mn^{2+} \rightarrow H_2O + Cr^{3+} + MnO_4^-$

   A) 1

   B) 2

   C) 5

   D) 6

   E) 10

4. Which element can have the highest positive oxidation number?

   A) O

   B) C

   C) Cl

   D) N

   E) Cr

5. *Magnesium reacts with dilute hydrochloric acid to produce hydrogen gas. Silver does not react in dilute hydrochloric acid. Based on this information, which of the following reactions will occur as written?*

A) $H_2(g) + Mg^{2+}(aq) \rightarrow 2H^+(aq) + Mg(s)$

B) $2Ag(s) + Mg^{2+}(aq) \rightarrow 2Ag^+(aq) + Mg(s)$

C) $2Ag^+(aq) + Mg(s) \rightarrow 2Ag(s) + Mg^{2+}(aq)$

D) $2Ag + 2H^+(aq) \rightarrow H_2(g) + 2Ag^+(aq)$

E) $H_2(g) + 2Ag(aq) \rightarrow 2Ag^+ + 2H^+(aq)$

Use the following information to answer Questions 6–8.
A cell is set up using the following half-reactions under standard conditions.

$$Mg^{2+} + 2e^- \rightarrow Mg \qquad E° = -2.37 \ V$$
$$Ag^+ + 1e^- \rightarrow Ag \qquad E° = +0.80 \ V$$
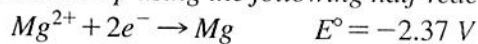
6. *What is the voltage of the cell?*

A) $+1.57 \ V$

B) $+3.17 \ V$

C) $+3.97 \ V$

D) $-0.77 \ V$

E) $+0.77 \ V$

7. *What are the products of the reaction?*

A) $Mg^{2+} + Ag^+$

B) $Mg^{2+} + Ag$

C) $Ag^+ + Mg$

D) $Ag^+ + Mg^{2+}$

E) $Mg + Ag$

8. *If the $[Mg^{2+}]$ is changed to 0.50 M, what will initially happen to the voltage?*

A) *no change*

B) *increase*

C) *decrease to a nonzero value*

D) *drop to zero*
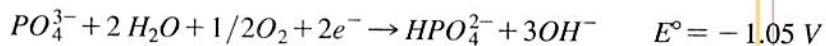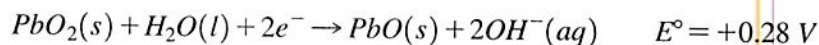
E) *There is not enough information to make a prediction.*

Free Response Questions

1. *Suppose that gold and silver half-cells are suitably connected.*

   $$Au^{3+} + 3e^- \rightarrow Au(s) \quad E° = +1.50 \ V$$

   $$Ag^+ + 1e^- \rightarrow Ag(s) \quad E° = +0.80 \ V$$
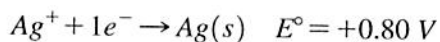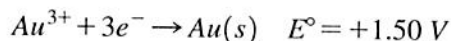
   a. i. *Identify the cathode and anode half-reactions.*

   ii. *Write the overall cell reaction.*

   iii. *Calculate $E°$ for the cell.*

   b. *Calculate $\Delta G°$ for the cell.*

   c. *Calculate the equilibrium constant for the cell reaction at 25°C.*

   d. *If $[Ag^+]$ is increased to 1.50 M, will the reaction be more spontaneous or less spontaneous? Will the cell voltage increase, decrease, or remain the same? Justify your answer.*

   e. *In a separate experiment, how many grams of gold can be plated onto a piece of jewelry if a 1.00 M solution of gold(III) nitrate is suitably electrolyzed for 45 min at 2.50 A?*

   f. *In yet another experiment, how many minutes are required to plate 1.00 g of silver onto an inert electrode at 1.25 A?*

2. *Consider the following half-reactions and their standard reduction potentials at 25 °C.*

   $$PbO_2(s) + H_2O(l) + 2e^- \rightarrow PbO(s) + 2OH^-(aq) \qquad E° = +0.28 \ V$$

   $$IO_3^- + 2 \ H_2O + 4 \ e^- \rightarrow IO^- + 4OH^- \qquad E° = +0.56 \ V$$

   $$PO_4^{3-} + 2 \ H_2O + 1/2O_2 + 2e^- \rightarrow HPO_4^{2-} + 3OH^- \qquad E° = -1.05 \ V$$

   a. i. *Which two half-reactions when combined will give the voltaic cell with the largest $E°$ for the cell?*

   ii. *Write the overall cell reaction that would take place.*

   iii. *Calculate $E°$ for the cell.*

   b. *Indicate how the E_{cell} will be affected by the following changes. Justify your answers.*

   i. *If the pH of both the anode and cathode compartments is decreased.*

   ii. *If $[OH^-]$ is fixed at 1.0 M, $O_2(g)$ is fixed at 1 atm, and all other ion concentrations are changed to 0.10 M.*

   iii. *If the temperature is increased while all concentrations remain at 1.0 M.*