TOPIC

# 20

# ELECTROCHEMISTRY

Students need to understand the concept of electrochemical cells, their structures, the chemical processes that take place in electrochemical cells, and the differences between voltaic and electrolytic cells. They must be able to calculate cell EMF and quantitatively determine spontaneity. Calculations using the Nernst equation relating cell EMF to concentrations need to be mastered as well as quantitative electrolysis determinations using Faraday's constant, time, amperage, and moles of substances. Pay particular attention to these sections in *Chemistry the Central Science.*

20.1 **Oxidation States and Oxidation-Reduction Reactions**

20.2 **Balancing Oxidation-Reduction Equations**

20.3 **Voltaic Cells**

20.4 **Cell EMF Under Standard Conditions**

20.5 **Free Energy and Redox Reactions**

20.6 **Cell EMF Under NonStandard Conditions**

20.9 **Electrolysis**

## Oxidation States and Oxidation-Reduction Reactions

Section 20.1
and
Review Section 4.4

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

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.*

**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.

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−. <br> 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? In which case(s) is/are oxidation number equal to charge?*

*Sulfate, thiosulfate, sulfide, sulfite, thiocyanate, sulfur, sulfur dioxide, sulfur trioxide. 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 have been assigned according to the rules given in Table 20.1.

$$2MnO_2(s) + Zn(s) + 2H_2O(l) \dashrightarrow 2MnO(OH)(s) + Zn(OH)_2(s)$$

$$\;\;\;4+\; 2-\qquad\;\; 0\qquad\;\; 1+\, 2-\qquad\;\; 3+\, 2-\, 2-1+\qquad 2+\, 2-1+$$
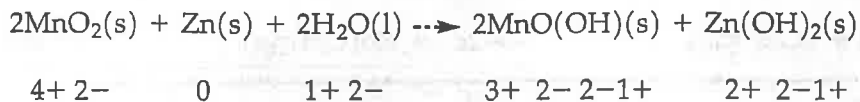
Notice that Mn changes oxidation numbers from 4+ to 3+ as it goes from $MnO_2$ to MnO(OH). Also Zn changes from 0 to 2+. $MnO_2$ is reduced because it has gained electrons. (The oxidation number of Mn has been reduced.) Zn is oxidized because it has lost electrons. (The oxidation number of Zn has increased.)

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.

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*

*In the following reaction, identify the oxidizing agent, the reducing agent, the substance oxidized, and the substance reduced: $N_2(g) + 3H_2(g) \dashrightarrow 2NH_3(g)$. Explain your reasoning. Write your answer in the space provided.*
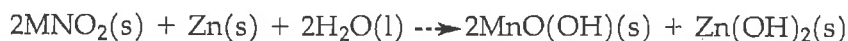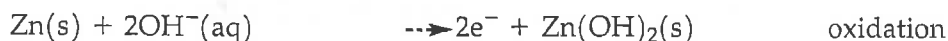
## Section 20.2    Balancing Oxidation-Reduction Equations

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.

$$2MnO_2(s) + 2H_2O(l) + 2e^- \dashrightarrow 2MnO(OH)(s) + 2OH^-(aq) \quad \text{reduction}$$

$$Zn(s) + 2OH^-(aq) \dashrightarrow 2e^- + Zn(OH)_2(s) \quad \text{oxidation}$$

$$2MNO_2(s) + Zn(s) + 2H_2O(l) \dashrightarrow 2MnO(OH)(s) + Zn(OH)_2(s)$$

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 20.1 illustrates some simplified rules for balancing half-reactions. For a more complete 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 $H^+ + OH^-$ on one side to yield water. ($H^+ + OH^- = H_2O$) |
| 7. Combine or cancel water molecules as needed. |

### Example:

*Balance the following equation in acidic solution.*

$$HOCl(aq) + NO(g) \dashrightarrow Cl_2(g) + NO_3^-(aq)$$

## 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.*
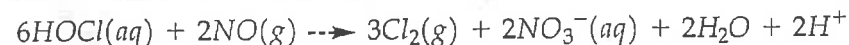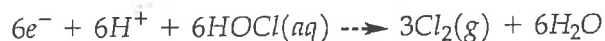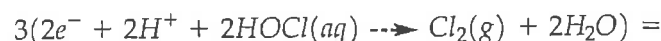
$$HOCl(aq) \dashrightarrow Cl_2(g) \qquad\qquad NO(g) \dashrightarrow \qquad NO_3^-(aq)$$

1. $2HOCl(aq) \dashrightarrow Cl_2(g)$
2. $2HOCl(aq) \dashrightarrow Cl_2(g) + 2H_2O$
3. $2H^+ + 2HOCl(aq) \dashrightarrow Cl_2(g) + 2H_2O$
4. $2e^- + 2H^+ + 2HOCl(aq) \dashrightarrow Cl_2(g) + 2H_2O$

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

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

*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 of the electrons in the final balanced equation.*

$$3(2e^- + 2H^+ + 2HOCl(aq) \dashrightarrow Cl_2(g) + 2H_2O) =$$
$$6e^- + 6H^+ + 6HOCl(aq) \dashrightarrow 3Cl_2(g) + 6H_2O$$
$$2(2H_2O + NO(g) \dashrightarrow NO_3^-(aq) + 4H^+ + 3e^-) =$$
$$4H_2O + 2NO(g) \dashrightarrow 2NO_3^-(aq) + 8H^+ + 6e^-$$

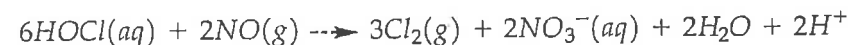$$\overline{6HOCl(aq) + 2NO(g) \dashrightarrow 3Cl_2(g) + 2NO_3^-(aq) + 2H_2O + 2H^+}$$

## Example:

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

## Solution:

*First apply Rules 1 through 4 as if the reaction were in acidic solution.*

*Then continue with Rules 5 through 7 to balance it in basic solution:*

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

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

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

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

## Section 20.3   Voltaic Cells

A **voltaic** (or 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.

Oxidation, the loss of electrons, takes place in the anode compartment. In Figure 20.1, the anode compartment contains a zinc metal anode and a zinc nitrate solution.

Reduction, the gain of electrons, takes place in the cathode compartment, consisting in Figure 20.1 of a copper metal cathode and a copper(II) nitrate solution.



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

Movement of cations →
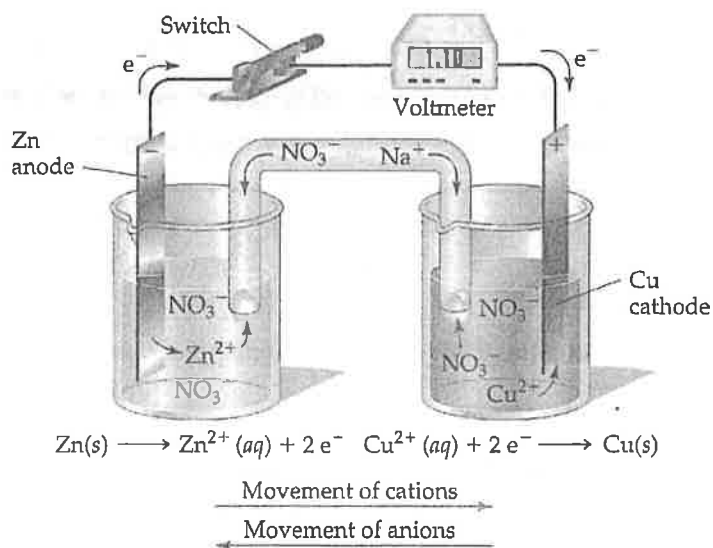
← Movement of anions

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.

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. (To examine an atomic view of an operating voltaic cell, see Figures 20.7 and 20.8 of *Chemistry the Central Science*.)

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

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

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

## Cell EMF Under Standard Conditions    Section 20.4

A potential difference exists between anode and cathode of a voltaic cell. As the redox reaction takes place this cell potential, also called electromotive force (emf), pushes electrons through the external circuit. The **cell potential**, $E_{cell}$, (also called **electromotive force, EMF**) 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 reaction.

A standard reduction potential 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 volts. The reduction half-reaction of the hydrogen electrode is:

$$2H^+(aq) + 2e^- \longrightarrow H_2(g) \qquad E°_{red} = 0.000 \text{ volts}$$
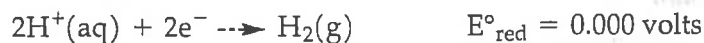
Table 20.3 lists the standard reduction potentials of several half-cells. (Appendix E of *Chemistry the Central Science* has a more complete list of standard reduction potentials.) For convenience, all half-reactions are written as reductions. The reverse reactions (oxidations) have the same cell voltage but with the opposite signs.

A table of standard reduction potentials is useful in determining the spontaneous 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

Table 20.3. Selected standard reduction potentials

| Oxidizing/reducing agents | Half-reaction | $E°_{red}$ (volts) Forward reaction | $E°_{ox}$ (volts) Reverse reaction |
|---|---|---|---|
| $F_2/F^-$ | $F_2(g) + 2e^- \longrightarrow 2F^-(aq)$ | +2.87 | −2.87 |
| $Cl_2/Cl^-$ | $Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$ | +1.359 | −1.359 |
| $Ag^+/Ag$ | $Ag^+(aq) + 1e^- \longrightarrow Ag(s)$ | +0.799 | −0.799 |
| $Cu^{2+}/Cu$ | $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ | +0.337 | −0.337 |
| $H^+/H_2$ | $2H^+(aq) + 2e^- \longrightarrow H_2(g)$ | 0.000 | 0.000 |
| $Zn^{2+}/Zn$ | $Zn^{2+}(aq) + 2e^- \longrightarrow Zn(S)$ | −0.762 | +0.762 |
| $Al^{3+}/Al$ | $Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$ | −1.66 | +1.66 |

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.

To determine the spontaneous 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. Similarly, to determine the cell potential of any two coupled half-reactions, change the sign of the potential for the reversed half-reaction and add it to the potential of the reduction half-reaction.

### Example:

*What is the reaction that occurs when a Ag half cell is coupled with a Cu half-cell?*
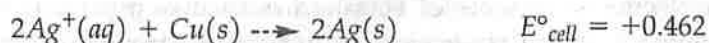
### Solution:

*From Table 20.3, the half-reactions are:*

|  | *half-reaction* | $E°_{red}(volts)$ | $E°_{ox}(volts)$ |
|---|---|---|---|
| $Ag^+/Ag$ | $Ag^+(aq) + 1e^- \longrightarrow Ag(s)$ | +0.799 | −0.799 |
| $Cu^{2+}/Cu$ | $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ | +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 $E°_{red}$!)*

$$2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s) \qquad\qquad E^\circ_{red} = +0.799$$

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^- \qquad\qquad E^\circ_{ox} = -0.337$$

$$2Ag^+(aq) + Cu(s) \longrightarrow 2Ag(s) \qquad\qquad E^\circ_{cell} = +0.462$$

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

**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 $E^\circ$ is not proportional to the balanced equation and should not be multiplied by 2!

Table 20.4 summarizes the process.

Table 20.4. Simplified rules for using a standard reduction potentials table to determine the overall reaction and the voltage, $E^\circ_{cell}$, 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, $E^\circ_{cell}$, by adding $E^\circ_{red}$ for the reduction half-reaction to $-E^\circ_{red}$ for the oxidation half-reaction. |
| $E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox}$ $\qquad\qquad$ ($E^\circ_{ox} = -E^\circ_{red}$ for the reversed reaction.) |

*Your Turn 20.3*

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

How to recognize common oxidizing and reducing agents.

**Oxidizing agents** are substances that take electrons away from another reactant in a redox reaction. In the process, oxidizing agents are reduced. They gain electrons. Any table of standard reduction potentials lists the relative strengths of oxidizing agents. In general, strong oxidizing agents have relatively high positive values of $E°_{red}$. The more positive the $E°_{red}$ value for a substance listed in a table of standard reduction potentials, the stronger the oxidizing agent. For example, $F_2(g)$ is the strongest oxidizing agent listed in Table 20.3.

**Reducing agents** are substances that provide electrons to another reactant. Reducing agents lose electrons. They are oxidized in redox reactions. The relative strengths of reducing agents are indirectly listed *as products* in tables of standard reduction potentials. The half reaction with the more negative reduction potential contains the product which is the stronger reducing agent.

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 stronger the oxidation potential. For example, Al(s) is the strongest reducing agent listed in Table 20.3.

Whether a substance acts as an oxidizing agent or a reducing agent depends on the relative values of $E°_{red}$ for their respective reduction half-reactions. For example, half-reactions for the reduction of $Mn^{2+}$ to Mn and $Fe^{2+}$ to Fe both have negative reduction potentials. $Fe^{2+}$ has the more positive $E°_{red}$ so when coupled with Mn, $Fe^{2+}$ will act as the oxidizing agent and Mn will be the reducing agent. However, if Fe and Ni are coupled, $Ni^{2+}$ will be the oxidizing agent and Fe will be the reducing agent.

|  | $E°_{red}$ (volts) | $E°_{ox}$ (volts) |
|---|---|---|
| $Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$ | −0.440 | +0.440 |
| $Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$ | −0.28 | +0.28 |
| $Mn^{2+}(aq) + 2e^- \quad Mn(s)$ | −1.18 | +1.18 |

Given reactants in word form, the AP exam requires students to predict products and write the formulas of reactants and products in net ionic form. Redox reactions are included on the AP exam.

**Recognize a redox reaction if:**

1. One reactant is a metal and the other is an aqueous metal ion. The metal will be oxidized to form an aqueous ion, usually but not always having a charge of 2+, and the aqueous ion will be reduced to the corresponding metal.
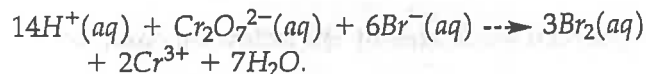
**Example:**

*A piece of solid zinc is placed in an aqueous solution of copper(II) sulfate.*

**Solution:**

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

2. One reactant is a polyatomic anion with a metallic element displaying its highest oxidation number and the other is an anion displaying an oxidation number lower than its maximum. The polyatomic ion reduces to an ion displaying the metal in a lower oxidation state. The anion is oxidized to a higher oxidation state.

**Example:**

*Acidic aqueous sodium dichromate is mixed with a solution of potassium bromide.*

**Solution:**

$$14H^+(aq) + Cr_2O_7^{2-}(aq) + 6Br^-(aq) \longrightarrow 3Br_2(aq) + 2Cr^{3+} + 7H_2O.$$

*Remember: The equation must account for each reactant and product. "Acidic solution" implies that $H^+(aq)$ is a reactant and $H_2O$ is often a product.*

3. An organic compound burned in air (or oxygen) produces carbon dioxide and water.

**Example:**

*Ethanol is burned in air.*

**Solution:**

$$CH_3CH_2OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$$
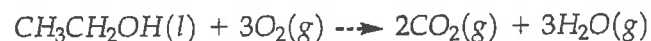
*If you cannot convert the organic name to a formula, for partial credit, re-write the name and finish the equation with $O_2$ as a reactant and carbon dioxide and water as products.*

4. A metal reacts with a non-metal to produce a binary salt.

**Example:**

*Solid sodium is mixed with chlorine gas.*

**Solution:**

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$
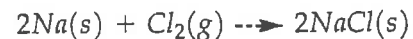
5. An active metal reacts with water to produce hydrogen gas and a hydroxide base.

**Example:**

*Solid lithium is placed in water.*

**Answer:**
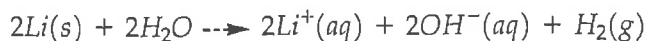
$$2Li(s) + 2H_2O \longrightarrow 2Li^+(aq) + 2OH^-(aq) + H_2(g)$$

*Remember that lithium must be oxidized because the metal is in its lowest oxidation state. Hydrogen is reduced because it can change oxidation states from 1+ to 0. Oxygen cannot be reduced because in water it already displays its lowest oxidation number (2−).*

## Section 20.5    Free Energy and Redox Reactions

A negative value for free energy, $\Delta G$ indicates a spontaneous process. A spontaneous reaction also has a positive value for cell potential, $E_{cell}$.

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

$$\Delta G° = -nFE°$$

$\Delta G$ 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 half are suitably connected at 298 K and standard conditions and that both aqueous solutions are 1.00 M concentrations.*

*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 spontaneous or nonspontaneous? Explain.*

*f.  Calculate the equibrium constant for this reaction.*

**Solution:**

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

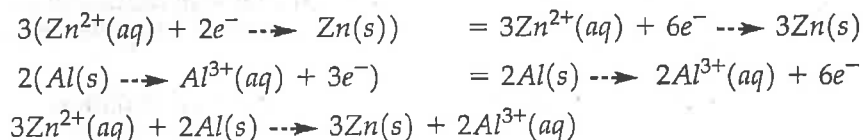|  |  |  | $E°_{red}$ | $E°_{ox}$ |
|---|---|---|---|---|
| $Zn^{2+}/Zn$ | $Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$ | | -0.762 | +0.762 |
| $Al^{3+}/Al$ | $Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$ | | -1.66 | +1.66 |

The reduction half-reaction is the $Zn^{2+}/Zn$ half-reaction because it has the
more positive $E°_{red}$.

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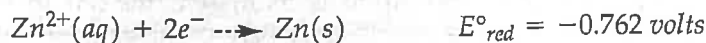
b. The oxidation half-reaction is the reverse of the listed $Al^{3+}/Al$ half-
   reaction:

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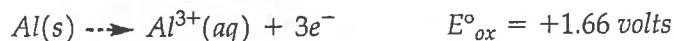
c. Multiply each half-reaction by coefficients that balance the electrons
   and add the half-reactions.

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

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

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

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

$$E°_{cell} = E°_{red} + E°_{ox} = +1.66 + (-0.762) = +0.90 \text{ volts}.$$

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

$$\Delta G° = -nFE°$$

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

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

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

$R = 8.314 \text{ J}/K \text{ mol}$

$T = $ absolute temperature

$K = $ the equilibrium constant

$\Delta G° = -RT \ln K$

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

$\ln K = 210$

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

*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 spontaneous reaction.*

## Section 20.6    Cell Emf Under Nonstandard Conditions

As a voltaic cell discharges, reactants are consumed and products are generated. The concentrations of reactants and products change. As the cell operates, the conditions become nonstandard and the voltage drops. The voltage of the cell is dependent on the concentrations of reactants and products, and can be calculated using the Nernst equation:

$$E = E° - (0.0592/n) \log Q \quad \text{when } T = 298 \text{ K}$$

E is the cell voltage under nonstandard conditions.

E° is the standard cell voltage (calculated from a table of reduction potentials).

Q is the reaction quotient.

n is the number of electrons transferred in the balanced equation.

0.0592 is a constant, which incorporates Faraday's constant, F, the universal gas constant, R, and the absolute temperature at 298 K.

### Example:

*What is the voltage of the Zn/Al cell in the previous example when $[Al^{3+}] = 1.60 \text{ M}$ and $[Zn^{2+}] = 0.10 \text{ M}$?*

### Solution:

*The balanced equation is: $3Zn^{2+}(aq) + 2Al(s) \longrightarrow 3Zn(s) + 2Al^{3+}(aq)$ Q is defined in the same way as the equilibrium constant and its value can be calculated from the given data:*

$$Q = [Al^{3+}]^2/[Zn^{2+}]^3 = (1.60)^2/(0.10)^3 = 2560$$

*From the previous example, the standard cell voltage, $E° = +0.90$ volts. Substituting into the Nerst equation we get:*

$$E = Eo - (0.0592/n) \log Q$$

$$E = +0.90 \text{ volts} - (0.0592/6) \log (2560)$$

$$E = +0.90 \text{ volts} - 0.034 \text{ volts} = 0.87 \text{ v}$$

*The cell voltage drops as the concentration of reactant decreases from 1 M standard conditions.*

**Common misconception:** Remember that E is the voltage of a cell at non-standard conditions and that E° is the voltage at standard conditions.

## Electrolysis     Section 20.9

**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-spontaneous chemical reaction to occur. An electrolytic cell converts electrical energy into chemical energy. Figure 20.2 illustrates an electrolytic cell.



$$2\ Cl^- \longrightarrow Cl_2(g) + 2\ e^- \qquad 2\ Na^+ + 2\ e^- \longrightarrow 2\ Na(l)$$

Anode oxidation:      $Cl^- + \rightarrow 1/2\ Cl_2(g) + 1\ e\text{-}$
Cathode reduction:    $Na^+ + 1\ e\text{-} \rightarrow Na(l)$
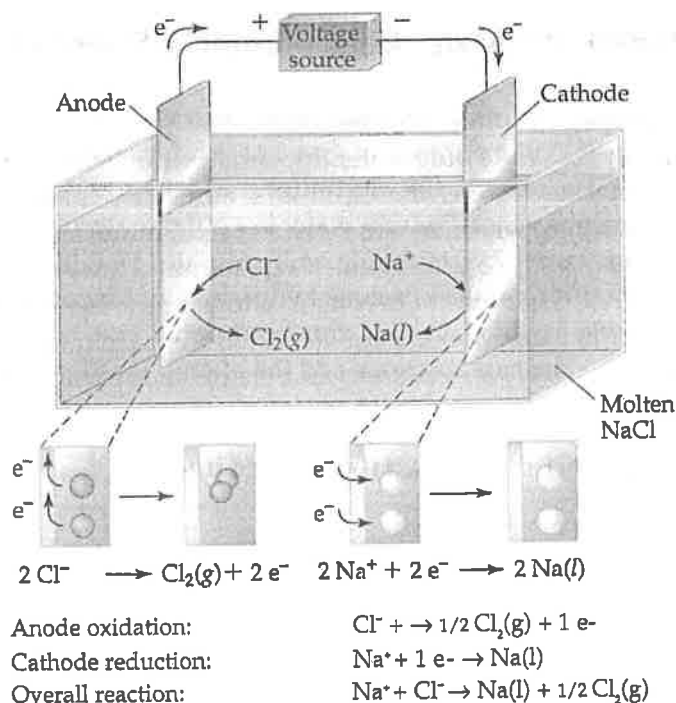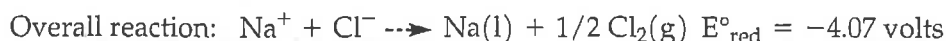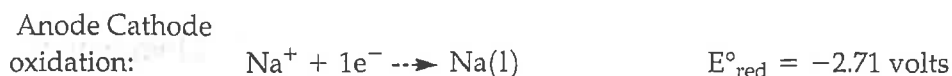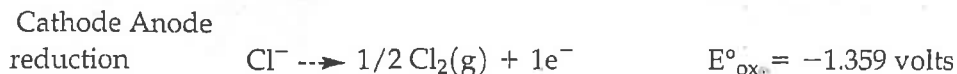Overall reaction:     $Na^+ + Cl^- \rightarrow Na(l) + 1/2\ Cl_2(g)$

Figure 20.2. Diagram of an electrolytic cell for the electrolysis of molten NaCl.

## The Electrolysis of Molten Sodium Chloride

Solid sodium chloride does not conduct electricity and cannot be electrolyzed because its ions are locked in place in a strong ionic lattice. Molten sodium chloride does conduct electricity because 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,
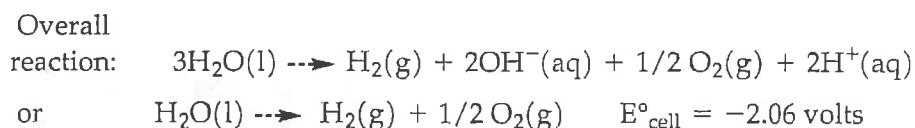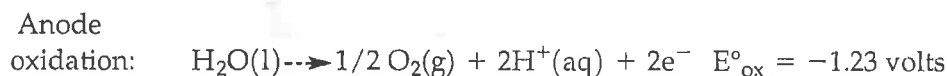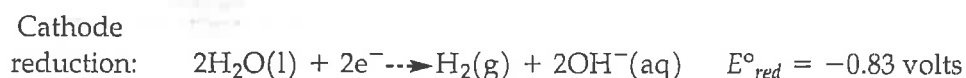
and give up their electrons to become chlorine gas. Positive sodium ions move to the cathode, collect electrons, and become liquid sodium. The half-reactions, the overall equation, and the corresponding voltages are:

Cathode Anode
reduction          $Cl^- \dashrightarrow 1/2\, Cl_2(g) + 1e^-$          $E°_{ox} = -1.359$ volts

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

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

Notice that the overall reaction has a negative voltage so it is nonspontaneous. It requires just over 4 volts to electrolyze molten sodium chloride. All electrolysis reactions are nonspontaneous.

## The Electrolysis of Water Using an Inert Electroylte

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:
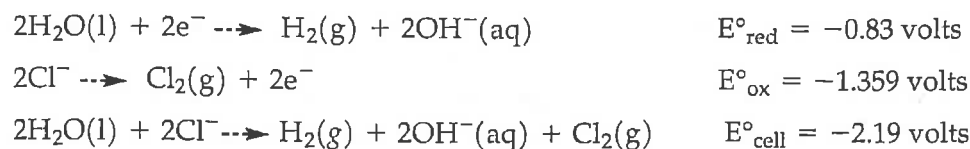
Cathode
reduction:     $2H_2O(l) + 2e^- \dashrightarrow H_2(g) + 2OH^-(aq)$     $E°_{red} = -0.83$ volts

Anode
oxidation:     $H_2O(l) \dashrightarrow 1/2\, O_2(g) + 2H^+(aq) + 2e^-$   $E°_{ox} = -1.23$ volts

Overall
reaction:      $3H_2O(l) \dashrightarrow H_2(g) + 2OH^-(aq) + 1/2\, O_2(g) + 2H^+(aq)$

or             $H_2O(l) \dashrightarrow H_2(g) + 1/2\, O_2(g)$     $E°_{cell} = -2.06$ volts

The electrolysis of water with an inert electrolyte requires just over two volts.

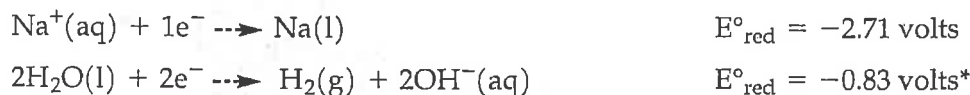### The Electrolysis of an Aqueous Sodium Chloride Solution

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.

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad E°_{red} = -0.83 \text{ volts}$$

$$2Cl^- \longrightarrow Cl_2(g) + 2e^- \qquad E°_{ox} = -1.359 \text{ volts}$$

$$2H_2O(l) + 2Cl^- \longrightarrow H_2(g) + 2OH^-(aq) + Cl_2(g) \qquad E°_{cell} = -2.19 \text{ volts}$$

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.
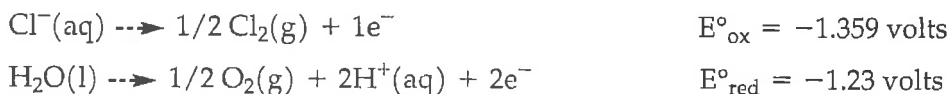
Possible cathode reductions:

$$Na^+(aq) + 1e^- \longrightarrow Na(l) \qquad E°_{red} = -2.71 \text{ volts}$$

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad E°_{red} = -0.83 \text{ volts*}$$

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. In general, 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 electrolyses 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:

$$Cl^-(aq) \longrightarrow 1/2\,Cl_2(g) + 1e^- \qquad E°_{ox} = -1.359 \text{ volts}$$

$$H_2O(l) \longrightarrow 1/2\,O_2(g) + 2H^+(aq) + 2e^- \qquad E°_{red} = -1.23 \text{ volts}$$

## 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 consists of a nickel anode and a steel cathode. 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, which replace the ions in solution.
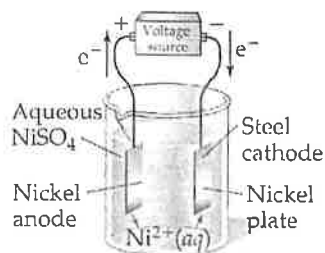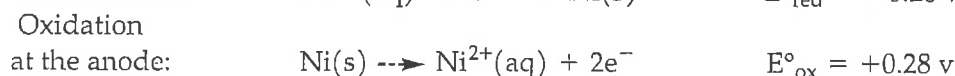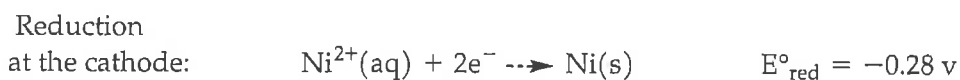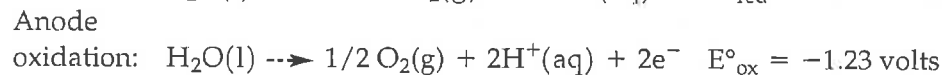


Figure 20.3. Electrolysis device for plating nickel onto a piece of steel.

The half-reactions are:

Reduction
at the cathode:           $Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$           $E°_{red} = -0.28$ v
Oxidation
at the anode:             $Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$           $E°_{ox} = +0.28$ 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:   $H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$       $E°_{red} = -0.83$ volts
Anode
oxidation:   $H_2O(l) \longrightarrow 1/2\ O_2(g) + 2H^+(aq) + 2e^-$   $E°_{ox} = -1.23$ volts
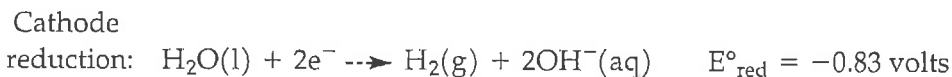
The nickel reactions predominate and the net effect is to move nickel atoms from the anode to the surface of the steel cathode.

## 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.

$$Ag^+(aq) + 1e^- \longrightarrow Ag(s)$$
$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$$
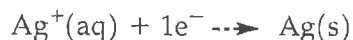
The amount of a substance that is oxidized or reduced in an electrolytic cell is directly proportional to the number of electrons passed through the cell. The

balanced half-reaction is a way to convert electrical quantities into moles of chemical quantities and vice versa.
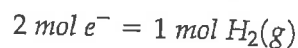
### Example:

*How many liters of dry hydrogen gas at 30°C and 720 torr can be obtained by the electrolysis of water for one hour at 2.50 amps?*

### 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 one second:*

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

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

$$1 \ mol \ e^- = 96485 \ C \quad (Faraday's \ constant)$$

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

$$V = nRT/P$$

$x \ mol \ H_2(g) = 1 \ hr(60 \ min/hr)(60 \ s/min)(2.50 \ C/s)$
$(1 \ mole \ e^-/96485 \ C)$

$(1 \ mol \ H_2/(2 \ mol \ e^-) = 0.0466 \ mol \ H_2.$

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

## 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 spontaneous.

   Reduction Potentials, $E°$

   1. $Cd^{2+} + 2e^- \longrightarrow Cd$      $-0.403\ V$

   2. $Mn^{2+} + 2e^- \longrightarrow Mn$      $-1.18\ V$

   3. $Cu^+ + 1e^- \longrightarrow Cu$      $+0.521\ V$

   4. $Fe^{3+} + 1e^- \longrightarrow Fe^{2+}$      $+0.771\ V$

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

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

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

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

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

3. What is the coefficient for $MnO_4^-$ when the following redox equation is balanced in acidic solution using the smallest whole-number coefficients?

   $$H^+ + Cr_2O_7^{2-} + Mn^{2+} \longrightarrow H_2O + Cr^{3+} + MnO_4^-$$

   A) 1

   B) 2

   C) 5

   D) 6

   E) 10

4.  A cell is set up using the following reactions: What is the voltage of
    the cell?

    $Mg^{2+} + 2e^- \longrightarrow Mg$         $E° = -2.37 \text{ volts}$

    $Ag^+ + 1e^- \longrightarrow Ag$         $E° = +0.80 \text{ volts}$

    A)  +1.57 volts

    B)  +3.17 volts

    C)  +3.97 volts

    D)  −0.77 volts

    E)  +0.77 volts

5.  All of these substances act as oxidizing agents except:

    A)  $H_2O_2$

    B)  $Cr_2O_7^{2-}$

    C)  $MnO_4^-$

    D)  $IO_3^-$

    E)  $Br^-$

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

    A)  O

    B)  C

    C)  Cl

    D)  N

    E)  Cr

7.  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
    spontaneously?

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

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

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

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

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

8. Which species can act as both an oxidizing agent and a reducing agent?

   A) $Cr_2O_7^{2-}$

   B) $S^{2-}$

   C) $H_2O_2$

   D) $Fe$

   E) $MnO_4^-$

9. Of the following, which is the strongest oxidizing agent?

   A) $IO_3^-$

   B) $Cl_2$

   C) $O_2$

   D) $PbO_2$

   E) $Co^{3+}$

10. Of the following, which is the strongest reducing agent?

   A) $F^-$

   B) $Ca$

   C) $Mn$

   D) $H_2O_2$

   E) $N_2H_4$

## Free Response Questions

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

   $$Au^{3+} + 3e^- \dashrightarrow Au(s) \qquad E^\circ = +1.50\ v$$
   $$Ag^+ + 1e^- \dashrightarrow Ag(s) \qquad E^\circ = +0.80\ v$$
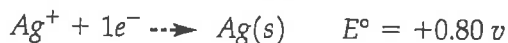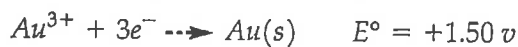
   a.  i. Indicate the cathode and anode half-reactions.

      ii. Write the overall cell reaction.

      iii. Calculate $E^\circ$ for the cell.

   b. Calculate $\Delta G^\circ$ for the cell.

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

   d. Calculate E for the cell if $[Ag^+] = 0.15\ M$ and $[Au^{3+}] = 0.75\ M$.

   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 minutes at 2.50 amps?

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

$$PbO_2(s) + H_2O(l) + 2e^- \longrightarrow PbO(s) + 2OH^-(aq) \quad E° = +0.28\ v$$

$$IO_3^- + 2H_2O + 4e^- \longrightarrow IO^- + 4OH^- \quad\quad\quad E° = +0.56\ v$$

$$PO_4^{3-} + 2H_2O + 1/2 O_2 + 2e^- \longrightarrow HPO_4^{2-} + 3OH^-$$
$$E° = -1.05\ v$$
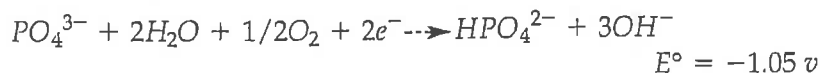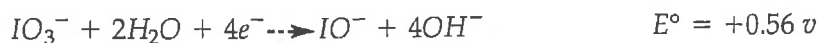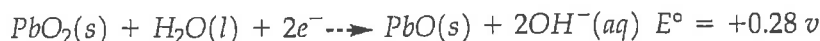
a. i. Which two half-reactions when combined will give the voltaic cell with the largest $E°$ for the cell?

   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 one atmosphere 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.

## Additional Practice in *Chemistry the Central Science*

For more practice working electrochemistry problems in preparation for the Advanced Placement examination try these problems in Chapter 20 of Chemistry the Central Science:

Additional Exercises: 19.93, 19.94, 19.95, 19.97, 19.99, 19.102, 19.107.
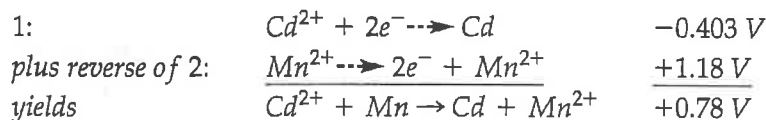
Integrated Exercises: 19.110, 19.111, 19.112, 19.114, 19.115, 19.116, 19.117, 19.118.

## Multiple Choice Answers and Explanations

1. A. The oxidation numbers of sulfur in $CuS$, $K_2S_2O_3$, $SO_2$, $Na_2SO_4$ are $-2$, $+2$, $+4$ and $+6$ respectively. As a monatomic ion in $CuS$, sulfur has a $-2$ charge so its oxidation number is equal to its charge. The oxidation number of each sulfur adds to the oxidation numbers of each oxygen to equal the charge in the polyatomic ion, $S_2O_3^{2-}$. $3(2-$ for each oxygen$) + 2(2+$ for each sulfur$)$ (note: in $S_2O_3^2$, one sulfur carries a $4+$ oxidation number where the other sulfur is zero, an average of $2+$ for each sulfur). The oxidation number of sulfur in $SO_2$ is $4+$ because it adds to the oxidation numbers of each oxygen to equal the zero charge on $SO_2$. $4 + 2(2-) = 0$.

*A 6+ oxidation number for sulfur in $SO_4^{2-}$ adds to the four 2−
oxidation numbers of oxygen to give a charge of
2−. $6 + 4(2-) = 2-$.*

2.  **C.** *For an overall reaction to be spontaneous the values of E° for the
two half-reactions must add to yield a positive E°. Half reaction 1
adds to the reverse of half-reaction 2 to give a positive E°.*

| | | |
|---|---|---|
| 1: | $Cd^{2+} + 2e^- \dashrightarrow Cd$ | −0.403 V |
| *plus reverse of* 2: | $Mn^{2+} \dashrightarrow 2e^- + Mn^{2+}$ | +1.18 V |
| *yields* | $Cd^{2+} + Mn \rightarrow Cd + Mn^{2+}$ | +0.78 V |

*The other combinations listed each yield a negative E°.*

3.  **D.** *Taking apart the unbalanced equation provides two skeletal half-
reactions and each is balanced according to the rules given in Table 20.2:*

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 more positive side.*

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

1.  $Mn^{2+} \dashrightarrow MnO_4^-$

2.  $4H_2O(l) + Mn^{2+} \dashrightarrow MnO_4^-$

3.  $4H_2O(l) + Mn^{2+} \dashrightarrow MnO_4^- + 8H^+(aq)$

4.  $4H_2O(l) + Mn^{2+} \dashrightarrow MnO_4^- + 8H^+(aq) + 5e^-$

$$Cr_2O_7^{2-} \dashrightarrow Cr^{3+}$$

1.  $Cr_2O_7^{2-} \dashrightarrow 2Cr^{3+}$

2.  $Cr_2O_7^{2-} \dashrightarrow 2Cr^{3+} + 7H_2O(l)$

3.  $14H^+(aq) + Cr_2O_7^{2-} \dashrightarrow 2Cr^{3+} + 7H_2O(l)$

4.  $6e^- + 14H^+(aq) + Cr_2O_7^{2-} \dashrightarrow 2Cr^{3+} + 7H_2O(l)$

*Multiplication of the Mn and Cr half-reactions to make the electrons
equal requires factors of 6 and 5, respectively. That means that in the
balanced equation, $MnO_4^-$ will have a coefficient of 6.*

*An alternate way to arrive at the answer is to assign oxidation
numbers to all the elements and note that Mn changes by 5 electrons
(from 2+ to 7+) and that Cr changes by 3 electrons (from 6+ to 3+)*

twice for a total of 6 electrons. The lowest common multiple of 5 and 6 is 30 so the Mn half-reaction must be multiplied by 6 giving the $MnO_4^-$ a coefficient of 6.

4.  **B.** The Ag half-reaction has the more positive voltage so it is the reduction. The Mg half-cell is the oxidation and its voltage changes to +2.37 volts.

    $E°_{cell} = E°_{red} + E°_{ox} = 0.80 + 2.37 = 3.17$ volts.

    Note: The stoichiometry is not taken into account because voltage is independent of the number of electrons transferred.

5.  **E.** An oxidizing agent is the substance reduced in a chemical reaction. Therefore, an oxidizing agent must contain an element with an oxidation number greater than the lowest possible oxidation number for that element. $Br^-$ has an oxidation number of $1-$ for Br which is the lowest possible oxidation number for bromine.

6.  **C.** Cl displays a $7+$ oxidation number in the perchlorate ion, $ClO_4^-$. Cr is $6+$ in $CrO_4^{2-}$. C is $4+$ in $CO_2$. Oxygen is $2+$ in $OF_2$.

7.  **C.** On the basis of their behavior in the presence of hydrochloric acid, Mg is a more active metal than is Ag. Thus, Mg will react with $Ag^+$ ions, but Ag will not react with $Mg^{2+}$. Also Ag, because it does not react with HCl, does not react with $H^+$. E cannot be correct because both $H_2$ and Ag are oxidized.

8.  **C.** An oxidizing agent is reduced. It gains electrons causing another species to lose electrons. A reducing agent is oxidized, losing electrons, causing another species to gain electrons. Although hydrogen peroxide is often considered an oxidizing agent, it commonly acts as a reducing agent. The oxidation number of oxygen in $H_2O_2$ is $1-$. Oxygen can either lose an electron to become 0 or gain an electron to become $2-$. The half-reactions are:

    As an oxidizing agent: $H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O(l)$

    As a reducing agent: $H_2O_2(aq) \longrightarrow O_2(g) + 2H^+(aq) + 2e^-$

    $Cr_2O_7^{2-}$ and $MnO_4^-$ can only be oxidizing agents because Cr and Mn, respectively, have their maximum oxidation numbers. They can only gain electrons. Similarly, Fe and $S^{2-}$ can only lose electrons because those atoms display their minimum oxidation numbers.

9.  E.  The correct answer requires access to a table of standard reduction potentials provided on the AP exam. The reactant with the most positive $E°_{red}$ value is the strongest oxidizing agent.

10. B.  The correct answer requires access to a table of standard reduction potentials provided on the AP exam. The reactant with the most positive $E°_{ox}$ value is the strongest reducing agent. However, the answer is not given directly on a table of standard reduction potentials. To determine the correct answer, choose the product of the reduction half-reaction having the most negative $E°_{red}$ value. The reverse of that half-reaction has the most positive $E°_{ox}$ value.

## Free Response Answers

1. a.   i. Cathode half-cell reaction:

$$Au^{3+} + 3e^- \longrightarrow Au(s) \qquad E° = +1.500\ v$$

Anode half-cell reaction:

$$Ag(s) \longrightarrow Ag^+ + 1e^- \qquad E° = -0.800\ v$$
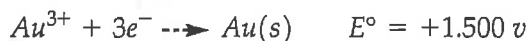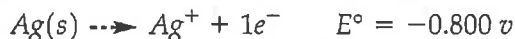
ii. Overall cell reaction:

$$Au^{3+} + 3Ag(s) \longrightarrow Au(s) \rightarrow \longrightarrow\ + 3Ag^+$$

iii. $E°_{cell} = E°_{ox} + E°_{red} = +1.50\ v - 0.800\ v = 0.700\ volts$

b.  $\Delta G° = -nFE° = -(3\ mole\ e^-)(96{,}500\ Coul/mole\ e^-)$
$(0.700\ J/Coul) = -203\ kJ$

$(1\ volt = 1\ J/Coul)$

c.  $\Delta G° = -RT\ ln\ K$

$-202\ kJ = (8.314\ J/mol\ K)(1\ kJ/1000\ J)(298\ K)\ ln\ K$

$ln\ K = +81.5$

$K = e^{+81.5} = 2.48 \times 10^{35}$

d.  $E = E° - (0.0592/n)\ log\ Q$

$Q = [Ag^+]^3/[Au^{3+}] = (0.15)^3/0.75 = 0.0045$

$E = (0.700) - (0.0592/3)\ log(0.0045) = 0.65\ volts$
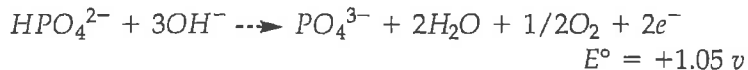
e.  $x\ g\ Au =$

$45\ min\ (60\ s/min)(2.50\ C/s)(1\ mol\ e^-/96500\ C)$

$(1\ mol\ Au/3\ mol\ e^-)(197\ g/mol) = 4.59\ g$

2. a.   i. $IO_3^- + 2H_2O + 4e^- \longrightarrow IO^- + 4OH^- \qquad E° = +0.56\ v$

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

ii. $2HPO_4^{2-} + 2OH^- + IO_3^- \dashrightarrow 2PO_4^{3-} + 2H_2O + IO^- + O_2$
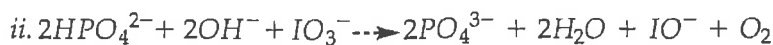
iii. $E^° = E^°_{ox} + E^°_{red} = +1.05\ v + 0.56\ v = +1.61\ volts.$

b. If the pH of both the anode and cathode compartments is decreased, the net effect will be to decrease $[OH^-]$ and the voltage will decrease, as evidenced by the Nernst equation.

i. $E = E^° - (0.0592/n)\ log\ ([PO_4^{3-}]^2[IO^-][O_2]/[HPO_4^{2-}]^2$
$[OH^-]^2[IO_3^-])$

ii. If $[OH^-]$ is fixed at 1.0 M and all other ion concentrations are changed to 0.10 M the voltage will remain the same because, other than hydroxide, there are three moles of ions on both sides of the balanced equation.

iii. If the temperature is increased while all concentrations remain at 1.0 M the voltage will drop because the 0.0592 term will become larger.

Also, the reaction is exothermic because the voltage is positive. Increasing temperature always favors the endothermic reaction (the reverse reaction).

## Your Turn Answers

20.1. $SO_4^{2-}$, 6+; $S_2O_3^{2-}$, 4+ and 0; $S^{2-}$, 2−; $SO_3^{2-}$, 4+; $SCN^-$, 2−; S, 0; $SO_2$, 4+; $SO_3$, 6+. Oxidation number and charge are equivalent only in sulfide, $S^{2-}$, and sulfur, S.

20.2. $N_2$ gains electrons and its oxidation number changes from 0 to 3−. $N_2$ is the substance reduced and is the oxidizing agent. $H_2$ loses electrons and its oxidation number changes from 0 to 1+. $H_2$ is the substance oxidized and is the reducing agent.

20.3. When coupled, the two half-reactions with the largest difference in $E^°$ value will give the most spontaneous reaction, the one with the largest positive cell voltage. Reverse the half-reaction with the most negative voltage and add it to the half-reaction with the most positive voltage. Use coefficients to balance the electrons. Change the sign of the $E^°$ for the reversed reaction and add it to the $E^°$ of the forward reaction.

| | |
|---|---|
| $3F_2(g) + 6e^- \dashrightarrow 6F^-(aq)$ | +2.87 volts |
| $2Al(s) \dashrightarrow 2Al^{3+}(aq) + 6e^-$ | +1.66 volts |
| $3F_2(g) + 2Al(s) \dashrightarrow 6F^-(aq) + 2Al^{3+}(aq)$ | +4.53 volts |