In the nineteenth century, railway tunnels were blasted through the Rocky Mountains to connect British Columbia with the rest of Canada. Workers used nitroglycerin to blast through the rock. This compound is so unstable, however, that accidents were frequent and many workers died. Alfred B. Nobel found a way to stabilize nitroglycerin, and make it safer to use, when he invented dynamite.

What makes nitroglycerin such a dangerous substance? Nitroglycerin, $C_3H_5(NO_3)_3$, gives off a large amount of energy when it decomposes. In fact, about 1500 kJ of energy is released for every mole of nitroglycerin that reacts. The fast, exothermic decomposition of nitroglycerin is accompanied by a tremendous shock wave, which is caused by the expansion of the gaseous products: nitrogen, oxygen, water, and carbon dioxide. Due to the great instability of nitroglycerin, simply jarring or shaking a container of nitroglycerin can initiate the decomposition reaction.

Energy changes accompany every chemical and physical process, from the decomposition of nitroglycerin to the vaporization of water. What causes these energy changes? How can you determine the energy change associated with a given chemical reaction or physical change? In this unit, you will explore the energy changes that accompany various chemical and physical processes.
Think about a prehistoric family group building a fire. It may seem as though this fire does not have much in common with a coal-burning power plant. Both the fire and the power plant, however, are technologies that harness energy-producing processes.

Humans continually devise new technologies that use chemical reactions to produce materials with useful properties. Since the invention of fire, humans have also worked to devise technologies that harness energy. These technologies depend on the fact that every chemical and physical process is accompanied by a characteristic energy change.

You take advantage of such energy changes every day, whether you are using ice cubes to cool a drink or a gas stove to cook a meal. Canadian society depends on the energy changes that are associated with physical and chemical changes.

In this chapter, you will learn about the energy changes associated with heating and cooling. Next, you will study the energy changes that accompany physical changes and chemical reactions. You will learn how to calculate the heat that is absorbed or released during physical or chemical changes. Finally, you will use your skills to analyze what happens as a substance is heated or cooled, changing its state once or more.
Temperature Change and Heat

All physical changes and chemical reactions are accompanied by changes in energy. These energy changes are crucial to life on Earth. For example, chemical reactions in your body generate the heat that helps to regulate your body temperature. Physical changes, such as evaporation, help to keep your body cool. On a much larger scale, there would be no life on Earth without the energy from the nuclear reactions that take place in the Sun.

The study of energy and energy transfer is known as thermodynamics. Chemists are interested in the branch of thermodynamics known as thermochemistry: the study of energy involved in chemical reactions. In order to discuss energy and its interconversions, thermochemists have agreed on a number of terms and definitions. You will learn about these terms and definitions over the next few pages. Then you will examine the energy changes that accompany temperature changes, chemical reactions, and physical changes.

Studying Energy Changes

The law of conservation of energy states that the total energy of the universe is constant. In other words, energy can be neither destroyed nor created. This idea can be expressed by the following equation:

\[ \Delta E_{\text{universe}} = 0 \]

Energy can, however, be transferred from one substance to another. It can also be converted into various forms. In order to interpret energy changes, scientists must clearly define what part of the universe they are dealing with. The system is defined as the part of the universe that is being studied and observed. In a chemical reaction, the system is usually made up of the reactants and products. By contrast, the surroundings are everything else in the universe. The two equations below show the relationship between the universe, a system, and the system’s surroundings.

\[ \text{Universe} = \text{System} + \text{Surroundings} \]

\[ \Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0 \]

This relationship is known as the first law of thermodynamics.

According to the first law of thermodynamics, any change in the energy of a system is accompanied by an equal and opposite change in the energy of the surroundings.

\[ \Delta E_{\text{system}} = -\Delta E_{\text{surroundings}} \]

Consider the chemical reaction that is taking place in the flask in Figure 16.1. A chemist would probably define the system as the contents of the flask—the reactants and products. Technically, the rest of the universe is the surroundings. In reality, however, the entire universe changes very little when the system changes. Therefore, the surroundings are usually considered to be only the part of the universe that is likely to be affected by the energy changes of the system. In Figure 16.1, the flask, the lab bench, the air in the room, and the student all make up the surroundings. The system is more likely to significantly influence its immediate surroundings than it is to influence a mountaintop in Japan (also, technically, part of the surroundings).
Depending on how they are separated from their surroundings, systems are defined in three different ways.

- An **open system**, as its name implies, is open to its surroundings. Both energy and matter may be exchanged between an open system and its surroundings. A reaction in an open beaker is an open system.

- In a **closed system**, matter cannot move between the system and surroundings. Energy, however, can be transferred between a closed system and its surroundings. A reaction in a stoppered Erlenmeyer flask is a closed system.

- An **isolated system** is completely insulated from the surroundings. Neither matter nor energy is exchanged between an isolated system and its surroundings. You will learn more about the importance of isolated systems in Chapter 17.

### Types of Energy

You may recall from earlier science courses that energy is classified into two fundamental types. These types of energy are:

- **kinetic energy** — the energy of motion
- **potential energy** — energy that is stored

If you pick up a rock and lift it several metres above the ground, the rock gains potential energy. Once you let go of the rock, the rock falls to the ground as the potential energy is converted to kinetic energy. As you will learn, energy changes involved in chemical and physical processes fit into one or both of these two categories.

The SI unit for both kinetic and potential energy is the **joule** (symbol J). The joule is derived from other SI units. One joule is equal to $1 \text{ kg} \left( \frac{\text{m}^2}{\text{s}^2} \right)$.

### Temperature Change and Heat

Temperature, $T$, is a measure of the average kinetic energy of the particles that make up a substance or system. You can think of temperature as a way of quantifying how hot or cold a substance is, relative to another substance.

![Figure 16.2](image)  
**Figure 16.2**  
Celsius degrees and Kelvin degrees are the same size. The Kelvin scale begins at absolute zero. This is the temperature at which the particles in a substance have no kinetic energy. Therefore, Kelvin temperatures are never negative. By contrast, $0 \degree \text{C}$ is set at the melting point of water. Celsius temperatures can be positive or negative.
Temperature is measured in either Celsius degrees (°C) or kelvins (K). The Celsius scale is a relative scale. It was designed so that the boiling point of water is at 100°C and the melting point of water is at 0°C. The Kelvin scale, on the other hand, is an absolute scale. It was designed so that 0 K is the temperature at which a substance possesses no kinetic energy. The relationship between the Kelvin and Celsius scales is shown in Figure 16.2 on the previous page, and by the following equation.

\[ T_{\text{Kelvin}} = T_{\text{Celsius}} + 273.15 \]

Temperature change is an indication of a change in kinetic energy. The temperature variable that is used is the change in temperature, symbolized \( \Delta T \). The change in temperature is always equal to the final temperature subtracted from the initial temperature, as shown by the following equation.

\[ \Delta T = T_f - T_i \]

A positive value for \( \Delta T \) indicates an increase in temperature. A negative value for \( \Delta T \) indicates a decrease in temperature.

**Transfer of Kinetic Energy**

*Heat*, \( q \), refers to the transfer of kinetic energy between objects with different temperatures. Heat, therefore, has the same units as energy—joules (J).

According to the particle model of matter, matter is made up of particles in constant motion. When a substance absorbs heat, the average speed of the particles in the object increases. Therefore the temperature of the substance increases. Figure 16.3 models what happens when hot chocolate is heated on a stove.

![Figure 16.3](image)

**Figure 16.3** The length of each arrow represents the speed of the particle. As the hot chocolate absorbs heat, the average speed of the particles increases.

According to the first law of thermodynamics, any energy released by a system is gained by the surroundings, and vice versa. When the energy is transferred as heat, you can express the relationship as follows.

\[ q_{\text{system}} = -q_{\text{surroundings}} \]

When substances with different temperatures come into contact, kinetic energy is transferred as heat from the particles of the warmer substance to the particles of the cooler substance.
For example, hot chocolate at 75°C has a higher temperature than your body, which is about 37°C. You can feel the difference as warmth when you drink the hot chocolate, as shown in Figure 16.4.

As you drink, the particles in the hot chocolate transfer kinetic energy as heat to particles in your mouth. The particles in the hot chocolate slow down, and the particles in your mouth speed up.

The moving particles in the hot chocolate also transfer kinetic energy as heat to the particles in the mug. The average speed of the particles of the mug increases and the temperature of the mug increases as a result. You feel the increased kinetic energy of the particles of the mug as warmth. The particles in the mug transfer kinetic energy as heat to the particles in your fingertips.

When you blow on hot chocolate to cool it, as shown in Figure 16.5, what happens? You cause high-pressure air to move over the surface of the liquid. As the air leaves your mouth, it begins to expand and cool. As the air moves across the surface of the hot chocolate, the particles in the hot chocolate transfer some kinetic energy to the particles of the cool air. The hot chocolate cools down.

Temperature is an important factor in the transfer of kinetic energy as heat. What other factors are important? Work through the following ThoughtLab to find out.
Two students performed an experiment to determine what factors need to be considered when determining the quantity of thermal energy lost or gained by a substance undergoing an energy change. They set up their experiment as follows.

**Part A**
The students placed two different masses of water, at the same initial temperature, in separate beakers. They placed an equal mass of ice (from the same freezer) in each beaker. Then they monitored the temperature of each beaker. Their results are listed in the table below.

### Different Masses of Water

<table>
<thead>
<tr>
<th>Beaker</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of water (g)</td>
<td>60.0</td>
<td>120.0</td>
</tr>
<tr>
<td>Initial temperature of water (°C)</td>
<td>26.5</td>
<td>26.5</td>
</tr>
<tr>
<td>Mass of ice added (g)</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Final temperature of mixture (°C)</td>
<td>9.7</td>
<td>17.4</td>
</tr>
<tr>
<td>Temperature change (°C)</td>
<td>16.8</td>
<td>9.1</td>
</tr>
</tbody>
</table>

**Part B**
The students placed equal masses of canola oil and water, at the same initial temperature, in separate beakers. They placed equal masses of ice (from the same freezer) in the two beakers. Then they monitored the temperature of each beaker. Their results are listed in the following table.

### Different Liquids

<table>
<thead>
<tr>
<th>Beaker</th>
<th>1 (canola oil)</th>
<th>2 (water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of liquid (g)</td>
<td>60.0</td>
<td>60.0</td>
</tr>
<tr>
<td>Initial temperature of liquid (°C)</td>
<td>35.0</td>
<td>35.0</td>
</tr>
<tr>
<td>Mass of ice added (g)</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Final temperature of mixture (°C)</td>
<td>16.9</td>
<td>16.9</td>
</tr>
<tr>
<td>Temperature change (°C)</td>
<td>29.8</td>
<td>18.1</td>
</tr>
</tbody>
</table>

**Procedure**

1. For each part of the experiment, identify
   (a) the variable that was changed by the students (the manipulated variable)
   (b) the variable that changed as a result of changing the manipulated variable (the responding variable)
   (c) the variables that were kept constant to ensure a fair test (the controlled variables)

2. Interpret the students’ results by answering the following questions.
   (a) If ice is added to two different masses of water, how does the temperature change?
   (b) If ice is added to two different liquids, how does the temperature change?

**Analysis**

3. Think about your interpretation of the students’ experiment and the discussion prior to this ThoughtLab. What are three important factors to consider when measuring the thermal energy change of a substance?
Mass and Energy Transfer

The ThoughtLab on page 631 gave you some insight into the factors that are important when measuring energy changes. How can you use these factors to calculate the amount of kinetic energy that is transferred as heat?

First you must examine each factor and determine its relationship to heat. You have already learned that a change in temperature indicates a change in energy. For a given object or sample, the larger the temperature change, the larger the energy change. How does the mass of a substance affect energy transfer? To answer that question, think about water.

About 70% of Earth’s surface is covered with water. This enormous mass of water absorbs and releases tremendous amounts of energy. Water makes our climate more moderate by absorbing heat in hot weather and releasing heat in cold weather. The greater the mass of the water, the greater the amount of heat it can absorb and release. Mass is directly related to heat transfer. Mass is therefore a variable in the calculation of heat energy. It is symbolized by a lower-case $m$.

Type of Substance and Energy Transfer

In the ThoughtLab, you probably noticed that the quantity of heat being transferred depends on the type of substance. When you added equal masses of ice to the same mass of oil and water, the temperature change of the oil was almost double the temperature change of the water. “Type of substance” cannot be used as a variable, however, when calculating energy changes. Instead, we use a variable that reflects the individual nature of different substances: specific heat capacity. The specific heat capacity of a substance is the quantity of energy, in joules (J), that is required to change one gram (g) of the substance by one degree Celsius (°C). The specific heat capacity of a substance reflects how well the substance can store energy. A substance with a large specific heat capacity can absorb and release more energy than a substance with a smaller specific heat capacity. The symbol that is used for specific heat capacity is a lower-case $c$. The units are J/g·°C.

The specific heat capacity of water is relatively large: 4.184 J/g·°C. This value helps to explain how water can absorb and release enough energy to moderate Earth’s temperature. Examine the values in Table 16.1. Notice that the specific heat capacities of most substances shown are much lower than the specific heat capacity of water.

Areas without much water, such as Canada’s prairie provinces, experience huge variations in temperature from summer to winter. Provinces near the Atlantic and Pacific Oceans, however, such as Newfoundland and Labrador or British Columbia, experience much smaller variations in year-round temperatures. These more moderate temperatures are due to the ability of water to absorb and release large quantities of heat.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Specific heat capacity (J/g · °C at SATP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements</td>
<td></td>
</tr>
<tr>
<td>aluminum</td>
<td>0.900</td>
</tr>
<tr>
<td>carbon (graphite)</td>
<td>0.711</td>
</tr>
<tr>
<td>copper</td>
<td>0.385</td>
</tr>
<tr>
<td>gold</td>
<td>0.129</td>
</tr>
<tr>
<td>hydrogen</td>
<td>14.267</td>
</tr>
<tr>
<td>iron</td>
<td>0.444</td>
</tr>
<tr>
<td>Compounds</td>
<td></td>
</tr>
<tr>
<td>ammonia (liquid)</td>
<td>4.70</td>
</tr>
<tr>
<td>ethanol</td>
<td>2.46</td>
</tr>
<tr>
<td>water (solid)</td>
<td>2.01</td>
</tr>
<tr>
<td>water (liquid)</td>
<td>4.184</td>
</tr>
<tr>
<td>water (gas)</td>
<td>2.01</td>
</tr>
<tr>
<td>Other materials</td>
<td></td>
</tr>
<tr>
<td>air</td>
<td>1.02</td>
</tr>
<tr>
<td>concrete</td>
<td>0.88</td>
</tr>
<tr>
<td>glass</td>
<td>0.84</td>
</tr>
<tr>
<td>granite</td>
<td>0.79</td>
</tr>
<tr>
<td>wood</td>
<td>1.76</td>
</tr>
</tbody>
</table>
Calculating Heat Transfer

You have just considered three variables: change in temperature (\(\Delta T\)), mass (\(m\)), and type of substance, which is characterized by specific heat capacity (\(c\)). The formula in Figure 16.6 shows how to combine these variables to calculate the heat involved.

\[
q = m \cdot c \cdot \Delta T
\]

How do you solve heat problems using \(q = mc\Delta T\)? Go back to the ThoughtLab. Some of the data in this ThoughtLab can be used to illustrate the calculation of heat transfer, as shown below.

Sample Problem

Heat Transferred From Water to Ice

**Problem**

In the ThoughtLab, 10.0 g of ice was added to 60.0 g of water. The initial temperature of the water was 26.5°C. The final temperature of the mixture was 9.7°C. How much heat was lost by the water?

**What Is Required?**

You need to calculate the quantity of heat (\(q\)) that was lost by the water.

**What Is Given?**

You know the mass of the water. You also know the initial and final temperatures of the water.

- Mass of water (\(m\)) = 60.0 g
- Initial temperature (\(T_i\)) = 26.5°C
- Final temperature (\(T_f\)) = 9.7°C

**Plan Your Strategy**

You have enough information to solve this problem using \(q = mc\Delta T\). Use the initial and final temperatures to calculate \(\Delta T\). You need the specific heat capacity (\(c\)) of liquid water. This is given in Table 16.1 (4.184 J/g·°C). Because you are concerned only with the water, you will not use the mass of the ice.

Why does water have such a high specific heat capacity? Do some research to find out. **Hint:** Water’s specific heat capacity has something to do with bonding.
Act on Your Strategy

Substitute the values into the following heat formula, and solve.
Remember that \( \Delta T = T_f - T_i \)
\[
q = mc\Delta T \\
= (60.0 \text{ g})(4.184 \frac{\text{J}}{\text{g} \cdot \degree \text{C}})(9.7\degree \text{C} - 26.5\degree \text{C}) \\
= -4.22 \times 10^3 \text{ (g)(}\frac{1}{\text{g} \cdot \degree \text{C}})\text{(C)} \\
= -4.22 \times 10^3 \text{ J (or } -4.22 \text{ kJ)}
\]
The water lost \(4.22 \times 10^3\) J of heat.

Check Your Solution

The water lost heat, so the heat value should be negative. Heat is measured in joules or kilojoules. Make sure that the units cancel out to give the appropriate unit for your answer.

Practice Problems

1. 100 g of ethanol at 25°C is heated until it reaches 50°C. How much heat does the ethanol gain? **Hint:** Find the specific heat capacity of ethanol in Table 16.1.

2. In Part A of the ThoughtLab on page 631, the students added ice to 120.0 g of water in beaker 2. Calculate the heat lost by the water. Use the information given for beaker 2, as well as specific heat capacities in Table 16.1.

3. Beaker A contains 50 g of liquid at room temperature. The beaker is heated until the liquid gains 10°C. Beaker B contains 100 g of the same liquid at room temperature. This beaker is also heated until the liquid gains 10°C. In which beaker does the liquid absorb the most heat? Explain.

4. As the diagram below illustrates, the sign of the heat value tells you whether a substance has lost or gained heat energy. Consider the following descriptions. Write each heat value, and give it the appropriate sign to indicate whether heat was lost from or gained by the system.

   (a) In Part A of the ThoughtLab on page 631, the ice absorbed the heat that was lost by the water. When ice was added to 60.0 g of water, it absorbed 4.22 kJ of heat. When ice was added to 120.0 g of water, it absorbed 4.6 kJ of heat.

   (b) When 2.0 L of water was heated over a campfire, the water gained 487 kJ of energy.

   (c) A student baked a cherry pie and put it outside on a cold winter day. There was a change of 290 kJ of heat energy in the pie.
In the Sample Problem, heat was lost by the water. Therefore the value of \( q \) was negative. If the value of \( q \) is positive, this indicates that heat is gained by a substance.

The heat equation \( q = mc\Delta T \) can be rearranged to solve for any of the variables. For example, in Part B of the ThoughtLab on page 631, ice was added to both canola oil and water. How can you use the information given in Part B to calculate the specific heat capacity of the canola oil?

**Math Link**

The specific heat capacity

\[
q = mc \Delta T
\]

Units: \( \text{kJ} = \text{kg} \cdot \frac{4.184 \text{ kJ}}{\text{kg} \cdot ^\circ \text{C}} \cdot ^\circ \text{C} \)

**Sample Problem**

**Calculating Specific Heat Capacity**

**Problem**

Calculate the specific heat capacity of canola oil, using the information given in Part B of the ThoughtLab on page 631. Note that the ice gained \( 4.0 \times 10^3 \text{ J} \) of energy when it came in contact with the canola oil.

**What Is Required?**

You need to calculate the specific heat capacity (\( c \)) of the canola oil.

**What Is Given?**

From the ThoughtLab, you know the mass (\( m \)) and the initial and final temperatures of the canola oil.

- Mass of oil (\( m \)) = 60.0 g
- Initial temperature (\( T_i \)) = 35.0\(^\circ\)C
- Final temperature (\( T_f \)) = 5.2\(^\circ\)C

You also know the quantity of heat gained by the ice. This must be the same as the heat lost by the oil.

Heat gained by the ice = Heat lost by the canola oil = \( 4.0 \times 10^3 \text{ J} \)

**Plan Your Strategy**

Rearrange the equation \( q = mc\Delta T \) to solve for \( c \). Then substitute the values for \( q \), \( m \), and \( \Delta T (T_f - T_i) \) into the equation.

**Act on Your Strategy**

\[
c = \frac{q}{m\Delta T} = \frac{-4.0 \times 10^3 \text{ J}}{(60.0 \text{ g})(5.2 \text{ C} - 35.0\text{ C})} = 2.2437 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} = 2.24 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}}
\]

**Check Your Solution**

The specific heat capacity should be positive, and it is. It should have the units \( \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \).
Heat Capacity

Consider the bathtub and teacup shown in Figure 16.8. Both are filled with water at 20°C. The water in the bathtub and the water in the teacup have the same heat capacity, but the water in the bathtub has a much greater mass. Therefore, it would take a great deal more energy to heat the water in the bathtub to 60°C than it would to heat the water in the teacup to 60°C. Although all water has the same specific heat capacity, different samples of water have different masses. Different samples of water have different heat capacities if they have different masses.

5. Solve the equation \( q = mc\Delta T \) for the following quantities.
   (a) \( m \)
   (b) \( c \)
   (c) \( \Delta T \)

6. You know that \( \Delta T = T_f - T_i \). Combine this equation with the heat equation, \( q = mc\Delta T \), to solve for the following quantities.
   (a) \( T_i \) (in terms of \( q \), \( m \), \( c \), and \( T_f \))
   (b) \( T_i \) (in terms of \( q \), \( m \), \( c \), and \( T_f \))

7. How much heat is required to raise the temperature of 789 g of liquid ammonia, from 25.0°C to 82.7°C?

8. A solid substance has a mass of 250.00 g. It is cooled by 25.00°C and loses 4937.50 J of heat. What is its specific heat capacity? Look at Table 16.1 to identify the substance.

9. A piece of metal with a mass of 14.9 g is heated to 98.0°C. When the metal is placed in 75.0 g of water at 20.0°C, the temperature of the water rises by 28.5°C. What is the specific heat capacity of the metal? Assume all heat released by metal is absorbed by the water.

10. A piece of gold (\( c = 0.129 \) J/g°C) with mass of 45.5 g and a temperature of 80.5°C is dropped into 192 g of water at 15.0°C. What is the final temperature of the water? (Hint: Use the equation \( q_w = -q_g \)).

Practice Problems

The water in the bathtub has a higher heat capacity than the water in the teacup.
Heat capacity, \( C \), relates the heat of a given sample, object, or system to its change in temperature. Heat capacity is usually expressed in units of kJ/°C. When you know the specific heat capacity and mass of a sample, you can determine the heat capacity using the following equation.

\[
C = m \times c
\]

where \( C \) = heat capacity (kJ/°C)  
\( m \) = mass (kg)  
\( c \) = specific heat capacity (kJ/kg °C)

Given the heat capacity of a sample, object, or system, you can determine the heat associated with a given temperature change, using the following equation.

\[
q = C \Delta T
\]

Practice using the equations above in the following Practice Problems. You will need to refer to Table 16.1.

**Practice Problems**

11. A bathtub contains 100.0 kg of water.
   (a) What is the heat capacity, \( C \), of the water in the bathtub?
   (b) How much heat is transferred to the surroundings as the water in the bathtub cools from 60.0°C to 20.0°C? Use your answer from (a) in your calculations.
   (c) Calculate the heat transferred in (b) using a different method.

12. A teacup contains 0.100 kg of water.
   (a) What is the heat capacity, \( C \), of the water in the teacup?
   (b) How much heat is transferred to the surroundings as the water in the teacup cools from 60.0°C to 20.0°C? Use your answer from (a) in your calculations.
   (c) Calculate the heat transferred in (b) using a different method.

13. A ring of pure gold with a mass of 18.8 g is tossed into a fire, and then removed with a pair of tongs. The initial temperature of the ring was 23.2°C and the final temperature of the ring is 55.8°C.
   (a) What is the heat capacity of the ring?
   (b) How much heat did the ring absorb from the fire?

14. Because humans are about 85% water, the specific heat capacity of a human is sometimes approximated as 0.85 times the specific heat capacity of water.
   (a) Using the above approximation, what is the heat capacity of a human that has a mass of 68.0 kg?
   (b) How much heat is required to raise the temperature of a 68.0 kg human by 1.00°C?

**Section Summary**

In this section, you have learned about the factors involved in temperature change and kinetic energy transfer as heat. So far, you have focussed on changes in kinetic energy. In the next section, you will learn about physical and chemical processes, which involve a change in potential energy.
In your own words, state the first law of thermodynamics. Then express the first law of thermodynamics as an equation.

Define the term “heat.”

What are three important factors to consider when measuring heat transfer?

In Part B of the ThoughtLab on page 631, 60.0 g of water was in beaker 2. The initial temperature of the water was 35.0°C, and the final temperature was 16.9°C.

(a) Calculate the heat that was lost by the water in beaker 2.

(b) Where did the heat go?

When iron nails are hammered into wood, friction causes the nails to heat up.

(a) Calculate the heat that is gained by a 5.2 g iron nail as it changes from 22.0°C to 38.5°C. (See Table 16.1.)

(b) Calculate the heat that is gained by a 10.4 g iron nail as it changes from 22.0°C to 38.5°C.

(c) Calculate the heat that is gained by the 5.2 g nail if its temperature changes from 22.0°C to 55.0°C.

A 23.9 g silver spoon is put in a cup of hot chocolate. It takes 0.343 kJ of energy to change the temperature of the spoon from 24.5°C to 85.0°C. What is the specific heat capacity of solid silver?

(b) What is the heat capacity, C, of the silver spoon?

The specific heat capacity of aluminum is 0.902 J/g°C. The specific heat capacity of copper is 0.389 J/g°C. The same amount of heat is transferred to equal masses of these two metals. Which metal increases more in temperature? Explain your answer.

You have prepared some hot chocolate to take with you on a hike. You are about to fill your Thermos™ bottle with the hot chocolate when your friend stops you. Your friend suggests you rinse the inside of the bottle with hot water before filling the bottle with hot chocolate.

(a) Explain in detail why rinsing the bottle with hot water will help keep your hot chocolate hot.

(b) A Thermos™ bottle has a vacuum between its inner layer and its outer layer. Explain why the vacuum insulation helps to keep cold drinks cold and hot drinks hot.

(c) What kind of system (open, closed, or insulated) is hot chocolate inside a sealed Thermos™ bottle? Explain your answer.
In the previous section, you explored what happens when the average kinetic energy of the particles in a substance changes. You saw that a change in average kinetic energy can be observed by monitoring temperature change. For example, you saw how the energy change of water relates to the temperature change, the mass of the water, and its specific heat capacity.

What happens during a phase change? What happens during a chemical reaction? These changes involve changes in the potential energy of a system, not the kinetic energy.

Chemists use the term enthalpy change ($\Delta H$) to refer to the potential energy change of a system during a process such as a chemical reaction or a physical change. Enthalpy changes are measured at constant pressure. The units of enthalpy change are kJ/mol.

**Enthalpy Changes in Chemical Changes**

The enthalpy change of a chemical reaction represents the difference between the potential energy of the products and the potential energy of the reactants. In chemical reactions, potential energy changes result from chemical bonds being broken and formed. Chemical bonds are sources of stored energy (potential energy). *Breaking a bond is a process that requires energy. Creating a bond is a process that releases energy.* Figure 16.9 represents these ideas.

Chemists define the total internal energy of a substance at a constant pressure as its enthalpy, $H$. Chemists do not work with the *absolute* enthalpy of the reactants and products in a physical or chemical process. Instead, they study the enthalpy change, that accompanies a process. That is, they study the *relative* enthalpy of the reactants and products in a system. This is like saying that the distance between your home and your school is 2 km. You do not usually talk about the *absolute* position of your home and school in terms of their latitude, longitude, and elevation. You talk about their *relative* position, in relation to each other.

![Figure 16.9](image) This illustration shows bonds being broken and made during a chemical reaction. If the bonds are strong, there is a large change in energy. If the bonds are weak, there is a small change in energy.
A chemical bond is caused by the attraction between the electrons and nuclei of two atoms. Energy is needed to break a chemical bond, just like energy is needed to break a link in a chain. On the other hand, making a chemical bond releases energy. The strength of a bond depends on how much energy is needed to break the bond.

Consider the combustion reaction that takes place when nitrogen reacts with oxygen.

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

In this reaction, one mole of nitrogen-nitrogen triple bonds and one mole of oxygen-oxygen double bonds are broken. Two moles of nitrogen-oxygen bonds are formed. This reaction absorbs energy. In other words, more energy is released to form two nitrogen-oxygen bonds than is used to break one nitrogen-nitrogen bond and one oxygen-oxygen bond. When a reaction results in a net *absorption* of energy, it is called an **endothermic reaction**.

On the other hand, when a reaction results in a net *release* of energy, it is called an **exothermic reaction**. In an exothermic reaction, more energy is released to form bonds than is used to break bonds. Therefore, energy is released. Figure 16.10 shows the relationship between bond breaking, bond formation, and endothermic and exothermic reactions.

- **Endothermic**
  - Heat gained by a process
  - Temperature of surroundings decreases

- **Exothermic**
  - Heat lost by a process
  - Temperature of surroundings increases

**Figure 16.10** The overall change in potential energy when bonds break and form determines whether a reaction is exothermic or endothermic.

**Representing Enthalpy Changes**

The enthalpy change of a chemical reaction is known as the **enthalpy of reaction**, $\Delta H_{\text{rxn}}$. The enthalpy of reaction is dependent on conditions such as temperature and pressure. Therefore, chemists often talk about the **standard enthalpy of reaction**, $\Delta H^\circ_{\text{rxn}}$: the enthalpy change of a chemical reaction that occurs at SATP (25°C and 100 kPa). Often, $\Delta H^\circ_{\text{rxn}}$ is written simply as $\Delta H^\circ$. The $^\circ$ symbol is called “nought.” It refers to a property of a substance at a standard state or under standard conditions. You may see the enthalpy of reaction referred to as the **heat of reaction** in other chemistry books.
Representing Exothermic Reactions

There are three different ways to represent the enthalpy change of an exothermic reaction. The simplest way is to use a thermochemical equation: a balanced chemical equation that indicates the amount of heat that is absorbed or released by the reaction it represents. For example, consider the exothermic reaction of one mole of hydrogen gas with half a mole of oxygen gas to produce liquid water. For each mole of hydrogen gas that reacts, 285.8 kJ of heat is produced. Notice that the heat term is included with the products because heat is produced.

\[
H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(ℓ) + 285.8 \text{ kJ}
\]

You can also indicate the enthalpy of reaction as a separate expression beside the chemical equation. For exothermic reactions, \( \Delta H^\circ \) is always negative.

\[
H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(ℓ) \quad \Delta H^\circ_{\text{rxn}} = -285.8 \text{ kJ/mol}
\]

A third way to represent the enthalpy of reaction is to use an enthalpy diagram. Examine Figure 16.11 to see how this is done.

Representing Endothermic Reactions

The endothermic decomposition of solid magnesium carbonate produces solid magnesium oxide and carbon dioxide gas. For each mole of magnesium carbonate that decomposes, 117.3 kJ of energy is absorbed. As for an exothermic reaction, there are three different ways to represent the enthalpy change of an endothermic reaction.

You can include the enthalpy of reaction as a heat term in the chemical equation. Because heat is absorbed in an endothermic reaction, the heat term is included on the reactant side of the equation.

\[
117.3 \text{ kJ} + \text{MgCO}_3(s) \rightarrow \text{MgO}(s) + \text{CO}_2(g)
\]

You can also indicate the enthalpy of reaction as a separate expression beside the chemical reaction. For endothermic reactions, the enthalpy of reaction is always positive.

\[
\text{MgCO}_3(s) \rightarrow \text{MgO}(s) + \text{CO}_2(g) \quad \Delta H^\circ_{\text{rxn}} = 117.3 \text{ kJ/mol}
\]

Finally, you can use a diagram to show the enthalpy of reaction. Figure 16.12 shows how the decomposition of solid magnesium carbonate can be represented graphically.

Enthalpy of Reaction

The enthalpy change associated with a reaction depends on the amount of reactants involved. For example, the thermochemical equation for the decomposition of magnesium carbonate, shown above, indicates that 117.3 kJ of energy is absorbed when one mole, or 84.32 g, of magnesium carbonate decomposes. The decomposition of two moles of magnesium carbonate absorbs twice as much energy, or 234.6 kJ.

\[
117.3 \text{ kJ} + 2\text{MgCO}_3(s) \rightarrow 2\text{MgO}(s) + 2\text{CO}_2(g)
\]

Enthalpy of reaction is linearly dependent on the amount of substances that react. That is, if the amount of reactants doubles, the enthalpy change also doubles.

In other words, when you multiply the stoichiometric coefficients of a thermochemical equation by any factor, you must multiply the heat term or enthalpy expression by the same factor.
Enthalpy and Catalysts

In Chapter 12, you learned that catalysts change the rate of a reaction by providing an alternative pathway. The catalyst itself is the same at the beginning and at the end of the reaction.

Does using a catalyst affect the enthalpy change of the reaction? No. For a given process, the reactants and products are the same, regardless of whether a catalyst is used or not. The catalyst itself is regenerated unchanged after the reaction. The change in potential energy between the reactants and products is the same, and the catalyst itself has no net change in potential energy. The enthalpy change is therefore the same whether a catalyst is used or not.

Standard Molar Enthalpy of Formation

In a formation reaction, a substance is formed from elements in their standard states. The enthalpy change of a formation reaction is called the standard molar enthalpy of formation, \( \Delta H^0_f \). The standard molar enthalpy of formation is the quantity of energy that is absorbed or released when one mole of a compound is formed directly from its elements in their standard states. A more comprehensive list is provided in Appendix E.

Some standard molar enthalpies of formation are listed in Table 16.2.

Table 16.2 Selected Standard Molar Enthalpies of Formation

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta H^0_f ) kJ/mol</th>
<th>Formation equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(g)</td>
<td>−110.5</td>
<td>( C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) )</td>
</tr>
<tr>
<td>CO_2(g)</td>
<td>−393.5</td>
<td>( C_2(g) + O_2(g) \rightarrow CO_2(g) )</td>
</tr>
<tr>
<td>CH_4(g)</td>
<td>−74.6</td>
<td>( C(s) + 2H_2(g) \rightarrow CH_4(g) )</td>
</tr>
<tr>
<td>CH_3OH(l)</td>
<td>−238.6</td>
<td>( C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(l) )</td>
</tr>
<tr>
<td>C_2H_5OH(l)</td>
<td>−277.6</td>
<td>( 2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH(l) )</td>
</tr>
<tr>
<td>C_6H_6(l)</td>
<td>+49.0</td>
<td>( 6C(s) + 3H_2(g) \rightarrow C_6H_6(l) )</td>
</tr>
<tr>
<td>C_6H_12O_6(s)</td>
<td>−1274.5</td>
<td>( 6C(s) + 6H_2(g) + 3O_2(g) \rightarrow C_6H_12O_6(s) )</td>
</tr>
<tr>
<td>H_2O(l)</td>
<td>−285.8</td>
<td>( H_2(s) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) )</td>
</tr>
<tr>
<td>H_2O(g)</td>
<td>−241.8</td>
<td>( H_2(s) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) )</td>
</tr>
<tr>
<td>CaCl_2(s)</td>
<td>−795.4</td>
<td>( Ca(s) + Cl_2(g) \rightarrow CaCl_2(s) )</td>
</tr>
<tr>
<td>CaCO_3(s)</td>
<td>−1206.9</td>
<td>( Ca(s) + C(s) + \frac{3}{2}O_2(g) \rightarrow CaCO_3(s) )</td>
</tr>
<tr>
<td>NaCl(s)</td>
<td>−411.1</td>
<td>( Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s) )</td>
</tr>
<tr>
<td>HCl(g)</td>
<td>−92.3</td>
<td>( \frac{1}{2}H_2(s) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g) )</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>−167.5</td>
<td>( \frac{1}{2}H_2(s) + \frac{1}{2}Cl_2(g) \rightarrow HCl(aq) )</td>
</tr>
</tbody>
</table>

When writing a formation equation, always write the elements in their standard states. For example, examine the equation for the formation of water directly from its elements under standard conditions.

\[
H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H^0_f = −285.8 \text{ kJ}
\]

A formation equation should show the formation of exactly one mole of the compound of interest. The following equation shows the formation of benzene, C_6H_6, under standard conditions.

\[
6C_{(\text{graphite})} + 3H_2(g) \rightarrow C_6H_6(l) \quad \Delta H^0_f = 49.1 \text{ kJ}
\]
Standard Molar Enthalpy of Combustion

The standard molar enthalpy of combustion, $\Delta H_{\text{comb}}^0$, is the enthalpy associated with the combustion of 1 mol of a given substance. The change in enthalpy is measured for the products and reactants in their standard states. For example, for methane, $\Delta H_{\text{comb}}^0 = -965.1 \text{ kJ/mol}$. You can represent the standard molar enthalpy of combustion using a thermochemical equation or using an enthalpy diagram, as shown in Figure 16.13.

$$\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l) + 965.1 \text{ kJ}$$

Notice that water is shown in the liquid form. Although water is formed as vapour during a combustion reaction, the enthalpy change for a standard molar enthalpy of combustion is measured with the energy change required for products to cool to SATP taken into consideration.

Table 16.3 lists selected standard molar enthalpies of combustion for the first eight straight-chain alkanes.

Practice representing formation and combustion reactions by working through the following problems.

### Practice Problems

15. Write a balanced thermochemical equation to represent the standard molar enthalpy of formation of each of the following substances. Include the heat term within the equation.

   - (a) $\text{H}_2\text{O}(g)$
   - (b) $\text{CaCl}_2(s)$
   - (c) $\text{CH}_4(g)$
   - (d) $\text{C}_6\text{H}_6(l)$
   - (e) Repeat (c) and (d), showing the standard molar enthalpy of formation in a different way.

16. Draw an enthalpy diagram to represent the standard molar enthalpy formation of sodium chloride.

17. Write a balanced thermochemical equation to represent the standard molar enthalpy of combustion of each of the following alkanes (see Table 16.3). Remember: the products and reactants must be in their standard states.

   - (a) ethane
   - (b) propane
   - (c) butane
   - (d) pentane

18. Draw an enthalpy diagram to represent the standard molar enthalpy of the combustion of heptane (see Table 16.3). Remember: the products and reactants must be in their standard states.

### Calculating Enthalpy Changes

The energy released or absorbed during a chemical reaction depends on the reactants involved. For example, the reaction of hydrogen and oxygen to form water releases heat to the surroundings, while the reaction of magnesium carbonate to form magnesium oxide and carbon dioxide absorbs heat from the surroundings. For each chemical reaction at SATP, there is a specific enthalpy change.
What other factors affect the enthalpy change of a given chemical reaction? Compare the warmth you feel from a burning wooden match and the warmth you feel from a roaring bonfire. Both involve the same chemical reactions (the combustion of wood, primarily cellulose), but the heat released in each case is clearly different. There is a great deal more cellulose and oxygen involved in the reactions in the bonfire compared to the burning matchstick. Therefore, the amount of reactants present plays a role in the energy change. As you know, the symbol for amount is $n$, and the unit is the mole (mol).

The heat released or absorbed by a system during a chemical change can be calculated using the relationship shown in Figure 16.14.

Work through the following Sample Problem to learn how to use the formula in Figure 16.14 for formation and combustion reactions. Then try the Practice Problems that follow.

**Sample Problem**

**Heat of Formation and Combustion Reactions**

**Problem**

Methane is the main component of natural gas. Natural gas undergoes combustion to provide energy for heating homes and cooking food.

(a) How much heat is released when 50.00 g of methane forms from its elements?

(b) How much heat is released when 50.00 g of methane undergoes complete combustion?

**What Is Required?**

(a) You need to determine $q$ for the formation reaction that produces 50.00 g of methane.

(b) You need to determine $q$ for the combustion reaction that consumes 50.00 g of methane.

**What Is Given?**

$m = 50.00 \text{ g}$

From Table 16.2, you can see that for methane, $\Delta H^0_f = -74.6 \text{ kJ/mol}$.

From Table 16.3, you can see that for methane, $\Delta H^0_{\text{comb}} = -965.1 \text{ kJ/mol}$.

**Plan Your Strategy**

**Step 1** Determine molar mass, $M$, for methane.

**Step 2** Determine $n$ based on the formula $n = \frac{m}{M}$.

**Step 3** (a) Determine $q$ for the formation reaction using $q = n\Delta H^0_f$.

(b) Determine $q$ for the combustion reaction using $q = n\Delta H^0_{\text{comb}}$.

**Act on Your Strategy**

**Step 1** For methane, $M = 12.01 \text{ g/mol} + (4 \times 1.01 \text{ g/mol}) = 16.05 \text{ g/mol}$

**Step 2**

$n = \frac{m}{M}$

$= \frac{50.00 \text{ g}}{16.05 \text{ g/mol}}$

$= 3.115 \text{ mol}$
Step 3 (a) \[ q = n\Delta H^\circ_f \]
\[ = (3.115 \text{ mol})(-74.6 \text{ kJ/mol}) \]
\[ = -232 \text{ kJ} \]

Therefore, 232 kJ of heat is released when 50.0 g of methane forms from its elements at SATP.

(b) \[ q = n\Delta H^\circ_{\text{comb}} \]
\[ = (3.115 \text{ mol})(-965.1 \text{ kJ/mol}) \]
\[ = -3.006 \times 10^3 \text{ kJ} \]

Therefore, \( 3.006 \times 10^3 \text{ kJ} \) of heat is released to the surroundings when 50.0 g of methane undergoes complete combustion.

Check Your Solution

The units are correct. The sign of the answer is negative, meaning heat is released by the reactions to the surroundings. As a quick check, use approximate numbers.

(a) There are about 3 mol of methane present, and the enthalpy of formation is about \(-75 \text{ kJ/mol}\). \(3(-75) = -225\), which is close to the actual solution.

(b) The enthalpy of combustion is about \(-1000 \text{ kJ}\). \(3(-1000) = 3000\), which is close to the actual solution.

Practice Problems

19. (a) Hydrogen gas and oxygen gas react to form 0.534 g of liquid water. How much heat is released to the surroundings?

(b) Hydrogen gas and oxygen gas react to form 0.534 g of gaseous water. How much heat is released to the surroundings?

20. Carbon and oxygen react to form carbon dioxide. At STP, the carbon dioxide has a volume of 78.2 L. How much heat was released to the surroundings during the reaction?

21. Determine the heat released by the combustion of each of the following samples of hydrocarbons.

(a) 56.78 g pentane, C\(_5\)H\(_{12}\)\((\ell)\)

(b) 1.36 kg octane, C\(_8\)H\(_{18}\)\((\ell)\)

(c) \(2.344 \times 10^4 \text{ g hexane, C}_6\text{H}_{14}(\ell)\)

22. How much heat is released by the combustion of a sample of methane, CH\(_4\)(g), that has a volume of 5.34 mL at STP?

23. What mass of methanol, CH\(_3\)OH\((\ell)\), is formed from its elements if \(2.34 \times 10^4 \text{ kJ}\) of energy is released during the process?

Enthalpy Changes and Changes of State

Like chemical reactions, changes of state involve changes in the potential energy of a system only. The temperature of the system undergoing the state change remains constant. Because energy is absorbed or released as heat, however, the temperature of the surroundings often changes.
The energy changes associated with changes of state are important in regulating body temperature. When you sweat, for example, the water absorbs heat from your skin as the water vaporizes. Cats lick their fur, and the vaporizing liquid helps keep them cool. Dogs cool off in a similar way, as shown in Figure 16.15. Again, the evaporating water absorbs heat from their mouths and helps keep them cool.

In general, the energy change associated with a physical change is smaller than the energy change associated with a chemical change. In the case of molecular substances, for example, changes of state involve the breaking of intermolecular forces. Intermolecular forces are generally much weaker than chemical bonds. The energy released or absorbed when intermolecular bonds form or break is much less than the energy released or absorbed when chemical bonds form or break.

Figure 16.16 summarizes the terminology and enthalpy changes associated with changes of state. Note that in general, enthalpy changes for changes of state between liquid and gas are greater than changes of state between liquid and solid. For example, when a solid melts to form a liquid the attractive forces between particles are not completely broken. The particles remain close together. When a liquid changes to a gas, however, the attractive forces are completely broken as relatively great distances separate the particles from each other. The difference in potential energy between a liquid and a gas is much greater than the difference in potential energy between a solid and a liquid.

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For example, when one mole of water melts, it absorbs 6.02 kJ of energy.

\[ \text{H}_2\text{O}(s) + 6.02 \text{ kJ} \rightarrow \text{H}_2\text{O}(l) \]
\[ \text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H = 6.02 \text{ kJ/mol} \]

Normally, however, chemists represent enthalpy changes associated with phase changes using modified \( \Delta H \) symbols. These symbols are described below.

- **molar enthalpy of vaporization,** \( \Delta H_{\text{vap}} \): the enthalpy change for the state change of one mole from liquid to gas
- **molar enthalpy of condensation,** \( \Delta H_{\text{cond}} \): the enthalpy change for the state change of one mole of a substance from gas to liquid
- **molar enthalpy of melting,** \( \Delta H_{\text{melt}} \): the enthalpy change for the state change of one mole of a substance from solid to liquid
- **molar enthalpy of freezing,** \( \Delta H_{\text{fre}} \): the enthalpy change for the state change of one mole of a substance from liquid to solid

Vaporization and condensation are opposite processes. Thus, the enthalpy changes for these processes have the same value but opposite signs. For example, 6.02 kJ of heat is needed to vaporize one mole of water. Therefore, 6.02 kJ of heat is released when one mole of water freezes.

\[ \Delta H_{\text{vap}} = -\Delta H_{\text{cond}} \]

Similarly, melting and freezing are opposite processes.

\[ \Delta H_{\text{melt}} = -\Delta H_{\text{fre}} \]

Several molar enthalpies of melting and vaporization are shown in Table 16.4. Notice that the same units (kJ/mol) are used for the enthalpies of melting, vaporization, condensation, and freezing. Also notice that energy changes associated with changes of state can vary widely.

**Table 16.4 Enthalpies of Melting and Vaporization for Several Substances**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Enthalpy of melting, ( \Delta H_{\text{melt}} ) (kJ/mol)</th>
<th>Enthalpy of vaporization, ( \Delta H_{\text{vap}} ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>argon</td>
<td>1.3</td>
<td>6.3</td>
</tr>
<tr>
<td>diethyl ether</td>
<td>7.3</td>
<td>29</td>
</tr>
<tr>
<td>ethanol</td>
<td>5.0</td>
<td>40.5</td>
</tr>
<tr>
<td>mercury</td>
<td>23.4</td>
<td>59</td>
</tr>
<tr>
<td>methane</td>
<td>8.9</td>
<td>0.94</td>
</tr>
<tr>
<td>sodium chloride</td>
<td>27.2</td>
<td>207</td>
</tr>
<tr>
<td>water</td>
<td>6.02</td>
<td>40.7</td>
</tr>
</tbody>
</table>

**Enthalpy of Solution**

Another type of physical change that involves a heat transfer is dissolution. When 1 mol of a solute dissolves in a solvent, the enthalpy change that occurs is called the **molar enthalpy of solution,** \( \Delta H_{\text{soln}} \). Dissolution can be either endothermic or exothermic.

Manufacturers take advantage of endothermic dissolution to produce cold packs that athletes can use to treat injuries. One type of cold pack contains water and a salt, such as ammonium nitrate, in separate compartments. When you crush the pack, the membrane that divides the compartments breaks, and the salt dissolves. This dissolution process is endothermic. It absorbs heat for a short time, so the cold pack feels cold. Figure 16.7 on the next page shows how a cold pack works.
This person’s shoulder was injured. Using a cold pack helps to reduce the inflammation of the joint.

Some types of hot packs are constructed in much the same way as the cold packs described above. They have two compartments. One compartment contains a salt, such as calcium chloride. The other compartment contains water. In hot packs, however, the dissolution process is exothermic. The process releases heat to the surroundings.

The molar enthalpy of solution, $\Delta H_{\text{soln}}$, of ammonium nitrate is $25.7 \text{ kJ/mol}$.

$$\text{NH}_4\text{NO}_3(s) + 25.7 \text{ kJ} \rightarrow \text{NH}_4\text{NO}_3(aq)$$

The molar enthalpy of solution, $\Delta H_{\text{soln}}$, of calcium chloride is $-82.8 \text{ kJ/mol}$.

$$\text{CaCl}_2(s) \rightarrow \text{CaCl}_2(aq) + 82.8 \text{ kJ}$$

**Heat Absorbed or Released by a Physical Change**

You can determine the heat absorbed or released by a state change or dissolution using the equation $q = n\Delta H$, just as you did with chemical reactions. Work through the following problems to practice determining $q$ for physical changes. Refer to Table 16.4 for enthalpies of melting and vaporization.

**Practice Problems**

24. An ice cube with a mass of 8.2 g is placed in some lemonade. The ice cube melts completely. How much heat does the ice cube absorb from the lemonade as it melts?

25. A teacup contains 0.100 kg of water at its freezing point. The water freezes solid.
   (a) How much heat is released to the surroundings?
   (b) How much heat would be required to melt the ice in the teacup?
26. A sample of liquid mercury vaporizes. The mercury is at its boiling point and has a mass of 0.325 g.
   (a) Is heat absorbed from the surroundings or released to the surroundings?
   (b) How much heat is absorbed or released to the surroundings by the process?

27. The molar enthalpy of solution for sodium chloride, NaCl, is 3.9 kJ/mol.
   (a) Write a thermochemical equation to represent the dissolution of sodium chloride.
   (b) Suppose you dissolve 25.3 g of sodium chloride in a glass of water at room temperature. How much heat is absorbed or released by the process?
   (c) Do you expect the glass containing the salt solution to feel warm or cool? Explain your answer.

28. What mass of diethyl ether, C₄H₁₀O, can be vaporized by adding 80.7 kJ of heat?

29. 3.97 × 10⁴ J of heat is required to vaporize 100 g of benzene, C₆H₆. What is the molar enthalpy of vaporization of benzene?

Section Summary
In this section, you learned that chemical reactions and physical changes involve changes in potential energy. In the next section, you will incorporate what you know about changes in kinetic energy and potential energy. You will analyze what happens when you heat a solid until it melts, then continue to heat the liquid until it vaporizes. You will track the temperature change and comment on whether a change in kinetic energy or potential energy is taking place.

Section Review

1. In your own words, explain why exothermic reactions have ΔH < 0.

2. Label each thermochemical equation with the most specific form(s) of ΔH. Remember to pay attention to the sign of ΔH.
   (a) Ag(s) + \( \frac{1}{2} \) Cl₂(g) → AgCl(s) + 127.0 kJ (at 25°C and 100 kPa)
   (b) 44.0 kJ + H₂O(l) → H₂O(g) (at 25°C and 100 kPa)
   (c) C₂H₄(g) + 3O₂(g) → 2CO₂(g) + 2H₂O(g) + energy

3. A pot of water boils on a stove. The temperature of the liquid water remains at 100°C.
   (a) What type of energy change is taking place within the water—a change in kinetic energy or a change in potential energy?
   (b) Explain why the temperature of the water does not change as the water boils, even though heat is continuously absorbed by the water from the stove element.
   (c) How much heat is needed to boil 2.32 kg of water at 100°C?
A group of campers light a bonfire by touching the flame from a butane lighter to some kindling. They roast marshmallows over the blaze. Describe the energy transfers involved using the terms potential energy, kinetic energy, temperature, system, surroundings, endothermic, exothermic, and combustion reaction.

Acetylene, $C_2H_2$, undergoes complete combustion in oxygen. Carbon dioxide and water are formed. The standard molar enthalpy of the complete combustion of acetylene is $1.3 \times 10^3 \text{ kJ/mol}$.

(a) Write a thermochemical equation for this reaction.

(b) Draw a diagram to represent the thermochemical equation.

(c) How much heat is released during the complete combustion of 2.17 g of acetylene?

Write an equation to represent each phase change in Table 16.4. Include the enthalpy change as a heat term in the equation.

When one mole of gaseous water forms from its elements, 241.8 kJ of energy is released. In other words, when hydrogen burns in oxygen or air, it produces a great deal of energy. Since the nineteenth century, scientists have been researching the potential of hydrogen as a fuel. One way in which the energy of the combustion of hydrogen has been successfully harnessed is as rocket fuel for aircraft.

(a) Write a thermodynamic equation for the combustion of hydrogen.

(b) Suggest three reasons why hydrogen gas is a desirable rocket fuel.

(c) Suggest challenges that engineers might have had to overcome in order to make hydrogen a workable rocket fuel for aircraft.

Calcium oxide, $\text{CaO}$, reacts with carbon in the form of graphite. Calcium carbide, $\text{CaC}_2$, and carbon monoxide, $\text{CO}$, are produced in an endothermic reaction.

$\text{CaO(s)} + 3\text{C(s)} + 462.3 \text{ kJ} \rightarrow \text{CaC}_2(s) + \text{CO(g)}$

(a) 246.7 kJ of heat is absorbed by the system. What mass of calcium carbide is produced?

(b) How much heat is absorbed by the system if 46.7 g of graphite reacts with excess calcium oxide?

(c) $1.38 \times 10^{24}$ formula units of calcium oxide react with excess graphite. How much energy is needed?
Heating and Cooling Curves

Water is a remarkable substance in many ways. For example, water is one of very few substances that is found naturally on Earth in all three states: gas, liquid, and solid. You observe water changing state all the time in your daily life. Water condenses in the air and falls as rain; when the sun comes out, the puddles evaporate. Icebergs melt as they travel through the ocean. Ice cubes form from liquid water in a freezer.

Chemists use heating curves and cooling curves to represent temperature and phase changes in substances such as water. A **cooling curve** shows how the temperature of a substance changes as heat is removed from it. A **heating curve** shows how the temperature of a substance changes as heat is added to it. Heating curves and cooling curves show temperature on the y-axis, and either heat transfer or time on the x-axis. Figure 16.18 shows a cooling curve that represents how the temperature of water changes as it cools from a gas at 130˚C to ice at –40˚C.

![Figure 16.18](image)

**Figure 16.18** This cooling curve shows the conversion of water vapour to ice as heat is removed from the system.

Refer to Figure 16.18 as you read about Stages 1–5.

**Stage 1** The gaseous water cools until it reaches the boiling point of water (100˚C). The average kinetic energy of the water particles is decreasing, therefore the temperature decreases.

**Stage 2** The gaseous water condenses, forming liquid water. Only potential energy is changing. Because the average kinetic energy of the water particles does not change, the temperature does not change.
Stage 3 The liquid water cools until it reaches the melting point of water (0°C). The average kinetic energy of the water particles is decreasing, therefore the temperature decreases.

Stage 4 The liquid water freezes, forming ice. Only potential energy is changing. The average kinetic energy of the particles does not change, therefore the temperature does not change.

Stage 5 The ice cools further. The average kinetic energy of the water particles is decreasing, therefore the temperature decreases.

Heating and cooling curves do not need to show all possible changes of state. For example, the cooling curve in Figure 16.19 shows the conversion of liquid mercury to solid mercury. As you now know, the flat portions of a heating or cooling curve occur at either the melting point or the boiling point of the substance. In this case, since the title of the curve indicates that the mercury started out as a liquid, you know that the flat portion represents the melting point (which is the same as the freezing point). Based on the graph, therefore, you can tell that the melting point of mercury is −39°C.

The heating curve in Figure 16.20 shows the conversion of liquid ethanol to gaseous ethanol. Since the title of the curve indicates that the ethanol started out as a liquid, you know that as heat is added, the liquid will eventually vaporize. While the liquid is vaporizing, the temperature does not change. Based on the graph, therefore, you can tell that the boiling point of ethanol is 78.5°C.

It is often helpful to draw heating curves and cooling curves when solving problems involving temperature change and state change. In the laboratory, you can determine melting points or boiling points by tracking temperature changes and constructing heating or cooling curves.

In the following ExpressLab, you will construct a heating curve and a cooling curve for lauric acid.
Chapter 16  Theories of Energy Changes • MHR

Total Heat Absorbed or Released by a System
As you discovered in the ExpressLab, substances undergo a sequence of temperature changes and state changes as they absorb or release heat. Suppose you wanted to determine how much heat is absorbed by a system that experiences both a temperature change and a change of state?

For example, suppose you are preparing to boil some water for pasta. You place 5 L of water at 10°C on the stove. Unfortunately, you forget about the water. When you return, the water has completely boiled away. You want to know how much heat was required to heat the liquid water to 100°C, and then completely vaporize it. How would you carry out this calculation?

Safety

Materials
10 g lauric acid  hot plate
test tube  thermometer
test tube tongs  stopwatch
250 mL beakers

Procedure
1. Read the procedure carefully. Prepare a data table as shown below to record your data.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Temperature (˚C) for cooling curve</th>
<th>Temperature (˚C) for heating curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2. Fill a 250 mL beaker with about 200 mL of warm water. Using the hot plate, heat the water to about 60˚C. Adjust the hot plate settings so that you maintain the temperature at 60˚C.

3. Place your sample of lauric acid in the 60˚C water on the hot plate. When the lauric acid starts to melt, place the thermometer in the test tube. Do not allow the thermometer to touch the bottom of the test tube.

4. When the temperature has reached about 55˚C, use the test tube holder to transfer the test tube to the test-tube holder.

5. Immediately record the temperature of the lauric acid. Every 30 seconds, record the temperature again. Stir the lauric acid gently with the thermometer.

6. Continue to record data until the lauric acid solidifies. Do not stop taking data until the temperature is well below the freezing point.

7. Check that your 60˚C bath is still at 60˚C. Return the test tube to the 60˚C bath.

8. Immediately record the temperature of the lauric acid. Every 30 seconds, record the temperature again. Stir the lauric acid gently with the thermometer once the lauric acid has melted somewhat. Stop recording data once the temperature reaches 55˚C.

9. Remove the thermometer and wipe it clean. Clean up as directed by your teacher.

10. Use your data to create two graphs: one to show cooling data and one to show heating data. Label your x-axis “time (s)” and your y-axis “temperature (˚C)”. Name your graphs appropriately.

Analysis
1. What is the freezing point of lauric acid? What is the melting point of lauric acid?

2. Your graphs will probably have both “flat” and “sloped” portions. Answer the following questions for each flat and sloped portion of each graph.

(a) What type of energy change (kinetic or potential) is taking place? How do you know?

(b) What is happening to the average speed of the lauric acid molecules?

3. Label the graph appropriately with the following labels: heating, cooling, melting, freezing, melting point, freezing point. (You will need to use some labels multiple times.)
You can calculate the heat required to heat and boil the water using the two equations you learned in sections 16.1 and 16.2.

\[ q = mc \Delta T \quad (\text{equation 1}) \]

\[ q = n \Delta H \quad (\text{equation 2}) \]

Recall that equation 1 is used to determine the heat absorbed or released by a system in which only the kinetic energy is changing. Conversely, equation 2 is used to determine the heat absorbed or released by a system in which only the potential energy is changing. You must use both equations, because heating the water involves a change in kinetic energy, while boiling the water involves a change in potential energy. Work through the following Sample Problem to see how to use the equations to determine the total heat absorbed by the water.

**Sample Problem**

**Determining the Overall Heat Transfer of a System**

**Problem**

How much heat is absorbed by 5.00 kg of water at 10.0°C if it is heated until it is converted completely into water vapour?

**What Is Required?**

You need to determine \( q \) for 5.00 kg of water heated from 10.0°C to the boiling point of water, plus \( q \) required for the change of state from water to steam.

**What Is Given?**

\( T_i = 10.0°C \)
\( T_f = 100.0°C \) (the boiling point of water)
\( m = 5.00 \text{ kg} = 5.00 \times 10^3 \text{ g} \)
\( c = 4.184 \text{ J/g °C} \) (from Table 16.1)
\( \Delta H_{\text{vap}} = 40.7 \text{ kJ/mol} \)

**Plan Your Strategy**

1. **Step 1** Use \( q_1 = mc \Delta T \) to determine the heat absorbed by the water as it heats from 10°C to 100°C.
2. **Step 2** Use \( q_2 = n \Delta H \) to determine the heat absorbed by the water as it vaporizes.
3. **Step 3** Add your answers together. Be sure to express both answers in kJ before adding them.

**Act on Your Strategy**

1. **Step 1**

\[ q_1 = mc \Delta T \]
\[ = (5.00 \times 10^3 \text{ g})(4.184 \text{ J/g °C})(100.0°C - 10.0°C) \]
\[ = (5.00 \times 10^3 \text{ g})(4.184 \text{ J/g °C})(90.0°C) \]
\[ = 1.88 \times 10^6 \text{ J} \]

The heat absorbed by the water as it heats to the boiling point is \( 1.88 \times 10^6 \text{ J} \).
Step 2  
\[ M = (2 \times 1.01 \text{ g/mol}) + 16.00 \text{ g/mol} = 18.02 \text{ g/mol} \]

\[ n = \frac{m}{M} = \frac{5.00 \times 10^3 \text{ g}}{18.02 \text{ g/mol}} = 277 \text{ mol} \]

\[ q_2 = n\Delta H_{vap} = (277)(40.7 \text{ kJ/mol}) = 1.13 \times 10^4 \text{ kJ} \]

The water absorbs \(1.13 \times 10^4\) kJ of heat as it vaporizes.

Step 3  
Convert the answer from Step 1 to kJ before adding the answers together.

\[ q_1 = (1.88 \times 10^6 \text{ J}) \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right) = 1.88 \times 10^3 \text{ kJ} \]

\[ q_{total} = q_1 + q_2 = 1.88 \times 10^3 \text{ kJ} + 1.13 \times 10^4 \text{ kJ} = 1.32 \times 10^4 \text{ kJ} \]

The total heat absorbed by the water is \(1.32 \times 10^4\) kJ.

Check Your Solution

The solution has the correct number of significant digits. The units are correct. Values for \(q_1\) and \(q_2\) are positive, which makes sense since the water absorbed heat as its temperature increased and as it changed state from liquid to gas.

Practice Problems

30. 1.451 kg of water at 25.2°C is added to a kettle and the water is completely vaporized.
   (a) Draw a heating curve for this process.
   (b) How much heat is required for the vaporization of all the water?

31. A metal bucket containing 532.1 g of ice at 0.00°C is placed on a wood-burning stove. The ice is melted and then heated to 45.21°C.
   (a) Draw a heating curve for this process.
   (b) How much heat is required to melt the ice and warm the water to 45.21°C?

32. A sample of liquid mercury having a mass of 0.0145 g cools from 35.1°C and forms solid mercury at −38.8°C. The melting point of mercury is −38.8°C and its specific heat capacity is \(0.140 \text{ J/g°C}\).
   (a) Draw a cooling curve for this process.
   (b) How much heat is released during this process?

33. A sample of 36.8 g of ethanol gas at 300.0°C is cooled to liquid ethanol at 25.5°C. The specific heat capacity of ethanol gas is 1.43 J/g°C, and the specific heat capacity of liquid ethanol is 2.45 J/g°C. The boiling point of ethanol is 78.5°C.
   (a) Draw a cooling curve for this process.
   (b) Calculate the heat released during this process.

34. Calculate the total heat released when 200 g of water vapour at 300.0°C is cooled until it reaches −20.0°C. The specific heat capacity of ice is 2.02 J/g°C. The specific heat capacity of water vapour is 1.99 J/g°C.
Section Summary

In this section, you learned how to calculate the total heat associated with changes involving both kinetic energy and potential energy. In Chapter 17, you will find out how to use changes in kinetic energy to determine potential energy changes associated with chemical reactions.

Section Review

1. The portions of heating curves and cooling curves that represent changes of state are horizontal (flat). Explain why this is the case.

2. Iron melts at 1535˚C. Draw a cooling curve to show what happens when molten iron at 1600˚C cools to solid iron at 50˚C. Label the axes and sections of your cooling curve appropriately.

3. A pure gold chain with a mass of 10.23 g is heated until it forms liquid gold at the melting point of 1064.2˚C. The temperature of the chain is initially 21.0˚C. The enthalpy of freezing for gold is 12.5 kJ/mol.
   (a) Draw a heating curve to represent what happens to the gold.
   (b) What is the total heat absorbed by the gold as it warms and then melts?

4. An ice cube with a mass of 3.375 g sits in an empty glass of water on a hot day. The ice cube is initially at −5.2˚C. It melts and the liquid water warms to 27.3˚C.
   (a) Draw a heating curve to represent what happens to the ice cube.
   (b) What is the total heat absorbed by the water as it warms from ice at −5.2˚C to liquid water at 27.3˚C? The specific heat capacity of ice is 2.02 J/g˚C.

5. 1.55 kg of water vapour at 125.4˚C cools to eventually form ice at −5.5˚C. The specific heat capacity of ice is 2.02 J/g˚C. The specific heat capacity of water vapour is 1.99 J/˚C.
   (a) Draw a cooling curve to represent the process.
   (b) How much heat is released during this process?

6. During cold weather, fruit farmers spray their fruit with water to prevent frost damage. Explain why this practice works.

7. Water vapour at 100˚C causes more severe burns than liquid water at 100˚C. Explain why this is the case.

8. If you became lost in a forest in winter, why would it be better to drink water from a stream rather than eat snow to quench your thirst?

9. Examine the heating curve for lead shown in Figure 16.21.
   (a) What is the boiling point of lead?
   (b) What is the melting point of lead?
   (c) A 500 g sample of solid lead at −25.0˚C is heated until it melts completely. How much heat is absorbed? The specific heat capacity of solid lead is 0.127 J/g˚C. The enthalpy of melting of lead is 5.08 kJ/mol.
Reflecting on Chapter 16

Summarize this chapter in the format of your choice. Here are a few ideas to use as guidelines:

• Explain what happens to the particles of a system during heat transfer.
• Describe heat in terms of transfer of kinetic energy.
• Explain how the temperature change of a substance depends on the nature of the substance, the heat absorbed or released, and the mass of the substance.
• Show how to calculate the heat absorbed or released by a system during a temperature change.
• Demonstrate various ways to communicate the enthalpy change associated with a process.
• Explain the relationship between enthalpy change and potential energy.
• Explain the energy changes related to bond breaking and bond making.
• List various processes that involve a change in enthalpy.
• Show how to calculate the heat absorbed or released by a system during a chemical or physical change.
• Explain what is happening to the particles of a substance during the different stages shown on a heating curve or a cooling curve.
• Show how to calculate the total heat absorbed or released during a multi-stage process that involves changes in both kinetic energy and potential energy.

Reviewing Key Terms

closed system cooling curve
endothermic reaction enthalpy change (\(\Delta H\))
exothermic reaction enthalpy of reaction
heat capacity (\(C\)) heat (\(q\))
isolated system heating curve
kinetic energy Joule (J)
potential energy open system
standard enthalpy of reaction specific heat capacity (\(c\))
system surroundings
thermochemical equation temperature (\(T\))
thermodynamics thermochemistry

Knowledge/Understanding

1. In your own words, define and distinguish between closed, open, and isolated systems.

2. The vaporization of liquid carbon disulfide, \(\text{CS}_2\), requires an energy input of 29 kJ/mol.
   (a) Is this reaction exothermic or endothermic?
   (b) What is the molar enthalpy of vaporization of carbon disulfide?
   (d) Write a thermochemical equation to represent the vaporization of carbon disulfide.
   Include 29 kJ as a heat term in the equation.
   (e) Draw and label an enthalpy diagram for the vaporization of liquid carbon disulfide.

3. Describe the relationship between the amount of heat released by water and the following factors:
   (a) the mass of the water
   (b) the temperature change of the water

4. (a) What are the products of the complete combustion of a hydrocarbon?
   (b) What products can form if the combustion is incomplete?
   (c) Why can incomplete combustion be dangerous if it occurs in your home?
   (d) Under what circumstances does incomplete combustion take place?

5. Define and distinguish between kinetic energy and potential energy and give one example of each of the following types of changes.
   (a) a process that involves changes in kinetic energy only
   (b) a process that involves changes in potential energy only
   (c) a process that involves changes in both potential and kinetic energy

6. State the first law of thermodynamics and express the law as an equation.

7. Explain briefly why areas of land that are not close to water tend to experience large variations in temperature, as compared to areas of land near lakes or oceans.

8. Define and distinguish between heat capacity and specific heat capacity. Use examples in your answer.

9. Explain how sweating helps your body to cool off on a hot day.

Answers to questions highlighted in red type are provided in Appendix A.
10. An equal amount of heat is absorbed by a 25 g sample of aluminum \((c = 0.900 \ J/\text{g}^\circ\text{C})\) and a 25 g sample of nickel \((c = 0.444 \ J/\text{g}^\circ\text{C})\). Which metal will show a greater increase in temperature? Explain your answer.

11. To make four cups of tea, 1.00 kg of water is heated from 22.0°C to 99.0°C. How much heat is added?

12. A sample of graphite with a mass of 2.35 kg experiences a temperature increase of 3.45°C. How much heat did the graphite absorb? Refer to Table 16.1 for the specific heat capacity of graphite.

13. In an ice cube tray in a freezer, 98.4 g of water at 0.00°C freezes solid. How much heat is released when the water freezes?

14. Hydrogen sulfide gas, \(\text{H}_2\text{S(g)}\), has a distinct, powerful smell of rotten eggs. The gas undergoes a combustion reaction with oxygen to produce gaseous sulfur dioxide and gaseous water. The molar enthalpy of combustion of hydrogen sulfide gas is \(-519 \ kJ/mol\).
   (a) Write a balanced thermochemical equation to represent the combustion of hydrogen sulfide gas.
   (b) How much heat is released when 15.0 g of hydrogen sulfide gas undergoes combustion?
   (c) A sample of hydrogen sulfide gas undergoes combustion. 47.2 kJ of heat are released. What volume of sulfur dioxide at STP is produced by the reaction?

15. A 10.0 g sample of pure acetic acid, \(\text{CH}_3\text{COOH}\), is completely burned in oxygen. 144.77 kJ of heat are released. What is the molar enthalpy of combustion of acetic acid?

16. The molar enthalpy of combustion of methanol, \(\text{CH}_3\text{OH(ℓ)}\), is \(-727 \ kJ/mol\).
   (a) Write a balanced thermochemical equation to show the complete combustion of methanol to form water and carbon dioxide.
   (b) 44.3 g of methanol undergoes complete combustion. How much heat is released?
   (c) A sample of methanol undergoes complete combustion to form 56.2 L of carbon dioxide at STP. How much heat is released?

17. The standard molar enthalpy of formation of poisonous hydrogen cyanide gas, \(\text{HCN(g)}\), is 135 kJ/mol.
   (a) Write a balanced thermochemical equation to show the formation of 1 mol of hydrogen cyanide gas from its elements.
   (b) How much heat would be required to form 50.0 L of \(\text{HCN(g)}\) at STP from its elements?
   (c) How much heat would be released if 25.3 g of \(\text{HCN(g)}\) were decomposed to form its elements?

18. A certain type of hot pack uses the enthalpy of solution of calcium chloride to release heat. The molar enthalpy of solution of calcium chloride is \(-82.8 \ kJ/mol\).
   (a) Write a balanced thermochemical equation to show the enthalpy of solution of calcium chloride.
   (b) A hot pack contains 15.0 g of calcium chloride. How much heat is released when the 15.0 g of calcium chloride dissolves in water?
   (c) Assume that all of the heat released in question (b) is transferred to 215.0 g of calcium chloride solution. The initial temperature is 25°C. What is the final temperature of the solution? (Assume the solution has the same specific heat capacity as water.)

19. 2.5 kg of ice at \(-5.3°C\) is heated until it becomes water vapour at 250.0°C. The specific heat capacity of ice is 2.02 J/g°C. The specific heat capacity of water vapour is 1.99 J/g°C.
   (a) Calculate the total heat absorbed by the process.
   (b) Draw a heating curve to show the process.

20. Examine the heating curve on the following page to answer the following questions.
   (a) What is the melting point of methanol?
(b) What is the boiling point of methanol?
(c) The molar enthalpy of vaporization of methanol is 38 kJ/mol. 1.50 kg of liquid methanol at 25.0°C is heated to form methanol vapour at 65.0°C. How much heat is absorbed in the process? The specific heat capacity of liquid methanol is 2.350 J/g°C.

Making Connections
24. When walking briskly, you use about 20 kJ of energy per minute. Eating one serving of a whole wheat cereal (37.5 g) provides about 527.18 kJ of energy.
(a) How long could you walk after eating one serving of cereal?
(b) What mass of cereal would provide enough energy for you to walk for 4.0 h?
(c) An average apple provides 283 kJ of energy. How many apples would provide enough energy for you to walk for 4.0 h?

Answers to Practice Problems and Short Answers to Section Review Questions

Practice Problems
1. 6.2 × 10³ J  2. −4.6 × 10³ J  3. Beaker B 4. (a) +4.22 J; +4.6 J (b) +87 kJ (c) −290 kJ  5. (a) \( m = \frac{q}{c \Delta T} \) (b) \( c = \frac{q}{m \Delta T} \) (c) \( \Delta T = \frac{q}{mc} \)  6. (a) \( T_f = T_i - \frac{q}{mc} \) (b) \( T_i = T_f + \frac{q}{mc} \)  7. 2.14 × 10³ J
8. 0.7900 J/°C; granite 9. 1.21 J/°C  10. 15.5°C  11. (a) 418.4 kJ/°C (b) 1.67 × 10⁴ kJ (c) 1.67 × 10⁴ kJ
12. (a) 0.4184 kJ/°C (b) 167.6 kJ (c) 167.6 kJ  13. (a) 2.43 × 10⁻³ kJ/°C (b) 0.0792 kJ  14. (a) 224 kJ/°C (b) 224 kJ  15. (a) \( H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) + 241.8 \) kJ
(b) \( Ca(s) + Cl_2(g) \rightarrow CaCl_2(s) + 795.4 \) kJ  16. (a) \( \Delta H_f^\circ = +49 \) kJ/mol  17. (a) \( CaH_2(s) + 7/2O_2(g) \rightarrow 3H_2O(l) + 2CO_2(g) + 1250.9 \) kJ
(b) \( CaH_2(s) + 5O_2(g) \rightarrow 4H_2O(l) + 3CO_2(g) + 2323.7 \) kJ
(c) \( CaH_2(s) + 13/2O_2(g) \rightarrow 5H_2O(l) + 4CO_2(g) + 3003.0 \) kJ
(d) \( CaH_2(s) + 8O_2(g) \rightarrow 6H_2O(l) + 5CO_2(g) + 3682.3 \) kJ
18. (a) \( H_2O(l) + 3CO_2(g) \) should be shown below reactants \( (NaCl(s) + 1/2Cl_2(g)) \); \( \Delta H_f^\circ = -411.1 \) kJ/mol
19. (a) 8.46 kJ (b) 7.16 kJ (c) 1.37 × 10³ kJ
20. 2.896 × 10¹ kJ (b) 6.81 × 10¹ kJ (c) 1.186 × 10⁶ kJ
21. 0.230 kJ (b) 3.14 × 10³ g (c) 2.74 kJ  25. (a) 33.4 kJ
(b) 33.4 kJ  26. (a) absorbed (b) 0.0956 kJ
27. (a) \( NaCl(s) + 3.9 \) kJ/mol \( \rightarrow NaCl(aq) \) (b) 1.69 kJ (c) heat absorbed from water
28. 206 g (b) 3.10 × 10⁴ kJ/mol
29. 3.73 × 10¹ kJ  31. (b) 279 kJ (b) 1.84 × 10⁻³ kJ
33. (b) 48.8 kJ  34. 690 kJ

Section Review 16.1
(a) −4.54 × 10¹ J  (a) 38 J
(b) 76 J (c) 76 J  6. (a) 0.237 J/°C  (b) 5.66 J/°C
7. copper 16.2: 3(c) 5.24 × 10³ kJ
5. (a) \( CaH_2(s) + 5/2O_2(g) \rightarrow H_2O(l) + 2CO_2(g) + 1.3 \times 10³ \) kJ
c) 104 kJ  8. (a) 34.21 g (b) 599 kJ (c) 1.06 × 10⁴ kJ
16.3: 3(b) 2.03 kJ  4(b) 1.55 kJ  5(b) 4.76 × 10² kJ  9(a) 1749°C
(b) 327.5°C (c) 34.7 kJ

Communication
21. Aqueous hydrogen peroxide, \( H_2O_2(aq) \), decomposes slowly to form water and oxygen. When 1 mol of aqueous hydrogen peroxide decomposes, 94.64 kJ of heat is released. The rate of the reaction is increased by the addition of a catalyst such as manganese(IV) oxide, MnO₂.
(a) Write a thermochemical equation to show the decomposition of aqueous hydrogen peroxide.
(b) Does the heat released by the decomposition of hydrogen peroxide change if a catalyst is added to speed up the reaction? Explain your answer in detail.
22. You are heating soup on the stove, and leave a metal spoon in the pot of hot soup. You accidentally touch the hot spoon with your hand. Immediately you turn on the cold water tap and hold your hand under the cold water. Describe in detail how heat is transferred in this scenario, using your knowledge of kinetic energy and the particle model of matter.
23. Explain in detail how the energy changes involved in bond breaking and bond making determine whether a chemical reaction is endothermic or exothermic. Use a diagram to illustrate your explanation.
Why is it important to know how to determine the energy changes associated with chemical and physical changes?

Engineers need to know how much energy is released from different fuels when they design an engine and decide between different fuels. Firefighters need to know how much heat can be given off by the combustion of different materials so they can decide on the best way to fight a specific fire. Manufacturers of hot packs need to know how much heat is released by a given exothermic process so that their pack will warm but not harm the user.

How do you determine the heat absorbed or released by chemical and physical processes? In this section, you will learn some ways to determine the enthalpy changes of various processes by experiment, based on the heat they release or absorb. You will apply what you have learned by performing your own heat experiments. You will also learn how to use tabulated values to determine enthalpies of physical and chemical processes. Finally, you will examine the efficiency and environmental impact of traditional and alternative energy sources.

Different substances release different amounts of heat when they burn. What are some ways to determine the enthalpy of combustion of a substance?
In the ThoughtLab in section 16.1, two students used beakers with no lids when they measured change in temperature. The students assumed that energy was being exchanged only between the ice and the water. In fact, energy was also being exchanged with the beaker, the lab bench, and the surrounding air. As a result, the data that the students obtained had a large experimental error. How could the students have prevented this error?

Much of the technology in our lives is designed to stop the flow of kinetic energy as heat. Your home is insulated to prevent heat loss in the winter and heat gain in the summer. If you take hot soup to school for your lunch, you probably use a Thermos™ to prevent heat loss to the environment. Whenever there is a temperature difference between two objects, kinetic energy is transferred as heat from the hotter object to the colder object. You measure the heat being transferred in a reaction or other process by monitoring temperature change. Therefore, you must minimize any heat transfer between the system and portions of the surroundings whose temperature change you are not measuring.

**Calorimetry**

To measure the heat flow in a process, you need an isolated system, such as a Thermos™. As you learned in section 16.1, an isolated system stops matter and energy from flowing into or out of the system. You also need a known amount of a substance, usually water. The water absorbs the heat that is released by the process, or the water releases heat if the process is endothermic. To determine the heat flow, you can measure the temperature change of the water. With its large specific heat capacity (4.184 J/g·˚C) and its broad temperature range (0˚C to 100˚C), liquid water can absorb and release a lot of heat.

Water, a thermometer, and an isolated system are the basic components of a calorimeter. A calorimeter is a device that is used to measure changes in kinetic energy. The technological process of measuring changes in kinetic energy is called calorimetry.

**Using a Calorimeter**

In a coffee-cup calorimeter, shown in Figure 17.1, a known mass of water is inside the coffee cup. The water surrounds, and is in direct contact with, the process that produces the energy change. The initial temperature of the water is measured. Then the process takes place and the final temperature of the water is measured. The water is stirred to maintain even energy distribution, and the system is kept at a constant pressure. This type of calorimeter can measure heat changes during processes such as dissolving, neutralization, heating, and cooling.

The law of conservation of energy states that energy can be changed into different forms, but it cannot be created or destroyed. This law allows you to calculate the energy change in a calorimetry experiment. However, you need to make the assumptions listed on the following page.
• The system is isolated. (No heat is exchanged with the surroundings outside the calorimeter.)
• The amount of heat that is exchanged with the calorimeter itself is small enough to be ignored.
• If something dissolves or reacts in the calorimeter water, the solution still retains the properties of water. (For example, density and specific heat capacity remain the same.)

Once you make those assumptions, the following equation applies:

\[ q_{\text{system}} = -q_{\text{surroundings}} \]

The system is the chemical or physical process you are studying. The surroundings consist of the water or solution in the calorimeter. When a process causes an energy change in a calorimeter, the change in temperature is measured by a thermometer in the water. If you know the mass of the water and its specific heat capacity, you can calculate the change in kinetic energy caused by the process using the equation \( q = m \cdot c \cdot \Delta T \). See Figures 17.2 and 17.3 on the following page for examples.

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**Tools & Techniques**

**The First Ice Calorimeter**

A calorimeter measures the thermal energy that is absorbed or released by a material. Today we measure heat using joules (J) or calories (cal). Early scientists accepted one unit of heat as the amount of heat required to melt 1 kg of ice. Thus two units of heat could melt 2 kg of ice.

The earliest measurements of heat energy were taken around 1760, by a Scottish chemist named Joseph Black. He hollowed out a chamber in a block of ice. Then he wiped the chamber dry and placed a piece of platinum, heated to 38°C, inside. He used another slab of ice as a lid. As the platinum cooled, it gave up its heat to the ice. The ice melted, and water collected in the chamber. When the platinum reached the temperature of the ice, Black removed the water and weighed it to find out how much ice had melted. In this way, he measured the quantity of heat that was released by the platinum.

In 1780, two French scientists, Antoine Lavoisier and Pierre Laplace, developed the first apparatus formally called a calorimeter. Like Black, they used the amount of melted ice to measure the heat released by a material. Their calorimeter consisted of three concentric chambers. The object to be tested was placed in the innermost chamber. Broken chunks of ice were placed in the middle chamber.

Ice was also placed in the outer chamber to prevent any heat reaching the apparatus from outside. As the object in the inner chamber released heat, the ice in the middle chamber melted. Water was drawn from the middle chamber by a tube, and then measured.

Lavoisier made many important contributions to the science of chemistry. Unfortunately, his involvement with a company that collected taxes for the government led to his arrest during the French Revolution. He was beheaded after a trial that lasted less than a day.

---

*The original calorimeter used by Lavoisier and Laplace*
In the next Sample Problem, you will use what you have just learned to calculate the specific heat capacity of a metal.

Notice that all the materials in the calorimeter in the following Sample Problem have the same final temperature. A system is said to be at thermal equilibrium when all its components have the same temperature.

**Sample Problem**

**Determining a Metal’s Specific Heat Capacity**

**Problem**

A 70.0 g sample of a metal was heated to 95.0°C in a hot water bath. Then it was quickly transferred to a coffee-cup calorimeter. The calorimeter contained 100.0 g of water at an initial temperature of 19.8°C. The final temperature of the contents of the calorimeter was 22.6°C. What is the specific heat capacity of the metal?

**What Is Required?**

You need to calculate the specific heat capacity of the metal.

**What Is Given?**

You know the mass of the metal, and its initial and final temperatures.

Mass of metal \( (m_m) = 70.0 \text{ g} \)

Initial temperature of metal \( (T_i) = 95.0°C \)

Final temperature of metal \( (T_f) = 22.6°C \)

You also know the mass of the water, and its initial and final temperatures.

Mass of water \( (m_w) = 100.0 \text{ g} \)

Initial temperature of water \( (T_i) = 19.8°C \)

Final temperature of water \( (T_f) = 22.6°C \)

As well, you know the specific heat capacity of water: 4.184 J/g·°C.
Plan Your Strategy

Assume that the following relationship holds:

\[ q_{\text{system}} = -q_{\text{surroundings}} \]

In this case, the system is the metal and the water in the calorimeter is the surroundings.

Therefore,

\[ q_m = -q_w \]

Both \( q_m \) and \( q_w \) involve a temperature change only, not a change in potential energy.

Therefore,

\[ q_m = m_mC_m\Delta T_m \]

and

\[ q_w = m_wc_w\Delta T_w \]

Since \( q_m = -q_w \), then

\[ m_mC_m\Delta T_m = -m_wc_w\Delta T_w \]

Rearrange to solve for \( c_m \).

\[ c_m = \frac{-m_wc_w\Delta T_w}{m_m\Delta T_m} \]

It is very important that you do not mix up the given information. For example, when solving for \( \Delta T_w \), the temperature change of the water, make sure that you only use variables for the water. You must use the initial temperature of the water, 19.8°C, not the initial temperature of the metal, 95.0°C. Also, remember that \( \Delta T = T_f - T_i \).

Act on Your Strategy

Solve for \( c_m \).

\[ c_m = \frac{-m_wc_w\Delta T_w}{m_m\Delta T_m} \]

\[ = \frac{-100.0 \text{ g}(4.184 \text{ J/g°C})(22.6°C - 19.8°C)}{(70.0 \text{ g})(22.6°C - 95.0°C)} \]

\[ = -0.23 \text{ J/g°C} \]

The specific heat capacity of the metal is 0.23 J/g°C.

Check Your Solution

The specific heat capacity of the metal is positive, and it has the correct units. The specific heat capacity of the metal is much smaller than the specific heat capacity of water. This makes sense, since the metal released the same amount of heat as the water absorbed, but the temperature change of the metal was much greater.

Practice Problems

1. A 92.0 g sample of a substance, with a temperature of 55°C, is placed in a large-scale polystyrene calorimeter. The calorimeter contains 1.00 kg of water at 20.0°C. The final temperature of the system is 25.2°C.

   (a) How much heat did the substance release? How much heat did the water absorb?
   (b) What is the specific heat capacity of the substance?
Using a Calorimeter to Determine the Enthalpy of a Reaction

A coffee-cup calorimeter is well-suited to determining the enthalpy changes of reactions in dilute aqueous solutions. The water in the calorimeter absorbs (or provides) the energy that is released (or absorbed) by a chemical reaction. When carrying out an experiment in a dilute solution, the solution itself absorbs or releases the energy. You can calculate the amount of energy that is absorbed or released by the solution using \[ q = m \cdot c \cdot \Delta T \].

The mass, \( m \), is the mass of the solution. The following Sample Problem shows how calorimetry can be used to determine the enthalpy change of a chemical reaction.

**Sample Problem**

**Determining the Enthalpy of a Chemical Reaction**

**Problem**

Copper(II) sulfate, \( \text{CuSO}_4 \), reacts with sodium hydroxide, \( \text{NaOH} \), in a double displacement reaction. A precipitate of copper(II) hydroxide, \( \text{Cu(OH)}_2 \), and aqueous sodium sulfate, \( \text{Na}_2\text{SO}_4 \), is produced.

\[
\text{CuSO}_4(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Cu(OH)}_2(\text{s}) + \text{Na}_2\text{SO}_4(\text{aq})
\]

50.0 mL of 0.300 mol/L \( \text{CuSO}_4 \) solution is mixed with an equal volume of 0.600 mol/L \( \text{NaOH} \). The initial temperature of both solutions is 21.4˚C. After mixing the solutions in the coffee-cup calorimeter, the highest temperature that is reached is 24.6˚C. Determine the enthalpy change of the reaction. Then write the thermochemical equation.

**What Is Required?**

You need to calculate \( \Delta H \) of the given reaction.
What Is Given?
You know the volume of each solution. You also know the initial temperature of each solution and the final temperature of the reaction mixture.

Volume of CuSO₄ solution, \( V_{\text{CuSO}_4} = 50.0 \, \text{mL} \)
Volume of NaOH solution, \( V_{\text{NaOH}} = 50.0 \, \text{mL} \)
Initial temperature, \( T_i = 21.4^\circ \text{C} \)
Final temperature, \( T_f = 24.6^\circ \text{C} \)

Plan Your Strategy

Step 1
Determine the total volume by adding the volumes of the two solutions. Determine the total mass of the reaction mixture, assuming a density of 1.00 g/mL (the density of water).

Step 2
Determine the number of moles of CuSO₄ and NaOH that reacted. If necessary, determine the limiting reactant.

Step 3
Assume that \( q_{\text{system}} = -q_{\text{surroundings}} \) or \( q_{\text{rxn}} = -q_{\text{solution}} \).

\[
q_{\text{rxn}} \cdot \Delta H_{\text{rxn}} = q_{\text{solution}} = m_{\text{solution}} \cdot c_{\text{solution}} \cdot \Delta T_{\text{solution}}
\]

Since \( q_{\text{rxn}} = -q_{\text{solution}} \) you can use the equations above to solve for \( \Delta H_{\text{rxn}} \) as follows.

\[
\frac{n \cdot \Delta H_{\text{rxn}}}{n} = -m_{\text{solution}} \cdot c_{\text{solution}} \cdot \Delta T_{\text{solution}}
\]

Step 4
Use your \( \Delta H \) to write the thermochemical equation for the reaction.

Act on Your Strategy

Step 1
The total volume of the reaction mixture is
\( 50.0 \, \text{mL} + 50.0 \, \text{mL} = 100.0 \, \text{mL} \)
The mass of the reaction mixture, assuming a density of 1.00 g/mL, is
\[
m = DV = (1.00 \, \text{g/mL})(100.0 \, \text{mL}) = 1.00 \times 10^2 \, \text{g}
\]

Step 2
Calculate the number of moles of CuSO₄ as follows.
\[
n = c \cdot V = (0.300 \, \text{mol/L})(50.0 \times 10^{-3} \, \text{L}) = 0.0150 \, \text{mol}
\]
Calculate the number of moles of NaOH.
\[
n \, \text{mol NaOH} = (0.600 \, \text{mol/L})(50.0 \times 10^{-3} \, \text{L}) = 0.0300 \, \text{mol}
\]
The reactants are present in stoichiometric amounts. (There is no limiting reactant.) Use 0.0150 mol in Step 3, since the stoichiometric coefficient of CuSO₄ in the equation is 1.
\[
\Delta H_{\text{rxn}} = -\frac{m_{\text{solution}} \cdot c_{\text{solution}} \cdot \Delta T_{\text{solution}}}{n}
\]
\[
= -\frac{(100 \text{ g})(4.184 \text{ J/g} \cdot ^\circ \text{C})(24.6^\circ \text{C} - 21.4^\circ \text{C})}{0.0150 \text{ mol}}
\]
\[
= -8.9 \times 10^4 \text{ J/mol}
\]
\[
= -89 \text{ kJ/mol}
\]

The enthalpy change of the reaction is \(-89 \text{ kJ/mol CuSO}_4\).

**Step 4** The thermochemical equation is
\[
\text{CuSO}_4(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Cu(OH)}_2(\text{s}) + \text{Na}_2\text{SO}_4(\text{aq}) + 89 \text{ kJ}
\]

**Check Your Solution**
The solution has the correct number of significant digits. The units are correct. You know that the reaction was exothermic, because the temperature of the solution increased. The calculated value for \(\Delta H\) is negative, which is correct for an exothermic reaction.

**Practice Problems**

5. A chemist wants to determine the enthalpy of neutralization for the following reaction.
\[
\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\ell)
\]
The chemist uses a coffee-cup calorimeter to neutralize completely 61.1 mL of 0.543 mol/L HCl(\text{aq}) with 42.6 mL of sufficiently concentrated NaOH(\text{aq}). The initial temperature of both solutions is 17.8\(^\circ\)C. After neutralization, the highest recorded temperature is 21.6\(^\circ\)C. Calculate the enthalpy of neutralization, in kJ/mol of HCl. Assume that the density of both solutions is 1.00 g/mL.

6. A chemist wants to determine empirically the enthalpy change for the following reaction.
\[
\text{Mg}(s) + 2\text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2(\text{g})
\]
The chemist uses a coffee-cup calorimeter to react 0.50 g of Mg ribbon with 100 mL of 1.00 mol/L HCl(\text{aq}). The initial temperature of the HCl(\text{aq}) is 20.4\(^\circ\)C. After neutralization, the highest recorded temperature is 40.7\(^\circ\)C.

(a) Calculate the enthalpy change, in kJ/mol of Mg, for the reaction.

(b) State any assumptions that you made in order to determine the enthalpy change.

7. Nitric acid is neutralized with potassium hydroxide in the following reaction.
\[
\text{HNO}_3(\text{aq}) + \text{KOH}(\text{aq}) \rightarrow \text{KNO}_3(\text{aq}) + \text{H}_2\text{O}(\ell)
\]
\[
\Delta H_{\text{rxn}} = -53.4 \text{ kJ/mol}
\]
55.0 mL of 1.30 mol/L solutions of both reactants, at 21.4\(^\circ\)C, are mixed in a calorimeter. What is the final temperature of the mixture? Assume that the density of both solutions is 1.00 g/mL. Also assume that the specific heat capacity of both solutions is the same as the specific heat capacity of water. No heat is lost to the calorimeter itself.

In the following investigation, you will construct a coffee-cup calorimeter and use it to determine the enthalpy of a neutralization reaction.
Determining the Enthalpy of a Neutralization Reaction

The neutralization of hydrochloric acid with sodium hydroxide solution is represented by the following equation.

\[ \text{HCl}_{(aq)} + \text{NaOH}_{(aq)} \rightarrow \text{NaCl}_{(aq)} + \text{H}_2\text{O}_{(l)} \]

Using a coffee-cup calorimeter, you will determine the enthalpy change for this reaction.

**Question**

What is the enthalpy of neutralization for hydrochloric acid and sodium hydroxide solution?

**Prediction**

Will the neutralization reaction be endothermic or exothermic? Record your prediction, and give reasons.

**Safety Precautions**

If you get any hydrochloric acid or sodium hydroxide solution on your skin, flush your skin with plenty of cold water.

**Materials**

- 100 mL graduated cylinder
- 400 mL beaker
- 2 polystyrene cups that are the same size
- polystyrene lid
- thermometer
- stirring rod
- 1.00 mol/L \( \text{HCl}_{(aq)} \)
- 1.00 mol/L \( \text{NaOH}_{(aq)} \)

**Procedure**

1. Your teacher will allow the hydrochloric acid and sodium hydroxide solution to come to room temperature overnight.
2. Read the rest of this Procedure carefully before you continue. Set up a graph to record your temperature observations.
3. Build a coffee-cup calorimeter, using the diagram above as a guide. You will need to make two holes in the lid—one for the thermometer and one for the stirring rod. The holes should be as small as possible to minimize heat loss to the surroundings.
4. Rinse the graduated cylinder with a small quantity of 1.00 mol/L \( \text{NaOH}_{(aq)} \). Use the cylinder to add 50.0 mL of 1.00 mol/L \( \text{NaOH}_{(aq)} \) to the calorimeter. Record the initial temperature of the \( \text{NaOH}_{(aq)} \). (This will also represent the initial temperature of the \( \text{HCl}_{(aq)} \).) **CAUTION** The \( \text{NaOH}_{(aq)} \) can burn your skin.
5. Rinse the graduated cylinder with tap water. Then rinse it with a small quantity of 1.00 mol/L HCl\(_{(aq)}\). Quickly and carefully, add 50.0 mL of 1.00 mol/L HCl\(_{(aq)}\) to the NaOH\(_{(aq)}\) in the calorimeter. **CAUTION** The HCl\(_{(aq)}\) can burn your skin.

6. Cover the calorimeter. Record the temperature every 30 s, stirring gently and continuously.

7. When the temperature levels off, record the final temperature, \(T_f\).

8. If time permits, repeat steps 4 to 7.

**Analysis**

1. Determine the amount of heat that is absorbed by the solution in the calorimeter.

2. Use the following equation to determine the amount of heat that is released by the reaction:

   \[-q_{\text{reaction}} = q_{\text{solution}}\]

3. Determine the number of moles of HCl\(_{(aq)}\) and NaOH\(_{(aq)}\) that were involved in the reaction.

4. Use your knowledge of solutions to explain what happens during a neutralization reaction. Use equations in your answer. Was heat released or absorbed during the neutralization reaction? Explain your answer.

**Conclusion**

5. Use your results to determine the enthalpy change of the neutralization reaction, in kJ/mol of NaOH. Write the thermochemical equation for the neutralization reaction.

**Applications**

6. When an acid gets on your skin, why must you flush the area with plenty of water rather than neutralizing the acid with a base?

7. Suppose that you had added solid sodium hydroxide pellets to hydrochloric acid, instead of adding hydrochloric acid to sodium hydroxide solution?

---

(a) Do you think you would have obtained a different enthalpy change?

(b) Would the enthalpy change have been higher or lower?

(c) How can you test your answer? Design an investigation, and carry it out with the permission of your teacher.

(d) What change do you need to make to the thermochemical equation if you perform the investigation using solid sodium hydroxide?

8. In this investigation, you assumed that the heat capacity of your calorimeter was 0 J/°C.

(a) Design an investigation to determine the actual heat capacity of your coffee-cup calorimeter, \(C_{\text{calorimeter}}\). Include equations for any calculations you will need to do. If time permits, have your teacher approve your procedure and carry out the investigation. **Hint:** If you mix hot and cold water together and no heat is absorbed by the calorimeter itself, then the amount of heat absorbed by the cold water should equal the amount of heat released by the hot water. If more heat is released by the hot water than is absorbed by the cold water, the difference must be absorbed by the calorimeter.

(b) Include the heat capacity of your calorimeter in your calculations for \(\Delta H_{\text{neutralization}}\). Use the following equation:

\[-q_{\text{reaction}} = (m_{\text{solution}} \cdot c_{\text{solution}} \cdot \Delta T) + (C_{\text{calorimeter}} \cdot \Delta T)\]

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www.mcgrawhill.ca/links/atlchemistry

If you have access to probeware, go to the website above for a probeware investigation related to this investigation.
Determining Enthalpy of Solution

In section 16.2, you learned that some substances dissolve exothermically, and some substances dissolve endothermically. In the following ExpressLab, use a coffee-cup calorimeter to determine the molar enthalpy of solution for two different substances.

ExpressLab

The Energy of Dissolving

In this lab you will measure the heat of solution of two solids.

Safety Precautions

- NaOH and KOH can burn skin. If you accidentally spill NaOH or KOH on your skin, wash immediately with copious amounts of cold water.

Materials

- balance and beakers or weigh boats
- polystyrene calorimeter
- thermometer and stirring rod
- distilled water
- 2 pairs of solid compounds:
  - ammonium nitrate and potassium hydroxide
  - potassium nitrate and sodium hydroxide

Procedure

1. Choose one pair of chemicals from the list.
2. For each of the two chemicals, calculate the mass required to make 100.0 mL of a 1.00 mol/L aqueous solution.
3. Measure the required mass of one of the chemicals in a beaker or a weigh boat.
4. Measure exactly 100 g of distilled water directly into your calorimeter.
5. Measure the initial temperature of the water.
6. Pour one of the chemicals into the calorimeter. Put the lid on the calorimeter.
7. Stir the solution. Record the temperature until there is a maximum temperature change.
8. Dispose of the chemical as directed by your teacher. Clean your apparatus.
9. Repeat steps 3 to 8, using the other chemical.

Analysis

1. For each chemical you used, calculate the molar enthalpy of solution.
2. For each chemical you used, write a thermochemical equation and draw an enthalpy diagram to represent the dissolution process.
3. Which chemical dissolved endothermically? Which chemical dissolved exothermically?
4. As you learned in section 16.2, one type of cold pack contains a compartment of powder and a compartment of water. When the barrier between the two compartments is broken, the solid dissolves in the water and causes an energy change. Which of the two chemicals you tested could be used in this type of cold pack? Why?

Determining Enthalpy of Combustion

In chapter 16, you compared the molar enthalpies of combustion for short, straight-chain alkanes. In your everyday life, you may have encountered another type of hydrocarbon: paraffins. Paraffins are long-chain hydrocarbons. They are semisolid or solid at room temperature. One type of paraffin has been a household item for centuries—paraffin wax, \( \text{C}_{25}\text{H}_{52(s)} \), better known as candle wax. (See Figure 17.4)

Like other hydrocarbons, the paraffin wax in candles undergoes combustion when burned. It releases thermal energy in the process. In the following investigation, you will determine the molar enthalpy of combustion of paraffin.

Figure 17.4 Paraffin wax candles have been an important light source for hundreds of years.
The Enthalpy of Combustion of a Candle

You have probably gazed into the flame of a candle without thinking about chemistry! Now, however, you will use the combustion of candle wax to gain insight into the measurement of heat changes. You will also evaluate the design of this investigation and make suggestions for improvement.

**Question**

What is the molar enthalpy of combustion of candle wax?

**Prediction**

Will the enthalpy of combustion of candle wax be greater or less than the enthalpy of combustion of other fuels, such as propane and butane? Record your prediction, and give reasons.

**Safety Precautions**

- Tie back long hair and secure any loose clothing. Before you light the candle, check that there are no flammable solvents nearby.

**Materials**

- balance
- calorimeter apparatus (see the diagram to the right)
- thermometer
- stirring rod
- matches
- water
- candle

**Procedure**

1. Burn the candle to melt some wax. Use the wax to attach the candle to the smaller can lid. Blow out the candle.

2. Set up the apparatus as shown in the diagram, but do not include the large can yet. Adjust the ring stand so that the small can is about 5 cm above the wick of the candle. The tip of the flame should just touch the bottom of the small can.

3. Measure the mass of the candle and the lid.

4. Measure the mass of the small can. Measure the mass of the hanger.

5. Place the candle inside the large can on the retort stand.

6. Fill the small can about two-thirds full of cold water (10°C to 15°C). You will measure the mass of the water later.
7. Stir the water in the can. Measure the temperature of the water.

8. Light the candle. Quickly place the small can in position over the candle. **CAUTION** Be careful of the open flame.

9. Continue stirring. Monitor the temperature of the water until it has reached 10°C to 15°C above room temperature.

10. Blow out the candle. Continue to stir. Monitor the temperature until you observe no further change.

11. Record the final temperature of the water. Examine the bottom of the small can, and record your observations.

12. Measure the mass of the small can and the water.

13. Measure the mass of the candle, lid, and any drops of candle wax.

**Analysis**

1. (a) Calculate the mass of the water.
   (b) Calculate the mass of candle wax that burned.

2. Calculate the heat that was absorbed by the water.

**Conclusions**

3. (a) Assume that the candle wax is pure paraffin wax, \( \text{C}_{25}\text{H}_{52(s)} \). Calculate the molar enthalpy of combustion of paraffin wax.
   (b) Write a balanced thermochemical equation for the complete combustion of paraffin wax.
   (c) Draw an enthalpy diagram showing the complete combustion of paraffin wax.

4. (a) List some possible sources of error that may have affected the results you obtained.
   (b) Evaluate the design and the procedure of this investigation. Consider the apparatus, the combustion, and anything else you can think of. Make suggestions for possible improvements.

5. What if soot (unburned carbon) accumulated on the bottom of the small can? Would this produce a greater or a lower heat value than the value you expected? Explain.

6. The aluminum can absorbs some of the heat from the combustion reaction.
   (a) Repeat your determination of the molar enthalpy of combustion of paraffin as shown:
   \[ q_{\text{system}} = -(q_{\text{water}} + q_{\text{aluminum}}) \]
   \[ q_{\text{system}} = n \cdot \Delta H_{\text{comb}} \]
   (b) Is your result from 6. (a) more accurate than your result from 3. (a)? Is it more precise? Explain your answer.
Bomb Calorimetry

In Investigation 17-B, you constructed a calorimeter to determine the enthalpy of combustion of a paraffin wax. Your calorimeter was more flame-resistant than a coffee-cup calorimeter, but some heat was transferred to the air and the metal containers. To measure precisely and accurately the enthalpy changes of combustion reactions, chemists use a calorimeter called a bomb calorimeter, shown in Figures 17.5. and 17.6. A bomb calorimeter measures enthalpy changes during combustion reactions at a constant volume.

The bomb calorimeter works on the same general principle as the polystyrene calorimeter. The reaction, however, takes place inside an inner metal chamber, called a “bomb.” This “bomb” contains pure oxygen. The reactants are ignited using an electric coil. A known quantity of water surrounds the bomb and absorbs the energy that is released by the reaction.

A bomb calorimeter has many more parts than a polystyrene calorimeter. All of these parts can absorb or release small quantities of energy. Therefore, you cannot assume that the heat lost to the calorimeter is small enough to be negligible. To obtain precise heat measurements, you must know or find out the heat capacity of the bomb calorimeter. The heat capacity of a calorimeter takes into account the heat that all parts of the calorimeter can lose or gain. (See Figure 17.7)

\[ C_{\text{total}} = C_{\text{water}} + C_{\text{thermometer}} + C_{\text{stirrer}} + C_{\text{container}} \]

Figure 17.6 Figure 17.6 shows a chemist preparing a sample for testing in a bomb calorimeter.

Figure 17.7 The heat capacity of the calorimeter incorporates the heat capacity of all its components.
A bomb calorimeter is calibrated for a constant mass of water. Since the mass of the other parts remains constant, there is no need for mass units in the heat capacity value. The manufacturer usually includes the heat capacity value in the instructions for the calorimeter.

Heat calculations must be done differently when the heat capacity of a calorimeter is included. The next Sample Problem illustrates how to use the heat capacity of a calorimeter in your calculations.

---

**Sample Problem**

**Calculating Heat Change in a Bomb Calorimeter**

**Problem**

A laboratory decided to test the energy content of peanut butter. A technician placed a 16.0 g sample of peanut butter in the steel bomb of a calorimeter, along with sufficient oxygen to burn the sample completely. She ignited the mixture and took heat measurements. The heat capacity of the calorimeter was calibrated at 8.28 kJ/˚C. During the experiment, the temperature increased by 50.5˚C.

(a) What was the thermal energy released by the sample of peanut butter?

(b) What is the enthalpy of combustion of the peanut butter per gram of sample?

**What Is Required?**

(a) You need to calculate the heat \( q_{\text{sample}} \) lost by the peanut butter.

(b) You need to calculate the enthalpy change per gram of peanut butter.

**What Is Given?**

You know the mass of the peanut butter, the heat capacity of the calorimeter, and the change in temperature of the system.

- Mass of peanut butter \( m \) = 16.0 g
- Heat capacity of calorimeter \( C \) = 8.28 kJ/˚C
- Change in temperature \( \Delta T \) = 50.5˚C

**Plan Your Strategy**

(a) The heat capacity of the calorimeter takes into account the specific heat capacities and masses of all the parts of the calorimeter. Calculate the heat change of the calorimeter, \( q_{\text{cal}} \), using the equation

\[
q_{\text{cal}} = C \Delta T
\]

**Note:** \( C \) is the heat capacity of the calorimeter in J/˚C or kJ/˚C. It replaces the \( m \) and \( c \) in other calculations involving specific heat capacity.

First calculate the heat gained by the calorimeter. When the peanut butter burns, the heat released by the peanut butter sample equals the heat absorbed by the calorimeter.

\[
q_{\text{sample}} = -q_{\text{cal}}
\]

(b) To find the heat of combustion per gram, divide the heat by the mass of the sample.
Act on Your Strategy

(a) \[ q_{\text{cal}} = C \Delta T \]
\[ = (8.28\text{kJ/}^\circ\text{C})(50.5^\circ\text{C}) \]
\[ = 418.14(\text{kJ}/\ell)(\ell) \]
\[ = 418 \text{ kJ} \]

The calorimeter gained 418 kJ of thermal energy.

\[ q_{\text{sample}} = -q_{\text{cal}} \]
\[ = -418 \text{ kJ} \]

The sample of peanut butter released 418 kJ of thermal energy.

(b) Heat of combustion per gram
\[ = \frac{q_{\text{sample}}}{m} \]
\[ = \frac{-418 \text{ kJ}}{16.0 \text{ g}} \]
\[ = -26.2 \text{ kJ/g} \]

The heat of combustion per gram of peanut butter is \(-26.2 \text{ kJ/g}\).

Check Your Solution

Heat was released by the peanut butter, so the heat value is negative.

Practice Problems

8. Use the heat equation for a calibrated calorimeter, \( q_{\text{cal}} = C \Delta T \). Recall that \( \Delta T = T_f - T_i \). Solve for the following quantities.

(a) \( C \)  
(b) \( \Delta T \)  
(c) \( T_f \) (in terms of \( C \), \( \Delta T \), and \( T_i \))  
(d) \( T_i \) (in terms of \( C \), \( \Delta T \), and \( T_f \))

9. A lab technician places a 5.00 g food sample into a bomb calorimeter that is calibrated at 9.23 kJ/°C. The initial temperature of the calorimeter system is 21.0°C. After burning the food, the final temperature of the system is 32.0°C. What is the heat of combustion of the food in kJ/g?

10. A scientist places a small block of ice in an uncalibrated bomb calorimeter. The ice melts, gaining 10.5 kJ (10.5 × 10³ J) of heat. The liquid water undergoes a temperature change of 25.0°C. The calorimeter undergoes a temperature change of 1.2°C.

(a) What mass of ice was added to the calorimeter? (Use the heat capacity of liquid water.)

(b) What is the calibration of the bomb calorimeter in kJ/°C?

Section Summary

In this section, you measured the enthalpy changes of several processes using constant-pressure calorimeters. You learned how to carry out calculations involving data obtained from a bomb calorimeter. You determined the enthalpy associated with a neutralization reaction, a dissolution, and the combustion of a hydrocarbon. In section 17.2, you will learn several methods for calculating enthalpies of reaction based on tabulated thermochemical data. This skill will allow you to determine enthalpies of reaction without carrying out experiments.
List two characteristics of a calorimeter that are necessary for successful heat measurement.

A calorimeter is calibrated at 7.61 kJ/˚C. When a sample of coal is burned in the calorimeter, the temperature increases by 5.23˚C. How much heat was lost by the coal?

A reaction in a calorimeter causes 150 g of water to decrease in temperature by 5.0˚C. What is the kinetic energy change of the water?

What properties of polystyrene make it a suitable material for a constant-pressure calorimeter?

Suppose that you use concentrated reactant solutions in an experiment with a coffee-cup calorimeter. Should you make the same assumptions that you did when you used dilute solutions? Explain.

Concentrated sulfuric acid can be diluted by adding it to water. The reaction is extremely exothermic. In this question, you will design an experiment to measure the enthalpy change (in kJ/mol) for the dilution of concentrated sulfuric acid. Assume that you have access to any equipment in your school’s chemistry laboratory. Do not carry out this experiment.

(a) State the equipment and chemicals that you need.
(b) Write a step-by-step procedure.
(c) Set up an appropriate data table.
(d) State any information that you need.
(e) State any simplifying assumptions that you will make.

A chemist mixes 100.0 mL of 0.050 mol/L aqueous potassium hydroxide with 100.0 mL of 0.050 mol/L nitric acid in a coffee-cup calorimeter. The temperature of the reactants is 21.01˚C. The temperature of the products is 21.34˚C.

(a) Determine the molar enthalpy of neutralization of KOH\(_{aq}\) with HNO\(_3\)\(_{aq}\)
(b) Write a thermochemical equation and draw an enthalpy diagram for the reaction.
(c) If you performed this investigation, how would you change the procedure? Explain your answer.

From experience, you know that you produce significantly more heat when you are exercising than when you are resting. Scientists can study the heat that is produced by human metabolism reactions using a “human calorimeter.” Based on what you know about calorimetry, how would you design a human calorimeter? What variables would you control and study in an investigation using your calorimeter? Write a brief proposal outlining the design of your human calorimeter and the experimental approach you would take.
In section 17.1, you learned how to use a coffee-cup calorimeter to determine the heat that was released or absorbed in a chemical reaction. Coffee-cup calorimeters are generally used only for dilute aqueous solutions. There are many non-aqueous chemical reactions, however. There are also many reactions that release so much energy they are not safe to perform using a coffee-cup calorimeter. Imagine trying to determine the enthalpy of reaction for the detonation of nitroglycerin, an unstable and powerfully explosive compound. Furthermore, there are reactions that occur too slowly for the calorimetric method to be practical.

Chemists can determine the enthalpy change of any reaction using an important law, known as Hess’s law of heat summation. This law states that the enthalpy change of a physical or chemical process depends only on the beginning conditions (reactants) and the end conditions (products). The enthalpy change is independent of the pathway of the process and the number of intermediate steps in the process. It is the sum of the enthalpy changes of all the individual steps that make up the process.

For example, carbon and oxygen can form carbon dioxide via two pathways.

1. Carbon can react with oxygen to form carbon monoxide. The carbon monoxide then reacts with oxygen to produce carbon dioxide. The two equations below represent this pathway.

   \[ \text{C}(s) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}(g) \quad \Delta H^\circ = -110.5 \text{ kJ/mol} \]
   \[ \text{CO}(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta H^\circ = -283.0 \text{ kJ/mol} \]

2. Carbon can also react with oxygen to produce carbon dioxide directly.

   \[ \text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta H^\circ = -393.5 \text{ kJ/mol} \]

In both cases, the net result is that one mole of carbon reacts with one mole of oxygen to produce one mole of carbon dioxide. (In the first pathway, all the carbon monoxide that is produced reacts with oxygen to form carbon dioxide.) Notice that the sum of the enthalpy changes for the first pathway is the same as the enthalpy change for the second pathway.

Examine Figure 17.8 to see how to represent the two pathways using one enthalpy diagram.

**Figure 17.8** Carbon dioxide can be formed by the reaction of oxygen with carbon to form carbon monoxide, followed by the reaction of carbon monoxide with oxygen. Carbon dioxide can also be formed directly from carbon and oxygen. No matter which pathway is used, the enthalpy change of the reaction is the same.
One way to think about Hess’s law is to compare the energy changes that occur in a chemical reaction with the changes in the potential energy of a cyclist on hilly terrain. This comparison is shown in Figure 17.9.

Hess’s Law is valid because enthalpy is considered to be a state function. A state function is a property of a system that is determined only by the current conditions of the system. It is not dependent on the path taken by the system to reach those conditions. As you have seen, there are several different ways for a given change to occur. If the beginning and end conditions (e.g., substances present, temperature, pressure) of a system are the same, however, the enthalpy change is the same, regardless of the steps taken in between.

Hess’s law allows you to determine the energy of a chemical reaction without directly measuring it. In this section, you will examine two ways in which you can use Hess’s law to calculate the enthalpy change of a chemical reaction:

1. by combining chemical equations algebraically
2. by using the enthalpy of formation

You will also learn how to use bond energies and Hess’s law to estimate the enthalpy change of a chemical reaction.

**Combining Chemical Equations Algebraically**

According to Hess’s law, the pathway that is taken in a chemical reaction has no effect on the enthalpy change of the reaction. How can you use Hess’s law to calculate the enthalpy change of a reaction? One way is to add equations for reactions with known enthalpy changes, so that their net result is the reaction you are interested in.

For example, you can combine thermochemical equations (1) and (2) below to find the enthalpy change for the decomposition of hydrogen peroxide, equation (3).

\[
\begin{align*}
(1) \quad & \text{H}_2\text{O}_2(\ell) \rightarrow \text{H}_2(g) + \text{O}_2(g) \quad \Delta H^\circ = +188 \text{ kJ/mol} \\
(2) \quad & \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H^\circ = -286 \text{ kJ/mol} \\
(3) \quad & \text{H}_2\text{O}_2(\ell) \rightarrow \text{H}_2\text{O}(l) + \frac{1}{2} \text{O}_2(g) \quad \Delta H^\circ = ?
\end{align*}
\]
Carefully examine equation (3), the target equation. Notice that \( \text{H}_2\text{O}_2 \) is on the left (reactant) side, while \( \text{H}_2\text{O} \) and \( \frac{1}{2}\text{O}_2 \) are on the right (product) side. Now examine equations (1) and (2). Notice which sides of the equations \( \text{H}_2\text{O}_2 \) and \( \text{H}_2\text{O} \) are on. They are on the correct sides, based on equation (3). Also notice that hydrogen must cancel out when equations (1) and (2) are added. Since there is one mole of \( \text{H}_2(g) \) on the product side of equation (1) and one mole of \( \text{H}_2(g) \) on the reactant side of equation (2), these two terms cancel. Set up equations (1) and (2) as shown below. Add the products and the reactants. Then cancel any substances that appear on opposite sides.

\[
\begin{align*}
(1) & \quad \text{H}_2\text{O}_2(\text{l}) & \rightarrow & \text{H}_2(g) + \text{O}_2(g) & \Delta H^\circ = +188 \text{ kJ/mol} \\
(2) & \quad \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) & \rightarrow & \text{H}_2\text{O}(\text{l}) & \Delta H^\circ = -286 \text{ kJ/mol} \\
\text{H}_2\text{O}_2(\text{l}) + \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) & \rightarrow & \text{H}_2\text{O}(\text{l}) + \text{O}_2(g) + \text{H}_2(g) & \Delta H^\circ = ? \\
\text{or} & \quad \text{H}_2\text{O}_2(\text{l}) & \rightarrow & \text{H}_2\text{O}(\text{l}) + \frac{1}{2}\text{O}_2(g) & \Delta H^\circ = ?
\end{align*}
\]

Equations (1) and (2) add to give equation (3). Therefore, you know that the enthalpy change for equation (3) is the sum of the enthalpy changes of equations (1) and (2).

\[
\text{H}_2\text{O}_2(\text{l}) \rightarrow \text{H}_2\text{O}(\text{l}) + \frac{1}{2}\text{O}_2(g) \quad \Delta H^\circ = 188 \text{ kJ/mol} - 286 \text{ kJ/mol} = -98 \text{ kJ/mol}
\]

Figure 17.10 illustrates this combination of chemical equations in an enthalpy diagram.

In the previous example, you did not need to manipulate the two equations with known enthalpy changes. They added to the target equation as they were written. In many cases, however, you will need to manipulate the equations before adding them. There are two key ways in which you can manipulate an equation:

1. **Reverse an equation** so that the products become reactants and the reactants become products. When you reverse an equation, you need to change the sign of \( \Delta H^\circ \)(multiply by \(-1\)).

2. **Multiply each coefficient in an equation** by the same integer or fraction. When you multiply an equation, you need to multiply \( \Delta H^\circ \) by the same number.

Examine the following Sample Problem to see how to manipulate equations so that they add to the target equation. Try the problems that follow to practise finding the enthalpy change by adding equations.
Sample Problem

Using Hess’s Law to Determine Enthalpy Change

**Problem**

One of the methods that the steel industry uses to obtain metallic iron is to react iron(III) oxide, $\text{Fe}_2\text{O}_3$, with carbon monoxide, CO.

$$\text{Fe}_2\text{O}_3(s) + 3\text{CO}(g) \rightarrow 3\text{CO}_2(g) + 2\text{Fe}(s)$$

Determine the enthalpy change of this reaction, given the following equations and their enthalpy changes.

1. $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta H^\circ = -283.0 \text{ kJ/mol}$
2. $2\text{Fe}(s) + \frac{3}{2}\text{O}_2(g) \rightarrow \text{Fe}_2\text{O}_3 \quad \Delta H^\circ = -822.3 \text{ kJ/mol}$

**What Is Required?**

You need to find $\Delta H^\circ$ of the target reaction.

$$\text{Fe}_2\text{O}_3(s) + 3\text{CO}(g) \rightarrow 3\text{CO}_2(g) + 2\text{Fe}(s)$$

**What Is Given?**

You know the chemical equations for reactions (1) and (2), and their corresponding enthalpy changes.

**Plan Your Strategy**

**Step 1** Examine equations (1) and (2) to see how they compare with the target equation. Decide how you need to manipulate equations (1) and (2) so that they add to the target equation. (Reverse the equation, multiply the equation, do both, or do neither). Remember to adjust $\Delta H^\circ$ accordingly for each equation.

**Step 2** Write the manipulated equations so that their equation arrows line up. Add the reactants and products on each side, and cancel substances that appear on both sides.

**Step 3** Ensure that you have obtained the target equation. Add $\Delta H^\circ$ for the combined equations.

**Act on Your Strategy**

**Step 1** Equation (1) has CO as a reactant and CO$_2$ as a product, as does the target reaction. The stoichiometric coefficients do not match the coefficients in the target equation, however. To achieve the same coefficients, you must multiply equation (1) by 3.

Equation (2) has the required stoichiometric coefficients, but Fe and Fe$_2$O$_3$ are on the wrong sides of the equation. You need to reverse equation (2) and change the sign of $\Delta H^\circ$.

**Step 2** Multiply each equation as required, and add them.

$$3 \times (1) \quad 3\text{CO}(g) + \frac{3}{2}\text{O}_2(g) \rightarrow 3\text{CO}_2(g) \quad \Delta H^\circ = 3(-283.0 \text{ kJ/mol})$$

$$-1 \times (2) \quad 2\text{Fe}(s) + \frac{3}{2}\text{O}_2(g) \rightarrow \text{Fe}_2\text{O}_3 \quad \Delta H^\circ = -1(-822.3 \text{ kJ/mol})$$

$$\text{Fe}_2\text{O}_3(s) + \frac{3}{2}\text{O}_2(g) + 3\text{CO}(g) \rightarrow 3\text{CO}_2(g) + 2\text{Fe}(s) + \frac{3}{2}\text{O}_2(g)$$

or

$$\text{Fe}_2\text{O}_3(s) + 3\text{CO}(g) \rightarrow 3\text{CO}_2(g) + 2\text{Fe}(s)$$
Sometimes it is impractical to use a coffee-cup calorimeter to find the enthalpy change of a reaction. You can, however, use the calorimeter to find the enthalpy changes of other reactions, which you can combine to arrive at the desired reaction. In the following investigation, you will apply Hess’s law to determine the enthalpy change of a reaction.

Step 3  The desired equation is achieved. Therefore, you can calculate the enthalpy change of the target reaction by adding the heats of reaction for the manipulated equations.

\[ \Delta H' = 3(-283.0 \text{ kJ/mol}) + 824.2 \text{ kJ/mol} = -24.8 \text{ kJ/mol} \]

\[ \text{Fe}_2\text{O}_3(s) + 3\text{CO}(g) \rightarrow 3\text{CO}_2(g) + 2\text{Fe}(s) \quad \Delta H' = -24.8 \text{ kJ/mol} \]

Check Your Solution
The equations added correctly to the target equation. Check to ensure that you adjusted \( \Delta H' \) accordingly for each equation.

Practice Problems

11. Ethene, \( \text{C}_2\text{H}_4 \), reacts with water to form ethanol, \( \text{CH}_3\text{CH}_2\text{OH}(l) \).
\[ \text{C}_2\text{H}_4(g) + \text{H}_2\text{O}(l) \rightarrow \text{CH}_3\text{CH}_2\text{OH}(l) \]
Determine the enthalpy change of this reaction, given the following thermochemical equations.

(1) \( \text{CH}_3\text{CH}_2\text{OH}(l) + 3\text{O}_2(g) \rightarrow 3\text{H}_2\text{O}(l) + 2\text{CO}_2(g) \quad \Delta H' = -1367 \text{ kJ/mol} \)
(2) \( \text{C}_2\text{H}_4(g) + 3\text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l) + 2\text{CO}_2(g) \quad \Delta H' = -1411 \text{ kJ/mol} \)

12. A typical automobile engine uses a lead-acid battery. During discharge, the following chemical reaction takes place.
\[ \text{Pb}(s) + \text{PbO}_2(s) + 2\text{H}_2\text{SO}_4(l) \rightarrow 2\text{PbSO}_4(aq) + 2\text{H}_2\text{O}(l) \]
Determine the enthalpy change of this reaction, given the following equations.

(1) \( \text{Pb}(s) + \text{PbO}_2(s) + 2\text{SO}_3(g) \rightarrow 2\text{PbSO}_4(s) \quad \Delta H' = -775 \text{ kJ/mol} \)
(2) \( 3\text{O}_3(g) + \text{H}_2\text{O}(l) \rightarrow 2\text{H}_2\text{SO}_4(l) \quad \Delta H' = -133 \text{ kJ/mol} \)

13. Mixing household cleansers can result in the production of hydrogen chloride gas, \( \text{HCl(g)} \). Not only is this gas dangerous in its own right, but it also reacts with oxygen to form chlorine gas and water vapour.
\[ 4\text{HCl(g)} + \text{O}_2(g) \rightarrow 2\text{Cl}_2(g) + 2\text{H}_2\text{O}(g) \]
Determine the enthalpy change of this reaction, given the following equations.

(1) \( \text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{HCl}(g) \quad \Delta H' = -185 \text{ kJ/mol} \)
(2) \( \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H' = -285.8 \text{ kJ/mol} \)
(3) \( \text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H' = -40.7 \text{ kJ/mol} \)

14. Calculate the enthalpy change of the following reaction between nitrogen gas and oxygen gas, given thermochemical equations (1), (2), and (3).
\[ 2\text{N}_2(g) + 5\text{O}_2(g) \rightarrow 2\text{N}_2\text{O}_5(g) \]

(1) \( 2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l) \quad \Delta H' = -572 \text{ kJ/mol} \)
(2) \( \text{N}_2\text{O}_5(g) + \text{H}_2\text{O}(l) \rightarrow 2\text{HNO}_3(l) \quad \Delta H' = -77 \text{ kJ/mol} \)
(3) \( \frac{1}{2}\text{N}_2(g) + \frac{3}{2}\text{O}_2(g) + \frac{1}{2}\text{H}_2(g) \rightarrow \text{HNO}_3(l) \quad \Delta H' = -174 \text{ kJ/mol} \)
Hess’s Law and the Enthalpy of Combustion of Magnesium

Magnesium ribbon burns in air in a highly exothermic combustion reaction. (See equation (1).) A very bright flame accompanies the production of magnesium oxide, as shown in the photograph below. It is impractical and dangerous to use a coffee-cup calorimeter to determine the enthalpy change for this reaction.

\[
\text{(1) } \text{Mg}(s) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{MgO}(s)
\]

Instead, you will determine the enthalpy changes for two other reactions (equations (2) and (3) below). You will use these enthalpy changes, along with the known enthalpy change for another reaction (equation (4) below), to determine the enthalpy change for the combustion of magnesium.

\[
\text{(2) } \text{MgO}(s) + 2\text{HCl}(aq) \rightarrow \text{MgCl}_2(aq) + \text{H}_2\text{O}(l)
\]

\[
\text{(3) } \text{Mg}(s) + 2\text{HCl}(aq) \rightarrow \text{MgCl}_2(aq) + \text{H}_2(g)
\]

\[
\text{(4) } \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) + 285.8 \text{ kJ}
\]

Notice that equations (2) and (3) occur in aqueous solution. You can use a coffee-cup calorimeter to determine the enthalpy changes for these reactions. Equation (4) represents the formation of water directly from its elements in their standard state.

Question

How can you use equations (2), (3), and (4) to determine the enthalpy change of equation (1)?

Prediction

Predict whether reactions (2) and (3) will be exothermic or endothermic.

Materials

- coffee cup calorimeter (2 nested coffee cups sitting in a 250 mL beaker)
- thermometer
- 100 mL graduated cylinder
- scoopula
- electronic balance
- MgO powder
- Mg ribbon (or Mg turnings)
- sandpaper or emery paper
- 1.00 mol/L HCl(aq)

Safety Precautions

- Hydrochloric acid is corrosive. Use care when handling it.
- Be careful not to inhale the magnesium oxide powder.

Procedure

Part 1 Determining \(\Delta H\) of Equation (2)

1. Read the Procedure for Part 1. Prepare a fully-labelled set of axes to graph your temperature observations.
2. Set up the coffee-cup calorimeter. (Refer to Investigation 5-A) Using a graduated cylinder, add 100 mL of 1.00 mol/L HCl(aq) to the calorimeter. \text{CAUTION} HCl(aq) can burn your skin.
3. Record the initial temperature, \(T_i\), of the HCl(aq), to the nearest tenth of a degree.
4. Find the mass of no more than 0.80 g of MgO. Record the exact mass.

5. Add the MgO powder to the calorimeter containing the HCl(aq). Swirl the solution gently, recording the temperature every 30 s until the highest temperature, $T_f$, is reached.

6. Dispose of the reaction solution as directed by your teacher.

**Part 2 Determining $\Delta H$ of Equation (3)**

1. Read the Procedure for Part 2. Prepare a fully-labelled set of axes to graph your temperature observations.

2. Using a graduated cylinder, add 100 mL of 1.00 mol/L HCl(aq) to the calorimeter.

3. Record the initial temperature, $T_i$, of the HCl(aq), to the nearest tenth of a degree.

4. If you are using magnesium ribbon (as opposed to turnings), sand the ribbon. Accurately determine the mass of no more than 0.50 g of magnesium. Record the exact mass.

5. Add the Mg to the calorimeter containing the HCl(aq). Swirl the solution gently, recording the temperature every 30 s until the highest temperature, $T_f$, is reached.

6. Dispose of the solution as directed by your teacher.

**Analysis**

1. Use the equation $q = m \cdot c \cdot \Delta T$ to determine the amount of heat that is released or absorbed by reactions (2) and (3). List any assumptions you make.

2. Convert the mass of MgO and Mg to moles. Calculate $\Delta H$ of each reaction in units of kJ/mol of MgO or Mg. Remember to put the proper sign (+ or −) in front of each $\Delta H$ value.

3. Algebraically combine equations (2), (3), and (4), and their corresponding $\Delta H$ values, to get equation (1) and $\Delta H$ of the combustion of magnesium.

4. (a) Your teacher will tell you the accepted value of $\Delta H$ of the combustion of magnesium. Based on the accepted value, calculate your percent error.

   (b) Suggest some sources of error in the investigation. In what ways could you improve the procedure?

5. What assumption did you make about the amount of heat that was lost to the calorimeter? Do you think that this is a fair assumption? Explain.

6. Why was it fair to assume that the hydrochloric acid solution has the same density and specific heat capacity as water?

**Conclusion**

7. Explain how you used Hess’s law of heat summation to determine $\Delta H$ of the combustion of magnesium. State the result you obtained for the thermochemical equation that corresponds to chemical equation (1).

**Extension**

8. Design an investigation to verify Hess’s law, using the following equations.

   (1) $\text{NaOH}(s) \rightarrow \text{Na}^+(aq) + \text{OH}^-(aq)$

   (2) $\text{NaOH}(aq) + \text{H}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq) + \text{H}_2\text{O}(l)$

   (3) $\text{Na}^+(aq) + \text{OH}^-(aq) + \text{H}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq) + \text{H}_2\text{O}(l)$

Assume that you have a coffee-cup calorimeter, solid NaOH, 1.00 mol/L HCl(aq), 1.00 mol/L NaOH(aq), and standard laboratory equipment. Write a step-by-step procedure for the investigation. Then outline a plan for analyzing your data. Be sure to include appropriate safety precautions. If time permits, obtain your teacher’s approval and carry out the investigation.
Using Standard Molar Enthalpies of Formation

You have learned how to add equations with known enthalpy changes to obtain the enthalpy change for another equation. This method can be time-consuming and difficult, however, because you need to find reactions with known enthalpy changes that will add to give your target equation. There is another way to use Hess’s law to find the enthalpy of an equation.

**Formation Reactions**

In section 16.2, you learned about molar enthalpies of formation. Recall that in a formation reaction, a substance is formed from elements in their standard states. Table 17.1 shows some standard molar enthalpies of formation for easy reference. You will find additional standard molar enthalpies of formation listed in Appendix E.

*By definition, the enthalpy of formation of an element in its standard state is zero.*

The standard state of an element is usually its most stable form under standard conditions. Standard conditions are 25°C and 100 kPa (close to room temperature and pressure). Therefore, the standard state of nitrogen is N\(_2\)(g). The standard state of magnesium is Mg(s).

Some elements exist in more than one form under standard conditions. For example, carbon can exist as either graphite or diamond, as shown in Figure 17.11. Graphite is defined as the standard state of carbon. Therefore, the standard molar enthalpy of formation of graphite carbon is 0 kJ/mol. The standard molar enthalpy of formation of diamond is 1.9 kJ/mol. Another example is oxygen, O\(_2\)(g). Oxygen also exists in the form of ozone, O\(_3\)(g), under standard conditions. The diatomic molecule is defined as the standard state of oxygen, however, because it is far more stable than ozone. Therefore, the standard molar enthalpy of formation of oxygen gas, O\(_2\)(g), is 0 kJ/mol. The standard molar enthalpy of formation of ozone is 143 kJ/mol.

Recall from section 16.2 that a formation equation shows the formation of one mole of a substance from its elements in their standard states. For example, the following equation shows the formation of liquid water from its elements under standard conditions.

\[
\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H_f = -285.8 \text{ kJ/mol}
\]

Try the following problems to practice writing formation equations.

---

**Table 17.1** Selected Standard Molar Enthalpies of Formation

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\Delta H_f) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_(g))</td>
<td>-110.5</td>
</tr>
<tr>
<td>CO(_2(g))</td>
<td>-393.5</td>
</tr>
<tr>
<td>CH(_4(g))</td>
<td>-74.6</td>
</tr>
<tr>
<td>CH(<em>3)OH(</em>(l))</td>
<td>-238.6</td>
</tr>
<tr>
<td>C(_2)H(_6(l))</td>
<td>-277.6</td>
</tr>
<tr>
<td>C(_6)H(_6(l))</td>
<td>+49.0</td>
</tr>
<tr>
<td>C(_6)H(_12)O(_6(s))</td>
<td>-1274.5</td>
</tr>
<tr>
<td>H(<em>2)O(</em>(l))</td>
<td>-285.8</td>
</tr>
<tr>
<td>H(<em>2)O(</em>(g))</td>
<td>-241.8</td>
</tr>
<tr>
<td>CaCl(_2(s))</td>
<td>-795.4</td>
</tr>
<tr>
<td>CaCO(_3(s))</td>
<td>-1206.9</td>
</tr>
<tr>
<td>NaCl(_(s))</td>
<td>-411.1</td>
</tr>
<tr>
<td>HCl(_(g))</td>
<td>-92.3</td>
</tr>
<tr>
<td>HCl(_(aq))</td>
<td>-167.5</td>
</tr>
</tbody>
</table>

Figure 17.11 Carbon can exist as graphite or diamond under standard conditions. It can, however, have only one standard state. Carbon’s standard state is graphite.
Calculating Enthalpy Changes

You can calculate the enthalpy change of a chemical reaction by adding the heats of formation of the products and subtracting the heats of formation of the reactants. The following equation can be used to determine the enthalpy change of a chemical reaction.

$$\Delta H^\circ_{\text{rxn}} = \Sigma(n\Delta H^\circ_{f \text{ products}}) - \Sigma(n\Delta H^\circ_{f \text{ reactants}})$$

In this equation, \( n \) represents the molar coefficient of each compound in the balanced chemical equation and \( \Sigma \) means “the sum of.”

As usual, you need to begin with a balanced chemical equation. If a given reactant or product has a molar coefficient that is not 1, you need to multiply its \( \Delta H^\circ_{f} \) by the same molar coefficient. This makes sense because the units of \( \Delta H^\circ_{f} \) are kJ/mol. Consider, for example, the complete combustion of methane, \( \text{CH}_4(g) \).

$$\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)$$

Using the equation for the enthalpy change, and the standard enthalpies of formation in Appendix E, you can calculate the enthalpy change of this reaction.

$$\Delta H^\circ_{\text{rxn}} = [(\Delta H^\circ_{f \text{ of CO}_2(g)}) + 2(\Delta H^\circ_{f \text{ of H}_2\text{O}(g)})] - [(\Delta H^\circ_{f \text{ of CH}_4(g)}) + 2(\Delta H^\circ_{f \text{ of O}_2(g)})]$$

Substitute the standard enthalpies of formation from Appendix E to get the following calculation.

$$\Delta H^\circ_{\text{rxn}} = [(-393.5 \text{ kJ/mol}) + 2(-241.8 \text{ kJ/mol})] - [(-74.8 \text{ kJ/mol}) + 2(0 \text{ kJ/mol})]$$

$$= -802.3 \text{ kJ/mol of CH}_4$$

Practice Problems

15. Write a thermochemical equation for the formation of each substance. Be sure to include the physical state of all the elements and compounds in the equation. You can find the standard enthalpy of formation of each substance in Appendix E.

   (a) CH\(_4\)
   (b) NaCl
   (c) MgO
   (d) CaCO\(_3\)

16. Liquid sulfuric acid has a very large negative standard enthalpy of formation (−814.0 kJ/mol). Write an equation to show the formation of liquid sulfuric acid. The standard state of sulfur is rhombic sulfur (S\(_{(s)}\)).

17. Write a thermochemical equation for the formation of gaseous cesium. The standard enthalpy of formation of Cs\(_{(g)}\) is 76.7 kJ/mol.

18. Solid phosphorus is found in two forms: white phosphorus (P\(_4\)) and red phosphorus (P). White phosphorus is the standard state.

   (a) The enthalpy of formation of red phosphorus is −17.6 kJ/mol. Write a thermochemical equation for the formation of red phosphorus.

   (b) 32.6 g of white phosphorus forms red phosphorus. What is the enthalpy change?
How does this method of adding heats of formation relate to Hess’s law? Consider the equations for the formation of each compound that is involved in the reaction of methane with oxygen.

\[
\begin{align*}
(1) & \quad H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) \quad \Delta H^f = -241.8 \text{ kJ} \\
(2) & \quad C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H^f = -393.5 \text{ kJ} \\
(3) & \quad C(s) + 2H_2(g) \rightarrow CH_4(g) \quad \Delta H^f = -74.6 \text{ kJ}
\end{align*}
\]

There is no equation for the formation of oxygen, because oxygen is an element in its standard state.

By adding the formation equations, you can obtain the target equation. Notice that you need to reverse equation (3) and multiply equation (1) by 2.

\[
\begin{align*}
& \quad 2 \times (1) \quad 2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \quad \Delta H^f = 2(-241.8) \text{ kJ} \\
& \quad (2) \quad C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H^f = -393.5 \text{ kJ} \\
& \quad -1 \times (3) \quad CH_4(g) \rightarrow C(s) + 2H_2(g) \quad \Delta H^f = -1(-74.6) \text{ kJ}
\end{align*}
\]

\[
\begin{align*}
\text{or} & \quad CH_4(g) + 2O_2(g) + C(s) + 2H_2(g) \rightarrow 2H_2O(g) + CO_2(g) + C(s) + 2H_2(g)
\end{align*}
\]

Add the manipulated \( \Delta H^f \) values:

\[
\Delta H^\text{rxn} = 2(-241.8) \text{ kJ} - 393.5 \text{ kJ} + 74.6 \text{ kJ} = -802.3 \text{ kJ}
\]

This value of \( \Delta H^\text{f} \) is the same as the value you obtained using \( \Delta H^f \) data. When you used the addition method, you performed the same operations on the enthalpies of formation before adding them. Therefore, using enthalpies of formation to determine the enthalpy of a reaction is consistent with Hess’s law. Figure 17.12 shows the general process for determining the enthalpy of a reaction from enthalpies of formation.

It is important to realize that, in most reactions, the reactants do not actually break down into their elements and then react to form products. Since there is extensive data about enthalpies of formation, however, it is useful to calculate the overall enthalpy change this way. Moreover, according to Hess’s law, the enthalpy change is the same, regardless of the pathway. Examine the following Sample Problem to see how to use enthalpies of formation to determine the enthalpy change of a reaction. Then try the Practice Problems that follow.
Sample Problem

Using Enthalpies of Formation

Problem
Iron(III) oxide reacts with carbon monoxide to produce elemental iron and carbon dioxide. Determine the enthalpy change of this reaction, using known enthalpies of formation.

Fe₂O₃(s) + 3CO(g) → 3CO₂(g) + 2Fe(s)

What Is Required?
You need to find $\Delta H^\circ$ of the given chemical equation, using $\Delta H^\circ$ data.

What Is Given?
From Appendix E, you can obtain the enthalpies of formation.

$\Delta H^\circ$ of Fe₂O₃(s) = −824.2 kJ/mol
$\Delta H^\circ$ of CO(g) = −110.5 kJ/mol
$\Delta H^\circ$ of CO₂(g) = −393.5 kJ/mol
$\Delta H^\circ$ of Fe(s) = 0 kJ/mol (by definition)

Plan Your Strategy
Multiply each $\Delta H^\circ$ value by its molar coefficient from the balanced chemical equation. Substitute into the following equation, and then solve.

$\Delta H^\circ = \Sigma (n\Delta H^\circ_{\text{products}}) - \Sigma (n\Delta H^\circ_{\text{reactants}})$

Act on Your Strategy

$\Delta H^\circ = \Sigma (n\Delta H^\circ_{\text{products}}) - \Sigma (n\Delta H^\circ_{\text{reactants}})$

$= [3(\Delta H^\circ_{\text{CO}_2}) + 2(\Delta H^\circ_{\text{Fe}})] - [(\Delta H^\circ_{\text{Fe}_2\text{O}_3}) + 3(\Delta H^\circ_{\text{CO}})]$

$= [(−393.5 \text{ kJ/mol}) + 2(0 \text{ kJ/mol})] - [(−824.2 \text{ kJ/mol}) + 3(−110.5 \text{ kJ/mol})]$

$= −24.8 \text{ kJ/mol}$

$\therefore \text{Fe}_2\text{O}_3(s) + 3\text{CO}(g) \rightarrow 3\text{CO}_2(g) + 2\text{Fe}(s) \quad \Delta H^\circ = −24.8 \text{ kJ/mol}$

Check Your Solution
A balanced chemical equation was used in the calculation. The number of significant digits is correct. The units are also correct.

Practice Problems

19. Hydrogen can be added to ethene, C₂H₄, to obtain ethane, C₂H₆.

C₂H₄(g) + H₂(g) → C₂H₆(g)

Show that the equations for the formation of ethene and ethane from their elements can be algebraically combined to obtain the equation for the addition of hydrogen to ethene.

20. Zinc sulfide reacts with oxygen gas to produce zinc oxide and sulfur dioxide.

2ZnS(s) + 3O₂(g) → 2ZnO(s) + 2SO₂(g)

Write the chemical equation for the formation of the indicated number of moles of each compound from its elements. Algebraically combine these equations to obtain the given equation.
Using Bond Energies

As you learned in Chapter 5, a chemical bond is caused by the attractions among the electrons and nuclei of two atoms. Breaking bonds is an exothermic process, while making bonds is an endothermic process.

A specific amount of energy is needed to break each type of bond. The energy that is required to break a bond is called bond energy. Bond energy is usually measured in kJ/mol. Table 17.2 reproduces the bond energy table you saw in Chapter 5, for easy reference. You will find a more comprehensive list of bond energies in Appendix E.

Every chemical reaction involves bond breaking and bond formation. Since there are different types of bonds in the reactants and products, the total energy required for bond breaking and the total energy released when new bonds form are different. The difference represents the energy change for the reaction.

To use bond energies to estimate the enthalpy change for a reaction, add together the total bond energies of the reactants. Bond breakage requires energy, so the sign will be positive. From the total, subtract the total bond energies of the products. If the reaction is endothermic, the result will be positive. If the reaction is exothermic, the result will be negative. The following equation summarizes the process for using bond energies to estimate the enthalpy of a reaction.

\[
\Delta H_{\text{rxn}} = \sum \text{bond energies (reactants)} - \sum \text{bond energies (products)}
\]

Since bond energies are only a way of estimating the energy of a reaction, your answer will not agree exactly with the recognized enthalpy of reaction. Bond energies are not exact; rather, they are averages.

For example, the table shows that 413 kJ of energy is needed to break one mole of C—H bonds. In fact, breaking a C—H bond in a methane molecule (CH₄) would require a slightly different quantity of energy than breaking a C—H bond in, say, a molecule of dichloromethane (CH₂Cl₂). The value 413 kJ/mol is a value that reflects the average of known bond energies for C—H bonds in different molecules.

The Sample Problem on the following page shows you how to estimate enthalpy changes of reactions using average bond energies. Try the Practice Problems that follow to compare how this method of estimating enthalpy change compares with the other methods you have learned in this chapter.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Average bond energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—C</td>
<td>346</td>
</tr>
<tr>
<td>C≡C</td>
<td>610</td>
</tr>
<tr>
<td>C≡C</td>
<td>835</td>
</tr>
<tr>
<td>Si—Si</td>
<td>226</td>
</tr>
<tr>
<td>C—H</td>
<td>413</td>
</tr>
<tr>
<td>Si—H</td>
<td>318</td>
</tr>
<tr>
<td>H—H</td>
<td>432</td>
</tr>
<tr>
<td>C—O</td>
<td>358</td>
</tr>
<tr>
<td>C≡O</td>
<td>745</td>
</tr>
<tr>
<td>O—H</td>
<td>467</td>
</tr>
<tr>
<td>O≡O</td>
<td>498</td>
</tr>
</tbody>
</table>
Problem
Consider the following familiar combustion reaction.
\[ \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \]

(a) Use bond energies to estimate the enthalpy change for the combustion of methane.

(b) Compare your answer to the accepted value for the combustion of methane.

What Is Required?
(a) You need to determine the difference in energy between bonds formed in the products and bonds formed in the products.

(b) You need to find the accepted value for the combustion of methane.

What Is Given?
You know the equation for the combustion reaction.
From Table 17.2, you know the following bond energies:
- C—H (413 kJ/mol)
- O=O (498 kJ/mol)
- C=O (745 kJ/mol)
- O—H (467 kJ/mol)

Plan Your Strategy
(a) Draw Lewis dot diagrams or structural diagrams to determine the number and type of bonds broken in the reactants and the number and type of bonds formed in the products.

Then use the following equation to estimate the enthalpy change for the reaction.

\[ \Delta H_{\text{rxn}} = \sum \text{bond energies (reactants)} - \sum \text{bond energies (products)} \]

(b) Look up the accepted value for the standard molar enthalpy of combustion of methane in Table 16.3.

Act on Your Strategy

\[
\begin{align*}
\text{reactants:} & \\
\text{bonds broken:} & \text{413 kJ/mol} + 498 \text{ kJ/mol} \\
\text{products:} & \text{bonds formed:} \\
& 745 \text{ kJ/mol} + 467 \text{ kJ/mol} \\
\text{CH}_4 + 2\text{O}_2 & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \\
\end{align*}
\]

Bonds broken

\[
\sum \text{bond energies (reactants)} = (4 \times \text{C} - \text{H}) + (2 \times \text{O} = \text{O})
\]

\[= (4 \times 413 \text{ kJ/mol}) + (2 \times 498 \text{ kJ/mol})
\]

\[= 2648 \text{ kJ/mol} \]
Bonds formed

\[ \sum \text{bond energies (products)} = (2 \times C = O) + (4 \times O - H) \]
\[ = (2 \times 745 \text{ kJ/mol}) + (4 \times 467 \text{ kJ/mol}) \]
\[ = 3358 \text{ kJ/mol} \]

Estimated enthalpy change

\[ \Delta H_{\text{rxn}} = \sum \text{bond energies (reactants)} - \sum \text{bond energies (products)} \]
\[ = 2648 \text{ kJ/mol} - 3358 \text{ kJ/mol} \]
\[ = -710 \text{ kJ/mol} \]

(b) From Table 16.3, the standard molar enthalpy of combustion of methane is \(-965.1 \text{ kJ/mol}\).

Check Your Solution

The sign of your answer is negative, which makes sense for a combustion reaction. You know the combustion of methane is exothermic. Your answer is reasonably close to the accepted value. It is not surprising that the values are somewhat different, since you are using average bond energies. Also, the accepted value you used assumes that the water product is liquid, which accounts for some of the deviation.

Practice Problems

23. Consider the following equation for the combustion of butane.

\[ \text{C}_4\text{H}_{10(g)} + \frac{13}{2} \text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 5\text{H}_2\text{O}(g) \]

(a) Use bond energies to estimate the enthalpy change for the reaction as written.

(b) Compare your answer to the accepted value using the standard molar enthalpy of combustion of butane.

24. Consider the following equation for the formation of ammonia from its elements.

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \]

(a) Use bond energies to estimate the enthalpy change for the reaction as written (see Appendix E).

(b) Compare your answer to the accepted value using the standard molar enthalpy of formation of ammonia (see Appendix E).

25. (a) Use bond energies to estimate the standard molar enthalpy of formation of gaseous water.

(b) Compare your answer to the accepted value.

26. Consider the following equation for the reaction of methane with chlorine.

\[ \text{CH}_4(g) + 3\text{Cl}_2(g) \rightarrow \text{CHCl}_3(g) + 3\text{HCl}(g) \]

(a) Use bond energies to estimate the enthalpy change for the reaction (see Appendix E).

(b) Use standard molar enthalpies to determine the enthalpy change for the reaction. (For gaseous CHCl\(_3\), \(\Delta H^\circ_f = -103.18 \text{ kJ/mol}\).) Compare your results from (a) and (b).
Section Summary
In this section, you learned how to calculate the enthalpy change of a chemical reaction using Hess’s law of heat summation. In the next section, you will see how the use of energy affects your lifestyle and the environment.

Explain why you need to reverse the sign of $\Delta H^\circ$ when you reverse an equation. Use an example in your answer.

In section 5.3, you learned two methods for calculating enthalpy changes using Hess’s law. If you had only this textbook as a reference, which method would allow you to calculate enthalpy changes for the largest number of reactions? Explain your answer.

In the early 1960s, Neil Bartlett, at the University of British Columbia, was the first person to synthesize compounds of the noble gas xenon. A number of noble gas compounds (such as XeF$_2$, XeF$_4$, XeF$_6$, and XeO$_3$) have since been synthesized. Consider the reaction of xenon difluoride with fluorine gas to produce xenon tetrafluoride.

$$\text{XeF}_2(g) + F_2(g) \rightarrow \text{XeF}_4(s)$$

Use the standard molar enthalpies of formation on the right to calculate the enthalpy change for this reaction.

Calculate the enthalpy change of the following reaction, given equations (1), (2), and (3).

$$2\text{H}_3\text{BO}_3(aq) \rightarrow \text{B}_2\text{O}_3(s) + 3\text{H}_2\text{O}(l)$$

1. $\text{H}_3\text{BO}_3(aq) \rightarrow \text{HBO}_2(aq) + \text{H}_2\text{O}(l) \quad \Delta H^\circ = -0.02 \text{ kJ/mol}$
2. $\text{H}_2\text{B}_4\text{O}_7(s) + \text{H}_2\text{O}(l) \rightarrow 4\text{HBO}_2(aq) \quad \Delta H^\circ = -11.3 \text{ kJ/mol}$
3. $\text{H}_2\text{B}_4\text{O}_7(s) \rightarrow 2\text{B}_2\text{O}_3(s) + \text{H}_2\text{O}(l) \quad \Delta H^\circ = 17.5 \text{ kJ/mol}$

The standard molar enthalpy of formation of calcium carbonate is $-1207.6 \text{ kJ/mol}$. Calculate the standard molar enthalpy of formation of calcium oxide, given the following equation.

$$\text{CaO}(g) + \text{CO}_2(g) \rightarrow \text{CaCO}_3(s) \quad \Delta H^\circ = -178.1 \text{ kJ/mol}$$

A classmate is having difficulty understanding Hess’s law. Write a few paragraphs to explain the law. Include examples, diagrams, and an original analogy.

The combustion of acetylene gas, C$_2$H$_2(g)$, is highly exothermic, as shown in Figure 17.13. The following thermochemical equation represents the complete combustion of acetylene.

$$\text{C}_2\text{H}_2(g) + \frac{5}{2}\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + \text{H}_2\text{O}(g) + 1259 \text{ kJ}$$

(a) Draw structural diagrams to represent each of the molecules involved in the reaction.

(b) Use the information provided and Table 17.2 to estimate the bond energy of the carbon-carbon triple bond in acetylene.

(c) Compare your result to the average bond energy for a carbon-carbon triple bond listed in Table 17.2.
In this section, you will:

- **compare** physical, chemical, and nuclear changes in terms of the species and the magnitude of energy involved.
- **identify** and **describe** sources of energy including present sources and possible new ones.
- **communicate** your understanding of the following terms: *non-renewable*, *renewable*, *greenhouse gases*, *global warming*, *sustainable development*, *risk*, *benefit*, *risk-benefit analysis*.

**Section Preview/Outcomes**

Compared to many other countries, Canada has huge energy requirements per capita. This energy demand is due in part to Canada’s vast size compared to its population, and the energy required for transportation of goods and people as a result. Also, Canada’s northern climate means that for many months of the year, Canadians rely on natural gas, oil, or electricity to heat their homes.

Where does the energy come from? As you can see in Figure 17.14, most of Canada’s energy comes from chemical processes such as the combustion of petroleum, coal, or natural gas. A significant portion of energy is also derived from nuclear processes. Although the energy changes associated with physical processes are not used directly to provide energy for Canadian society on a large scale, changes of state play an important role in generating electricity. Most power plants, whether nuclear or chemical, use the heat generated by exothermic processes to convert water into steam. The steam moves a turbine, which generates electrical energy.

**Energy from Physical, Chemical, and Nuclear Processes**

How does the energy from physical, chemical, and nuclear processes compare?

- Changes of state involve the breaking of intermolecular bonds. Physical changes such as changes of state usually involve tens of kJ/mol. When water vapour condenses, 40.7 kJ/mol of heat is released.

---

**Figure 17.14** The energy that Canadians use comes from a variety of sources. What factors account for the changes you can see in this graph? How do you think energy use has changed since 1996?
• Chemical changes involve the breaking of chemical bonds, which are stronger than intermolecular bonds. Chemical changes usually involve hundreds or thousands of kJ/mol. For example, the molar enthalpy of combustion of coal is about 3900 kJ/mol.

• Nuclear changes involve changes within the nuclei of atoms. These types of changes involve enormous changes in energy. Nuclear changes involve millions and billions of kJ/mol. For example, nuclear power plants derive their energy from the fusion (splitting) of uranium-235. The fusion of 1 mol of uranium-235 releases about $2.1 \times 10^{10}$ kJ, or 21 billion kilojoules!

Figure 17.15 shows the energy changes associated with various different processes.

**Energy and Efficiency**

When you think about energy efficiency, what comes to mind? You may think about taking the stairs instead of the elevator, choosing to drive a small car instead of a sport utility vehicle, or turning off lights when you are not using them. What, however, does efficiency really mean? How do you quantify it?

There are several ways to define efficiency. One general definition says that energy efficiency is the ability to produce a desired effect with minimum energy expenditure. For example, suppose that you want to bake a potato. You can use a microwave oven or a conventional oven. Both options achieve the same effect (baking the potato), but the first option uses less energy. According to the general definition above, using the microwave oven is more energy-efficient than using the conventional oven. The general definition is useful, but it is not quantitative.

Another definition of efficiency suggests that it is the ratio of useful energy produced to energy used in its production, expressed as a percent. This definition quantitatively compares input and output of energy. When you use it, however, you need to be clear about what you mean by “energy used.” Figure 17.16 shows factors to consider when calculating efficiency or analyzing efficiency data.

**Figure 17.15** The energy changes of physical, nuclear, and chemical processes vary widely. Solar energy, necessary for life on earth, comes from nuclear reactions that take place in the sun.

**Figure 17.16** Efficiency is expressed as a percent. Always specify what is included in the “energy used” part of the ratio.
It is often difficult to determine how much energy is used to produce useful energy. Often an efficiency percent only takes into account the “ideal” energy output of a system, based on the energy content of the fuel.

**Efficiency and Natural Gas**

When discussing the efficiency of a fuel, you need to specify how that fuel is being used. Consider, for example, natural gas. Natural gas is primarily methane. Therefore, you can estimate an ideal value for energy production using the enthalpy of combustion of methane.

\[
\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \quad \Delta H^\circ = -802 \text{ kJ}
\]

In other words, 16 g of methane produces 802 kJ of heat (under constant pressure conditions).

When natural gas is used directly in cooking devices, its efficiency can be as high as 90%. Thus, for every 16 g of gas burned, you get about 720 kJ (0.90 \times 802 \text{ kJ}) of usable energy as heat for cooking. This is a much higher fuel efficiency than you can get with appliances that use electrical energy produced in a power plant that runs on a fuel such as coal.

If natural gas is used to produce electricity in a power plant, however, the efficiency is much lower—around 37%. Why? The heat from the burning natural gas is used to boil water. The kinetic energy of the resulting steam is transformed to mechanical energy for turning a turbine. The turbine generates the electrical energy. Each of these steps has an associated efficiency that is less than 100%. Thus, at each step, the overall efficiency of the fuel decreases.

**Thinking About the Environment**

Efficiency is not the only criterion for selecting an energy source. Since the 1970s, society has become increasingly conscious of the impact of energy technologies on the environment.

Suppose that you want to analyze the environmental impact of an energy source. You can ask the following questions:

- **Are any waste products or by-products of the energy production process harmful to the environment?** For example, any process in which a hydrocarbon is burned produces carbon dioxide, a compound known to contribute to global warming. Any combustion process provides the heat required to form oxides of nitrogen from nitrogen gas. Nitrogen oxides contribute to acid precipitation.

- **Is obtaining or harnessing the fuel harmful to the environment?** For example, oil wells and strip coal mines destroy habitat. Natural gas pipelines, shown in Figure 17.16, are visually unappealing. They also split up habitat, which harms the ecosystem.

- **Will using the energy source permanently remove the fuel from the environment?** A **non-renewable** energy source (such as coal, oil, or natural gas) is effectively gone once we have used it up. Non-renewable energy sources take millions of years to form. We use them up at a much faster rate than they can be replenished. An energy source that is clearly **renewable** is solar energy. The Sun will continue to radiate energy toward Earth over its lifetime—many millions of years. A somewhat renewable energy source is wood. Trees can be grown to replace those cut down. It takes trees a long time to grow, however, and habitat is often destroyed in the meantime.

![Figure 17.16](image) This gas pipeline harms the ecosystem by splitting up habitat.
Hot Ice
When engineers first began extending natural gas pipelines through regions of bitter cold, they noticed that their lines plugged with a dangerous slush of ice and gas. The intense pressure of the lines, combined with the cold, led to the formation of methane hydrates, a kind of gas-permeated ice. More than a mere nuisance, methane hydrate plugs were a potential threat to pipelines. The build-up of gas pressure behind a methane hydrate plug could lead to an explosion. Now, however, this same substance may hold the key to a vast fuel supply.

Methane hydrates form when methane molecules become trapped within an ice lattice as water freezes. They can form in very cold conditions or under high-pressure conditions. Both of these conditions are met in deep oceans and in permafrost. In Canada, hydrates have already been found in large quantities in the Canadian Arctic. Methane hydrate has a number of remarkable properties. For example, when brought into an oxygen atmosphere, the methane fumes can be ignited, making it appear that the ice is burning!

Methane releases 25% less carbon dioxide per gram than coal, and it emits none of the oxides of nitrogen and sulfur that contribute to acid precipitation. Therefore, using methane in place of other fossil fuels is very desirable. Methane hydrates seem to be an ideal and plentiful “pre-packaged” source of natural gas. Estimates of the exact amount of methane stored in hydrates suggest there could be enough to serve our energy needs anywhere from 350 years to 3500 years, based on current levels of energy consumption. This would constitute a significant source of fossil fuels, if we can find a way to extract the gas safely and economically.

Unfortunately, hydrates become unstable when the pressure or temperature changes. Even small changes in these conditions can cause hydrates to degrade rapidly. Methane hydrates are stable at ocean depths greater than 300 m, but offshore drilling at these depths has been known to disturb the hydrate formations, causing large, uncontrolled releases of flammable methane gas. Also, methane hydrates often hold sediment layers together. Therefore, in addition to the danger of a gas explosion, there is the danger of the sea floor collapsing where drilling occurs.

Methane is a significant greenhouse gas. A massive release of methane could cause catastrophic global climate change. Some researchers believe that the drastic climate change that occurred during the Pleistocene era was due to methane hydrate destabilization and widespread methane release.

Nonetheless, Canada, Japan, the United States, and Russia all have active research and exploration programs in this area. As global oil supplies dwindle, using methane hydrates might increasingly be seen as worth the risk and cost.

Making Connections
1. Compare using methane from natural gas with using methane from methane hydrates in terms of environmental impact and efficiency. You will need to do some research to find out extraction methods for each source of methane.

2. On the Internet, research one possible structure of methane hydrate. Create a physical model or a three-dimensional computer model to represent it. Use your model to explain why methane hydrates are unstable at temperatures that are warmer than 0°C.
Hydrocarbon Fuels and the Environment

Hydrocarbon fuels have changed the way we live. Our dependence on them, however, has affected the world around us. The greenhouse effect, global warming, acid rain, and pollution are familiar topics on the news today. Our use of petroleum products, such as oil and gasoline, is linked directly to these problems.

The Greenhouse Effect and Global Warming

Roads, expressways, service stations, and parking lots occupy almost 40% of Toronto. They are the result of our demand for fast and efficient transportation. Every day, Toronto’s vehicles produce nearly 16,000 t of carbon dioxide by the combustion of fossil fuels. Carbon dioxide is an example of a greenhouse gas. **Greenhouse gases** trap heat in Earth’s atmosphere and prevent the heat from escaping into outer space. Scientists think that a build-up of carbon dioxide in the atmosphere may lead to an increase in global temperature, known as **global warming**. The diagram below shows how these concepts are connected to fossil fuels.

Acid Rain

The combustion of fossil fuels releases sulfur and nitrogen oxides. These oxides react with water vapor in the atmosphere to produce acid rain. Some lakes in northern Canada are “dead” because acid rain has killed the plants, algae, and fish that used to live in them. Forests in Québec and other parts of Canada have also been harmed by acid rain.

Oil Spill Pollution

Our society demands a regular supply of fossil fuels. Petroleum is transported from oil-rich countries to the rest of the world. If an oil tanker carrying petroleum has an accident, the resulting oil spill can be disastrous to the environment.
Everyday Oil Pollution

The biggest source of oil pollution comes from the everyday use of oil by ordinary people. Oil that is dumped into water in urban areas adds to oil pollution from ships and tankers. In total, three million tonnes of oil reach the ocean each year. This is equivalent to having an oil spill disaster every day!

A high school student did a home experiment to discover how much oil remains in “empty” motor oil containers that are thrown out. He collected 100 empty oil containers from a local gas station. Then he measured the amount of oil that was left in each container. He found an average of 36 mL per container. Over 130 million oil containers are sold and thrown out in Canada each year. Using these figures, he calculated that nearly five million litres of oil are dumped into landfill sites every year, just in “empty” oil containers!
Once oil reaches the environment, it is almost impossible to clean up. Oil leaking from a landfill site can contaminate drinking water in the area. Because oil can dissolve similar substances, pollutants such as chlorine and pesticides, and other organic toxins, mix with the oil. They are carried with it into the water system, increasing the problem.

**Solutions to Environmental Problems Caused by Fossil Fuels**

All of the problems described above hinge on our use of fossil fuels. Thus, cutting back on our use of fossil fuels will help to reduce environmental damage. Cutting back on fossil fuels, however, depends on the consumers who buy petrochemicals and use fossil fuels. In other words, it depends on you and the people you know.

Corporations that are looking for profit have little incentive to change their use of fossil fuels. For example, the technology is available to build cars that can drive about 32 km on a single litre of fuel. Because this technology is not financially profitable, cars are still being produced that drive about 8 km per litre of fuel. If consumers demand and purchase more fuel-efficient cars, however, car manufacturers will have an incentive to produce such cars. Tougher government standards may also help to push the vehicle industry towards greater fuel efficiency.

Governments can also bring about change by endorsing the principle of sustainable development. This principle was introduced at the 1992 Earth Summit Conference. **Sustainable development** takes into account the environment, the economy, and the health and needs of society. (See Figure 17.18.)

Hydrocarbon fuels and products can benefit our society if they are managed well. They can cause great environmental damage, however, if they are managed irresponsibly. With enough knowledge, you can learn to make informed decisions on these important issues. Here are some suggestions of ways you can reduce your consumption of petroleum products. Brainstorm with your classmates to think of other ways to reduce consumption.

- Contact your local government and local power companies. Suggest using alternative fuels, such as solar energy and wind power.
- Ride a bicycle or walk more.
- Express your concerns by writing letters to the government or to newspapers.
- Become more informed by researching issues that concern you.
- Fix oil leaks in vehicles, and avoid dumping oil down the sink.
- If you are cold at home, put on an extra sweater instead of turning up the heat.
Lamp Oil and the Petroleum Age

Abraham Gesner was born in 1797 near Cornwallis, Nova Scotia. Although Gesner became a medical doctor, he was much more interested in fossils. Gesner was fascinated by hydrocarbon substances, such as coal, asphaltum (asphalt), and bitumen. These substances were formed long ago from fossilized plants, algae, fish, and animals.

When Gesner was a young man, the main light sources available were fire, candles, and whale oil lamps. Gesner had made several trips to Trinidad. He began to experiment with asphaltum, a semisolid hydrocarbon from Trinidad’s famous “pitch lake.” In 1846, while giving a lecture in Prince Edward Island, he startled his audience by lighting a lamp that was filled with a fuel he had distilled from asphaltum. Gesner’s lamp fuel gave more light and produced less smoke than any other lamp fuel the audience had ever seen used.

Gesner needed a more easily obtainable raw material to make his new lamp fuel. He tried a solid, black, coal-like bitumen from Albert County, New Brunswick. This substance, called albertite, worked better than any other substance that Gesner had tested.

Making Kerosene

One residue from Gesner’s distillation process was a type of wax. Therefore, he called his lamp fuel kerosolain, from the Greek word for “wax oil.” He soon shortened the name to kerosene. To produce kerosene, Gesner heated chunks of albertite in a retort (a distilling vessel with a long downward-bending neck). As the albertite was heated, it gave off vapours. The vapours passed into the neck of the retort, condensed into liquids, and trickled down into a holding tank. Once Gesner had finished the first distillation, he let the tank’s contents stand for several hours. This allowed water and solid to settle to the bottom. Then he drew off the oil that remained on top.

Gesner distilled this oil again, and then treated it with sulfuric acid and calcium oxide. Finally he distilled the oil once more.

By 1853, Gesner had perfected his process. In New York, he helped to start the North American Kerosene Gas Light Company. Gesner distinguished between three grades of kerosene: grades A, B, and C. Grade C, he said, was the best lamp oil. Grades A and B could also be burned in lamps, but they were dangerous because they could cause explosions and fires.

Although Gesner never knew, his grades A and B kerosene became even more useful than the purer grade C. These grades were later produced from crude oil, or petroleum, and given a new name: gasoline!

Gesner laid the groundwork for the entire petroleum industry. All the basics of later petroleum refining can be found in his technology.

Making Connections

1. In the early nineteenth century, whales were hunted extensively for their oil, which was used mainly as lamp fuel. When kerosene became widely available, the demand for whale oil decreased. Find out what effect this had on whalers and whales.

2. How do you think the introduction of kerosene as a lamp oil changed people’s lives at the time? What conclusions can you draw about the possible impact of technology?
Analyzing Risks and Benefits of Energy Sources

A risk is a chance of possible negative or dangerous results. Riding a bicycle carries the risk of falling off. Driving a car carries the risk of an accident. Almost everything you do has some kind of risk attached. Fortunately most risks are relatively small, and they may never happen. Many of the activities that carry risks also carry benefits. A benefit is an advantage, or positive result. For example, riding a bicycle provides the benefits of exercise, transportation, and enjoyment. When deciding to do an activity, it may be a good idea to compare the risks and benefits involved. (See Figure 17.19.)

Risk-Benefit Analysis

Knowing more about an issue helps you assess its risks and benefits more accurately. How can you make the most informed decision possible? Follow these steps to do your own assessment of risks and benefits, called a risk-benefit analysis.

Step 1 Identify possible risks and benefits of the activity. Decide how to research these risks and benefits.

Step 2 Research the risks and benefits. You need information from reliable sources to make an accurate analysis.

Step 3 Weigh the effects of the risks and benefits. You may find that the risks are too great and decide not to do the activity. On the other hand, you may find that the benefits are greater than the risks.

Step 4 Compare your method for doing the activity with other possible methods. Do you use the safest method to do the activity? One method may be much safer than another.

Both efficiency and environmental impact are important factors to consider when comparing the risks and benefits of various energy sources. In the following ThoughtLab, you will conduct a risk-benefit analysis of an alternative or a conventional energy source.
Emerging Energy Sources

In the ThoughtLab above, you probably noticed that all energy sources have drawbacks as well as benefits. Scientists and engineers are striving to find and develop new and better energy sources. One energy source that engineers are trying to harness is nuclear fusion. Nuclear fusion provides a great deal of energy from readily available fuel (isotopes of hydrogen). In addition, nuclear fusion produces a more benign waste product than nuclear fission. Unfortunately, fusion is not yet practical and controllable on a large scale because of the enormous temperatures involved.

Chemists are also striving to find new sources for existing fuels that work well. The Chemistry Bulletin on page 695, for example, discussed a new potential source of methane.
Section Summary

In this section, you learned how efficiency can be defined in different ways for different purposes. You used your understanding of processes that produce energy to investigate the efficiency and environmental impact of different energy sources.

Section Review

1. Compare the energy changes associated with physical, chemical, and nuclear processes. Give one example of each process.

2. Your friend tells you about an energy source that is supposed to be 46% efficient. What questions do you need to ask your friend in order to clarify this claim?

3. Design an experiment to determine the efficiency of a laboratory burner. You will first need to decide how to define the efficiency, and you will also need to find out what fuel your burner uses. Include a complete procedure and safety precautions.

4. Some high-efficiency gas furnaces can heat with an efficiency of up to 97%. These gas furnaces work by allowing the water vapour produced during combustion to condense. Condensation is an exothermic reaction that releases further energy for heating. Explain why allowing the water to condense increases the energy output of the furnace.

5. The label on an electric kettle claims that the kettle is 95% efficient.
   (a) What definition of efficiency is the manufacturer using?
   (b) Write an expression that shows how the manufacturer might have arrived at an efficiency of 95% for the kettle.
   (c) Design a detailed experiment to test the manufacturer's claim. Include safety precautions.


7. Hydrogen is a very appealing fuel, in part because burning it produces only water. One of the challenges that researchers face in making hydrogen fuel a reality is how to produce hydrogen economically. Researchers are investigating methods of producing hydrogen indirectly. The following series of equations represent one such method.

   \[
   \begin{align*}
   3\text{FeCl}_2(s) + 4\text{H}_2\text{O}(g) & \rightarrow \text{Fe}_3\text{O}_4(s) + 6\text{HCl}(g) + \text{H}_2(g) \quad \Delta H^\circ = 318 \text{ kJ} \\
   \text{Fe}_3\text{O}_4(s) + \frac{3}{2}\text{Cl}_2(g) + 6\text{HCl}(g) & \rightarrow 3\text{FeCl}_3(s) + 3\text{H}_2\text{O}(g) + \frac{3}{2}\text{O}_2(g) \quad \Delta H^\circ = -249 \text{ kJ} \\
   3\text{FeCl}_3(s) & \rightarrow 3\text{FeCl}_2(s) + \frac{3}{2}\text{Cl}_2(g) \quad \Delta H^\circ = 173 \text{ kJ}
   \end{align*}
   \]

   (a) Show that the net result of the three reactions is the decomposition of water to produce hydrogen and oxygen.
   (b) Use Hess's law and the enthalpy changes for the reactions to determine the enthalpy change for the decomposition of one mole of water. Check your answer, using the enthalpy of formation of water.
Chapter 17  Measuring and Using Energy Changes • MHR

Reflecting on Chapter 17
Summarize this chapter in the format of your choice. Here are a few ideas to use as guidelines:
• Explain what a calorimeter is and how it is used to determine the energy changes associated with physical and chemical processes.
• Compare a coffee-cup calorimeter and a bomb calorimeter.
• Use examples and analogies to explain Hess's Law.
• Show how to calculate enthalpy of reaction using known enthalpies of reaction, and explain how this calculation relates to Hess’s law.
• Show how to calculate enthalpy of reaction using known enthalpies of formation, and explain how this calculation relates to Hess’s law.
• Describe how to use bond energies to estimate enthalpy of reaction. Explain why the result is an estimate only.
• Explain the concept of efficiency, and discuss the efficiency and environmental impact of conventional and alternative energy sources.

Reviewing Key Terms
benefit
bomb calorimeter
calorimeter
calorimetry
coffee-cup calorimeter
global warming
greenhouse gases
Hess’s law of heat summation
non-renewable
renewable
risk
risk-benefit analysis
state function
sustainable development
thermal equilibrium

Knowledge/Understanding
1. List three assumptions that you make when using a coffee-cup calorimeter.
2. A given chemical equation is tripled and then reversed. What effect, if any, will there be on the enthalpy change of the reaction?
3. Explain why two nested polystyrene coffee cups, with a lid, make a good constant-pressure calorimeter.
4. Write the balanced equation for the formation of each substance.
   (a) LiCl(s)
   (b) C₂H₅OH(ℓ)
   (c) NH₄NO₃(s)
5. If the enthalpy of formation of an element in its standard state is equal to zero, explain why the enthalpy of formation of iodine gas, I₂(g), is 21 kJ/mol.

Inquiry
6. In an oxygen-rich atmosphere, carbon burns to produce carbon dioxide, CO₂. Both carbon monoxide, CO, and carbon dioxide are produced when carbon is burned in an oxygen-deficient atmosphere. This makes the direct measurement of the enthalpy of formation of CO difficult. CO, however, also burns in oxygen, O₂, to produce pure carbon dioxide. Explain how you would experimentally determine the enthalpy of formation of carbon monoxide.
7. Two 30.0 g pieces of aluminium, Al, are placed in a calorimeter.
   (a) One piece of Al has an initial temperature of 100.0˚C. The other piece has an initial temperature of 20.0˚C. What is the temperature of the contents of the calorimeter after the system has reached thermal equilibrium?
   (b) Repeat the calculation in part (a) with the following change: The piece of Al at 20.0˚C has a mass of 50.0 g.
8. The complete combustion of 1.00 mol of sucrose, C₁₂H₂₂O₁₁, releases −5641 kJ of energy (at 25˚C and 100 kPa).
   C₁₂H₂₂O₁₁(s) + 12O₂(g) → 12CO₂(g) + 11H₂O(ℓ)
   (a) Use the enthalpy change of this reaction, and enthalpies of formation from Appendix E, to determine the enthalpy of formation of sucrose.
   (b) Draw and label an enthalpy diagram for this reaction.

Answers to questions highlighted in red type are provided in Appendix A.
9. A horseshoe can be shaped from an iron bar when the iron is heated to temperatures near 1500°C. The hot iron is then dropped into a bucket of water and cooled. An iron bar is heated to 1500°C and then cooled in 1000 g of water that was initially at 20.0°C. How much heat does the water absorb if its final temperature is 65.0°C?

10. A chemist wants to calibrate a new bomb calorimeter. He completely burns a mass of 0.930 g of carbon in a calorimeter. The temperature of the calorimeter changes from 25.00°C to 28.15°C. If the molar enthalpy of combustion of carbon is 394 kJ/mol, what is the heat capacity of the new calorimeter? What evidence shows that the reaction was exothermic?

11. 200 g of iron at 350°C is added to 225 g of water at 10.0°C. What is the final temperature of the iron-water mixture?

12. Fats have long hydrocarbon sections in their molecular structure. Therefore, they have many C—C and C—H bonds. Sugars have fewer C—C and C—H bonds but more C—O bonds. Explain why you can obtain more energy from burning a fat than from burning a sugar.

13. Use equations (1), (2), and (3) to find the enthalpy change of the formation of methane, CH₄, from chloroform, CHCl₃.

   \[ \text{CHCl}_3(i) + 3 \text{HCl}(g) \rightarrow \text{CH}_4(g) + 3 \text{Cl}_2(g) \]

   (1) \( \frac{1}{2} \text{H}_2(g) + \frac{1}{2} \text{Cl}_2(g) \rightarrow \text{HCl}(g) \) \[ \Delta H^\circ = -92.3 \text{ kJ} \]

   (2) \( \text{C}_6\text{H}_6(s) + 2 \text{H}_2(g) \rightarrow \text{CH}_4(g) \) \[ \Delta H^\circ = -74.8 \text{ kJ} \]

   (3) \[ \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \] \[ \Delta H^\circ = -242 \text{ kJ} \]

14. The following equation represents the combustion of ethylene glycol, \( (\text{CH}_2\text{OH})_2 \).

   \( (\text{CH}_2\text{OH})_2(l) + \frac{5}{2} \text{O}_2(g) \rightarrow 2 \text{CO}_2(g) + 3 \text{H}_2\text{O}(l) \)

   \[ \Delta H^\circ = -1178 \text{ kJ} \]

   Use known enthalpies of formation and the given enthalpy change to determine the enthalpy of formation of ethylene glycol.

15. Hydrogen peroxide, \( \text{H}_2\text{O}_2 \), is a strong oxidizing agent. It is used as an antiseptic in a 3.0% aqueous solution. Some chlorine-free bleaches contain 6.0% hydrogen peroxide.

   (a) Write the balanced chemical equation for the formation of one mole of \( \text{H}_2\text{O}_2(l) \).

   (b) Using the following equations, determine the enthalpy of formation of \( \text{H}_2\text{O}_2 \).

   (1) \( 2\text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g) \) \[ \Delta H^\circ = -196 \text{ kJ} \]

   (2) \( \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \) \[ \Delta H^\circ = -286 \text{ kJ} \]

16. Hydrogen cyanide is a highly poisonous gas. It is produced from methane and ammonia.

   \( \text{CH}_4(g) + \text{NH}_3(g) \rightarrow \text{HCN}(g) + 3\text{H}_2(g) \)

   Find the enthalpy change of this reaction, using the following thermochemical equations.

   (1) \( \text{H}_2(g) + 2\text{C}_{(\text{graphite})} + \text{N}_2(g) \rightarrow 2\text{HCl}(g) \) \[ \Delta H^\circ = 270 \text{ kJ} \]

   (2) \( \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \) \[ \Delta H^\circ = -92 \text{ kJ} \]

   (3) \( \text{C}_{(\text{graphite})} + 2\text{H}_2(g) \rightarrow \text{CH}_4(g) \) \[ \Delta H^\circ = -75 \text{ kJ} \]

17. The following equation represents the complete combustion of butane, \( \text{C}_4\text{H}_{10}(g) \).

   \( \text{C}_4\text{H}_{10}(g) + 6.5\text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 5\text{H}_2\text{O}(g) \)

   (a) Using known enthalpies of formation, calculate the enthalpy change of the complete combustion of \( \text{C}_4\text{H}_{10} \). (The enthalpy of formation of \( \text{C}_4\text{H}_{10} \) is \(-126 \text{ kJ/mol}\).)

   (b) Using known enthalpies of formation, calculate the enthalpy change of the complete combustion of ethane, \( \text{C}_2\text{H}_6 \), to produce carbon dioxide and water vapour. Express your answer in units of kJ/mol and kJ/g.

   (c) A 10.0 g sample that is 30% \( \text{C}_2\text{H}_6 \) and 70% \( \text{C}_4\text{H}_{10} \), by mass, is burned in excess oxygen. How much heat is released?

18. Design an investigation to determine the enthalpy change of the combustion of ethanol using a wick-type burner, similar to that in a kerosene lamp.

   (a) Draw and label a diagram of the apparatus.

   (b) Write a step-by-step procedure.

   (c) Prepare a table to record your data and other observations.

   (d) State any assumptions that you will make when carrying out the calculations.

**Communication**

19. Suppose that you need to determine the enthalpy change of a chemical reaction. Unfortunately, you are unable to carry out the reaction in your school laboratory. Does this mean that you cannot determine the enthalpy change of the reaction? Explain.
20. Acetylene, $\text{C}_2\text{H}_2$, and ethylene, $\text{C}_2\text{H}_4$, are both used as fuels. They combine with oxygen gas to produce carbon dioxide and water in an exothermic reaction. Acetylene also reacts with hydrogen to produce ethylene, as shown. $\text{C}_2\text{H}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_4(\text{g}) \quad \Delta H^\circ = -175.1 \text{ kJ}$

(a) Without referring to any tables or doing any calculations, explain how you know that $\text{C}_2\text{H}_2$ has a more positive enthalpy of formation than $\text{C}_2\text{H}_4$.

(b) Do you think $\text{C}_2\text{H}_2$ or $\text{C}_2\text{H}_4$ is a more energetic fuel? Explain.

Making Connections

21. When energy is “wasted” during an industrial process, what actually happens to this energy?

22. On an episode of *The Nature of Things*, Dr. David Suzuki made the following comment: “As a society and as individuals, we’re hooked on it [oil].” Discuss his comment. Explain how our society has benefitted from hydrocarbons. Describe some of the problems that are associated with the use of hydrocarbons. Also describe some possible alternatives for the future.

23. Consider methane, $\text{CH}_4$, and hydrogen, $\text{H}_2$, as possible fuel sources.

(a) Write the chemical equation for the complete combustion of each fuel. Then find the enthalpy of combustion, $\Delta H_{\text{comb}}$, of each fuel. Express your answers in kJ/mol and kJ/g. Assume that water vapour, rather than liquid water, is formed in both reactions.

(b) Which is the more energetic fuel, per unit mass?

(c) Consider a fixed mass of each fuel. Which fuel would allow you to drive a greater distance? Explain briefly.

(d) Describe how methane and hydrogen could be obtained. Which of these methods do you think is less expensive? Explain.

(e) Which fuel do you think is more environmentally friendly? Explain.

Answers to Practice Problem and Short Section Review Questions:

Practice Problems 1.(a) $-2.18 \times 10^4 \text{ J}$, $2.18 \times 10^4 \text{ J}$ (b) $8.01 \text{ J/g}$

2.(a) $6.34 \times 10^3 \text{ J}$, $-6.34 \times 10^3 \text{ J}$ (b) 92.3°C 3. 25 g 4.(a) 32.0 g (b) 26.0°C

5. $-51.2 \text{ kJ/mol}$ 6.(a) $-4.0 \times 10^5 \text{ kJ/mol}$ (b) The density and specific heat capacity of the solutions are assumed to be the same as the density and specific heat capacity of the water. It is assumed that no heat is lost to the calorimeter.

7. 29.7°C 8.(a) $C = q/\Delta T$ (b) $\Delta T = q/C$ (c) $T_1 = T_i + q/C$

(d) $T_1 = T_i - q/C$ 9. $-20.3 \text{ kJ/g}$ 10.(a) $1.00 \times 10^2 \text{ g}$ (b) $8.75 \text{ kJ/˚C}$

11. $-10 \text{ kJ}$ 12. $-509 \text{ kJ}$ 13. $-120 \text{ kJ}$

14. $+30 \text{ kJ}$ 15.(a) $\text{C}_3(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{H}_2(\text{g}) + 74.6 \text{ kJ}$

(b) $\text{Na}(\text{s}) + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{NaCl}(\text{s}) + 411.2 \text{ kJ}$ (c) $\text{Mg}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{MgO}_2(\text{s}) + 2.2 \text{ kJ}$

(d) $\text{Ca}(\text{s}) + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow \text{CaCO}_3(\text{s}) + 1207.6 \text{ kJ}$

16. $\text{H}_2(\text{g}) + \frac{1}{2}\text{S}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{SO}_4(\text{g}) + 814.0 \text{ kJ}$

17. $\text{Ca}(\text{s}) + 76.7 \text{ kJ} \rightarrow \text{Ca}(\text{g})$ 18.(a) $1/4\text{P}_4(\text{g}) \rightarrow \text{P}_4(\text{g}) + 17.6 \text{ kJ}$ (b) $-18.5 \text{ kJ}$

19. add the formation equation of ethene to the reverse of the formation equation of ethane 20. add the formation equation of sulfur dioxide, times two, to the formation equation of zinc oxide, times two, to the reverse of the formation equation of zinc sulfide times two 21. $-77.6 \text{ kJ/mol}$

22.(a) $-637.9 \text{ kJ}$ (b) $2.49 \times 10^5 \text{ kJ}$

23.(a) $-2225 \text{ kJ/mol}$ (b) $-3003 \text{ kJ/mol}$ 24.(a) 219 kJ (b) $-91.8 \text{ kJ}$ 25.(a) $-249 \text{ kJ/mol}$

(b) $-242 \text{ kJ/mol}$ 26.(a) $-519 \text{ J}$ (b) $-305 \text{ kJ}$

Section Review 17.1 2. $-39.8 \text{ kJ}$ 3. $-3.1 \times 10^3 \text{ J}$ 7.(a) $-55 \text{ kJ/mol}$ (b) $\text{KOH}(\text{aq}) + \text{HNO}_3(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{aq}) + \text{KNO}_3(\text{aq}) + 55 \text{ kJ}$

17.2 3. $-143 \text{ kJ}$ 4. $14.36 \text{ kJ}$ 5. $-636.0 \text{ kJ/mol}$ 7.(b) $584 \text{ kJ/mol}$ (a) $835 \text{ kJ/mol}$

17.3 7.(b) 242 kJ
Knowledge/Understanding

Multiple Choice
In your notebook, write the letter for the best answer to each question.

1. Which situation describes an exothermic reaction?
   (a) The energy that is released to form the product bonds is greater than the energy that is used to break the reactant bonds.
   (b) The energy that is released to form the product bonds is less than the energy that is used to break the reactant bonds.
   (c) The energy that is released to form the product bonds is equal to the energy that is used to break the reactant bonds.
   (d) The energy that is used to break the product bonds is greater than the energy that is released to form the reactant bonds.
   (e) The energy that is used to break the product bonds is less than the energy that is released to form the reactant bonds.

2. Beaker A contains 500 mL of a liquid. Beaker B contains 1000 mL of the same liquid. What happens when 200 kJ of heat is absorbed by the liquid in each beaker?
   (a) The temperature of the liquid increases the same amount in both beakers.
   (b) The temperature of the liquid decreases the same amount in both beakers.
   (c) The temperature of the liquid remains the same in both beakers.
   (d) The temperature change of the liquid in Beaker B is twice as large as the temperature change of the liquid in Beaker A.
   (e) The temperature change of the liquid in Beaker B is one half as large as the temperature change of the liquid in Beaker A.

3. Which of the following processes are exothermic?
   I. boiling water
   II. freezing water
   III. condensing steam
   IV. melting ice
   (a) I and II only
   (b) II and III only
   (c) I and IV only
   (d) II, III, and IV only
   (e) II and IV only

4. The $\Delta H^\circ_f$ of an element in its standard state is defined to be
   (a) 0 kJ/mol
   (b) 10 kJ/mol
   (c) −10 kJ/mol
   (d) greater than 0 kJ/mol
   (e) a unique value for each element

5. 10.9 kJ of heat is needed to vaporize 60.0 g of liquid Br$_2$ vapour at 60°C. What is the molar enthalpy of vaporization of Br$_2$ at 60°C?
   (a) 3.64 kJ/mol
   (b) 7.27 kJ/mol
   (c) 14.6 kJ/mol
   (d) 29.1 kJ/mol
   (e) 10.9 kJ/mol

6. What is the molar enthalpy of vaporization of water, given the following thermochemical equations?
   $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(g) + 241.8 \text{ kJ}$
   $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) + 285.8 \text{ kJ}$
   (a) 44.0 kJ/mol
   (b) −527.6 kJ/mol
   (c) −44.0 kJ/mol
   (d) 241.8 kJ/mol
   (e) −527.6 kJ/mol

7. Which substance has a standard enthalpy of formation, $\Delta H^\circ_f$, equal to zero?
   (a) gold, Au(s)
   (b) water, H$_2$O(l)
   (c) carbon monoxide, CO(s)
   (d) zinc, Zn
   (e) water, H$_2$O(g)

8. Which of the following statements are true?
   I. The temperature of the surroundings decreases when an endothermic reaction occurs.
   II. An endothermic reaction has a negative value of $\Delta H$.
   III. Heat is liberated when an exothermic reaction occurs.
   (a) I and II
   (b) I, II, and III
   (c) none of them
   (d) II and III only
   (e) I and III only

Short Answer
In your notebook, write a sentence or a short paragraph to answer each question.

9. Distinguish between a closed system and an insulated system.

10. In your own words, define the terms “system” and “surroundings.” Use an example to illustrate your definition.

Answers to questions highlighted in red type are provided in Appendix A.
11. In a chemical reaction, bonds are formed and broken.
   (a) How would you characterize the enthalpy change of bond breaking?
   (b) How would you characterize the enthalpy change of bond formation?
   (c) State the relationship between the enthalpy change of the overall reaction (exothermic or endothermic) and bond breakage and formation.

12. “The reactants have more potential energy than the products.” What kind of reaction does this statement describe? Justify your answer.

13. Compare and contrast enthalpy of vaporization and enthalpy of condensation.

14. Four fuels are listed in the table below. Equal masses of these fuels are burned completely.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Heat of combustion at SATP (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>octane, C(<em>8)H(</em>{18})(ℓ)</td>
<td>5513</td>
</tr>
<tr>
<td>methane, CH(_4)(g)</td>
<td>890</td>
</tr>
<tr>
<td>ethanol, C(_2)H(_5)OH(ℓ)</td>
<td>1367</td>
</tr>
<tr>
<td>hydrogen H(_2)(g)</td>
<td>285</td>
</tr>
</tbody>
</table>

   (a) Put the fuels in order, from greatest to least amount of energy provided.
   (b) Write a balanced chemical equation for the complete combustion of each fuel.
   (c) Suggest one benefit and one risk of using hydrocarbon fuels.

15. You are given a 70 g sample of each of the following metals, all at 25°C. You heat each metal under identical conditions. Which metal will be first to reach 30°C? Which will be last? Explain your reasoning.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Specific Heat Capacity (J/g·°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>0.133</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.528</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.388</td>
</tr>
</tbody>
</table>

16. Describe the information that is included in the following thermochemical equation:
   \[ \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{HN}_3(\text{g}) + 92.2 \text{ kJ} \]

17. Define calorimetry. Describe two commonly used calorimeters.

18. When taking a calorimetric measurement, why do you need to know the heat capacity of the calorimeter?

19. Describe two exothermic processes and two endothermic processes.

20. Compare the following terms: specific heat capacity and heat capacity.
   (a) Write their symbols and their units.
   (b) Write a mathematical formula in which each term would be used.

**Inquiry**

21. When kerosene, C\(_{12}\)H\(_{26}\)(ℓ), is burned in a device such as a space heater, energy is released. Design an investigation to determine the amount of energy that is released, per gram of kerosene. Discuss potential problems with using a kerosene heater in a confined area, such as a camper trailer, where the supply of air may be limited. Support your discussion with balanced chemical equations.

22. A group of students tested two white, crystalline solids, A and B, to determine their enthalpies of solution. The students dissolved 10.00 g of each solid in 100.0 mL of water in a polystyrene calorimeter and collected the temperature data. They obtained the following data:

<table>
<thead>
<tr>
<th>Time</th>
<th>Temperature (A)</th>
<th>Temperature (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td>0.5</td>
<td>20.1</td>
<td>18.8</td>
</tr>
<tr>
<td>1.0</td>
<td>25</td>
<td>16.7</td>
</tr>
<tr>
<td>1.5</td>
<td>29.8</td>
<td>15.8</td>
</tr>
<tr>
<td>2.0</td>
<td>31.9</td>
<td>15.2</td>
</tr>
<tr>
<td>2.5</td>
<td>32.8</td>
<td>15</td>
</tr>
<tr>
<td>3.0</td>
<td>33</td>
<td>15</td>
</tr>
<tr>
<td>3.5</td>
<td>33</td>
<td>15.2</td>
</tr>
<tr>
<td>4.0</td>
<td>32.8</td>
<td>15.5</td>
</tr>
<tr>
<td>4.5</td>
<td>32.5</td>
<td>15.8</td>
</tr>
<tr>
<td>5.0</td>
<td>32.2</td>
<td>16.1</td>
</tr>
<tr>
<td>5.5</td>
<td>31.9</td>
<td>16.4</td>
</tr>
</tbody>
</table>

   (a) Graph the data in the table above, placing time on the x-axis and temperature on the y-axis. Use your graph to answer (b) to (d).
   (b) Classify the enthalpy of solution of each solid as exothermic or endothermic.
(c) From the data given, calculate the enthalpy of solution for each solid. Your answer should be in kJ/g.
(d) Is there any evidence from the data that the students’ calorimeter could have been more efficient? Explain your answer.

23. Butane, C₄H₁₀, is the fuel that is used in disposable lighters. Consider the following equation for the complete combustion of butane. C₄H₁₀(g) + 6.5O₂(g) → 4CO₂(g) + 5H₂O(l)
(a) Write a separate balanced chemical equation for the formation of C₄H₁₀, the formation of CO₂, and the formation of H₂O, directly from the elements in their standard states.
(b) Algebraically combine these equations to get the balanced chemical equation for the complete combustion of C₄H₁₀.

24. A piece of aluminium metal at 160.0°C is added to a calorimeter containing 80.0 g of ice at 0.0°C. Thermal equilibrium is reached at 15.0°C.
(a) What further pieces of data do you need to determine the mass of the aluminum?
(b) Locate the missing data in your textbook, and determine the mass of the aluminum.

25. 543 g of ice is removed from a freezer that has a temperature of −15.3°C. The ice is dropped into a bowl containing 4.00 L of water.
(a) If thermal equilibrium is reached at 38.6°C, calculate the initial temperature of the 4.00 L of water. The specific heat capacity of ice is 2.01 J/g°C.
(b) State the assumptions you made in order to answer the question.

26. A student wants to determine the enthalpy change associated with dissolving solid sodium hydroxide, NaOH, in water. The student dissolves 1.96 g of NaOH in 100.0 mL of water in a coffee-cup calorimeter. The initial temperature of the water is 23.4°C. After the NaOH dissolves, the temperature of the water rises to 28.7°C.
(a) Use these data to determine the enthalpy of dissolution of sodium hydroxide, in kJ/mol NaOH. Assume that the heat capacity of the calorimeter is negligible.
(b) Suppose that the heat capacity of the calorimeter was not negligible. Explain how the value of ΔH that you calculated in part (a) would compare with the actual ΔH.

27. Some solid ammonium nitrate, NH₄NO₃, is added to a coffee-cup calorimeter that contains water at room temperature. After the NH₄NO₃ has dissolved, the temperature of the solution drops to near 0°C. Explain this observation.

28. Consider the following chemical equations and their enthalpy changes.
CH₄(g) + 2O₂(g) → CO₂(g) + 2H₂O(g) ΔH = −8.0 × 10² kJ
CaO(s) + H₂O(l) → Ca(OH)₂(s) ΔH = −65 kJ
What volume of methane, at STP, would have to be combusted in order to release the same amount of energy as the reaction of 1.0 × 10² g of CaO with sufficient water?

29. The molar enthalpy of combustion of sucrose (table sugar), C₁₂H₂₂O₁₁, is 5.65 × 10³ kJ.
(a) Write a balanced thermochemical equation for the complete combustion of sucrose.
(b) Calculate the amount of energy that is released when 5.00 g of sucrose (about one teaspoon) is combusted.

30. Carbon monoxide reacts with hydrogen gas to produce a mixture of methane, carbon dioxide, and water. (This mixture is known as substitute natural gas.)
4CO(g) + 8H₂(g) → 3CH₄(g) + CO₂(g) + 2H₂O(l)
Use the following thermochemical equations to determine the enthalpy change of the reaction.
C(graphite) + 2H₂(g) → CH₄(g) + 74.8 kJ
CO(g) + ½O₂(g) → CO₂(g) + 283.1 kJ
H₂(g) + ½O₂(g) → H₂O(l) + 241.8 kJ
C(graphite) + ½O₂(g) → CO(g) + 110.5 kJ
H₂O(l) + 44.0 kJ → H₂O(g)

31. The decomposition of aqueous hydrogen peroxide, H₂O₂, can be catalyzed by different catalysts, such as aqueous sodium iodide, NaI, or aqueous iron(III) nitrate, Fe(NO₃)₃.
(a) The enthalpy change, in kJ/mol of H₂O₂, would be the same for this reaction, regardless of the catalyst. Explain why, with the help of a potential energy diagram.
(b) Design an investigation to verify your explanation in part (a). Do not attempt to carry out the investigation without the supervision of your teacher.
Communication

32. If a solution of acid accidentally comes in contact with your skin, you are told to run the affected area under cold water for several minutes. Explain why it is not advisable to simply neutralize the acid with a basic solution.

33. A classmate is having difficulty understanding how the concepts of system, insulated system, and surroundings are related to exothermic and endothermic reactions. Write a note to explain to your classmate how the concepts are related. Use diagrams to help clarify your explanation.

34. Consider the following data for the complete combustion of the C₁ to C₈ straight-chain alkanes.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>(\Delta H_{\text{comb}}) (kJ/mol of alkane)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane</td>
<td>CH₄</td>
<td>(-8.90 \times 10^2)</td>
</tr>
<tr>
<td>ethane</td>
<td>C₂H₆</td>
<td>(-1.56 \times 10^3)</td>
</tr>
<tr>
<td>propane</td>
<td>C₃H₈</td>
<td>(-2.22 \times 10^3)</td>
</tr>
<tr>
<td>butane</td>
<td>C₄H₁₀</td>
<td>(-2.88 \times 10^3)</td>
</tr>
<tr>
<td>pentane</td>
<td>C₅H₁₂</td>
<td>(-3.54 \times 10^3)</td>
</tr>
<tr>
<td>hexane</td>
<td>C₆H₁₄</td>
<td>(-4.16 \times 10^3)</td>
</tr>
<tr>
<td>heptane</td>
<td>C₇H₁₆</td>
<td>(-4.81 \times 10^3)</td>
</tr>
<tr>
<td>octane</td>
<td>C₈H₁₈</td>
<td>(-5.45 \times 10^3)</td>
</tr>
</tbody>
</table>

(a) Using either graph paper or spreadsheet software, plot a graph of \(\Delta H_{\text{comb}}\) (y-axis) versus the number of C atoms in the fuel (x-axis).

(b) Extrapolate your graph to predict \(\Delta H_{\text{comb}}\) of decane, C₁₀H₂₂.

(c) From your graph, develop an equation to determine \(\Delta H_{\text{comb}}\) of a straight-chain alkane, given the number of carbons. Your equation should be of the form \(\Delta H = \ldots\).

(d) Use the equation you developed in part (c) to determine \(\Delta H_{\text{comb}}\) of C₁₀H₂₂. How does this value compare with the value of \(\Delta H\) you determined by extrapolation from the graph? Explain why.

(e) Methane, ethane, propane, and butane are all gases at room temperature. You know that equal volumes of different gases contain the same number of moles under identical conditions of temperature and pressure. Which of these gases do you think would make the best fuel? Explain your answer.

Making Connections

35. Suppose that you are having a new home built in a rural area, where natural gas is not available. You have two choices for fuelling your furnace:

• propane, C₃H₈, delivered as a liquid under pressure and stored in a tank
• home heating oil, delivered as a liquid (not under pressure) and stored in a tank

What factors do you need to consider in order to decide on the best fuel? What assumptions do you need to make?

36. Suppose that you read the following statement in a magazine: 0.95 thousand cubic feet of natural gas is equal to a gigajoule, GJ, of energy. Being a media-literate student, you are sceptical of this claim and wish to verify it. The following assumptions/information may be useful.

• Natural gas is pure methane.
• Methane undergoes complete combustion.
• \(H₂O(ℓ)\) is formed, rather than \(H₂O(g)\).
• 1.00 mol of any gas occupies 24 L at 20°C and 100 kPa.
• 1 foot = 12 inches; 1 inch = 2.54 cm; 1 L = 1 dm³
Canadian engineer Dr. John Hopps, working with a team of medical researchers in the late 1940s, developed one of the most significant medical inventions of the twentieth century: the pacemaker. The photograph on the right shows a pacemaker embedded in the body of a heart patient. A modern pacemaker is essentially a tiny computer that monitors a person’s heartbeat and corrects irregularities as needed. Pacemakers are particularly useful in correcting a heartbeat that is too slow.

The pacemaker device is surgically placed in a “pocket” of tissue near the patient’s collarbone. One or more wires, called “leads,” are connected to the pacemaker and threaded down through a major vein to the patient’s heart. By sending electrical impulses along the leads to the heart, the pacemaker can induce a heartbeat.

A pacemaker obtains electrical energy from a tiny battery that lasts for about seven years before it must be replaced. But how do batteries supply electrical energy? The answer lies in a branch of chemistry known as electrochemistry. In this unit, you will learn about the connection between chemical reactions and electricity. You will also learn about the chemical reactions that take place inside batteries.
Kitchen chemistry is an important part of daily life. Cooks use chemistry all the time to prepare and preserve food. Even the simplest things you do in the kitchen can involve chemical reactions. For example, you have probably seen a sliced apple turn brown. The same thing happens to pears, bananas, avocados, and several other fruits. Slicing the fruit exposes the flesh to oxygen in the air. Compounds in the fruit react with oxygen to form brown products. An enzyme in the fruit acts as a catalyst, speeding up this reaction. How can you stop fruit from turning brown after it is sliced?

A Waldorf salad uses a simple method to prevent fruit from browning. This type of salad usually consists of diced apples, celery, and walnuts, covered with a mayonnaise dressing. The dressing keeps the air away from the food ingredients. Without air, the fruit does not turn brown.

Another way to solve this problem is to prevent the enzyme in the fruit from acting as a catalyst. Enzymes are sensitive to pH. Therefore, adding an acid such as lemon juice or vinegar to fruit can prevent the enzyme from acting. You may have noticed that avocado salad recipes often include lemon juice. In addition to hindering the enzyme, lemon juice contains vitamin C, which is very reactive toward oxygen. The vitamin C reacts with oxygen before the sliced fruit can do so.

In this chapter, you will be introduced to oxidation-reduction reactions, also called redox reactions. You will discover how to identify this type of reaction. You will also find out how to balance equations for a redox reaction.
The term oxidation can be used to describe the process in which certain fruits turn brown by reacting with oxygen. The original, historical definition of this term was “to combine with oxygen.” Thus, oxidation occurred when iron rusted, and when magnesium was burned in oxygen gas. The term reduction was used historically to describe the opposite of oxidation, that is, the formation of a metal from its compounds. An ore is a naturally occurring solid compound or mixture of compounds from which a metal can be extracted. Thus, the process of obtaining a metal from an ore was known as a reduction. Copper ore was reduced to yield copper, and iron ore was reduced to yield iron.

As you will learn in this chapter, the modern definitions for oxidation and reduction are much broader. The current definitions are based on the idea of electron transfers, and can now be applied to numerous chemical reactions.

When a piece of zinc is placed in an aqueous solution of copper(II) sulfate, the zinc displaces the copper in a single displacement reaction. This reaction is shown in Figure 18.1. As the zinc dissolves, the zinc strip gets smaller. A dark red-brown layer of solid copper forms on the zinc strip, and some copper is deposited on the bottom of the beaker. The blue colour of the solution fades, as blue copper(II) ions are replaced by colourless zinc ions.
The reaction in Figure 18.1 is represented by the following equation.

\[
\text{Zn}(s) + \text{CuSO}_4(\text{aq}) \rightarrow \text{Cu}(s) + \text{ZnSO}_4(\text{aq})
\]

This equation can be written as a total ionic equation.

\[
\text{Zn}(s) + 2\text{Cu}^{2+}(\text{aq}) + 2\text{SO}_4^{2-}(\text{aq}) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(\text{aq}) + 2\text{SO}_4^{2-}(\text{aq})
\]

The sulfate ions are *spectator ions*, meaning ions that are not involved in the chemical reaction. By omitting the spectator ions, you obtain the following net ionic equation.

\[
\text{Zn}(s) + 2\text{Cu}^{2+}(\text{aq}) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(\text{aq})
\]

Notice what happens to the reactants in this equation. The zinc atoms *lose* electrons to form zinc ions. The copper ions *gain* electrons to form copper atoms.

The following chemical definitions describe these changes.

- **Oxidation** is the loss of electrons.
- **Reduction** is the gain of electrons.

In the reaction of zinc atoms with copper(II) ions, the zinc atoms lose electrons and undergo oxidation. In other words, the zinc atoms are *oxidized*. The copper(II) ions gain electrons and undergo reduction. In other words, the copper(II) ions are *reduced*. Because oxidation and reduction both occur in the reaction, it is known as an **oxidation-reduction reaction** or **redox reaction**.

Notice that electrons are transferred from zinc atoms to copper(II) ions. The copper(II) ions are responsible for the oxidation of the zinc atoms. A reactant that oxidizes another reactant is called an **oxidizing agent**. The oxidizing agent accepts electrons in a redox reaction. In this reaction, copper(II) is the oxidizing agent. The zinc atoms are responsible for the reduction of the copper(II) ions. A reactant that reduces another reactant is called a **reducing agent**. The reducing agent gives or donates electrons in a redox reaction. In this reaction, zinc is the reducing agent.

A redox reaction can also be defined as a reaction between an oxidizing agent and a reducing agent, as illustrated in Figure 18.2.
Try the following practice problems to review your understanding of net ionic equations, and to work with the new concepts of oxidation and reduction.

**Practice Problems**

1. Write a balanced net ionic equation for the reaction of zinc with aqueous iron(II) chloride. Include the physical states of the reactants and products.

2. Write a balanced net ionic equation for each reaction, including physical states.
   (a) magnesium with aqueous aluminum sulfate
   (b) a solution of silver nitrate with metallic cadmium

3. Identify the reactant oxidized and the reactant reduced in each reaction in question 2.

4. Identify the oxidizing agent and the reducing agent in each reaction in question 2.

**Half-Reactions**

To monitor the transfer of electrons in a redox reaction, you can represent the oxidation and reduction separately. A **half-reaction** is a balanced equation that shows the number of electrons involved in either oxidation or reduction. Because a redox reaction involves both oxidation and reduction, two half-reactions are needed to represent a redox reaction. One half-reaction shows oxidation, and the other half-reaction shows reduction.

As you saw earlier, the reaction of zinc with aqueous copper(II) sulfate can be represented by the following net ionic equation.

\[
\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(aq)
\]

Each neutral Zn atom is oxidized to form a Zn\(^{2+}\) ion. Thus, each Zn atom must lose two electrons. You can write an oxidation half-reaction to show this change.

\[
\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^-
\]

Each Cu\(^{2+}\) ion is reduced to form a neutral Cu atom. Thus, each Cu\(^{2+}\) ion must gain two electrons. You can write a reduction half-reaction to show this change.

\[
\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)
\]

If you look again at each half-reaction above, you will notice that the atoms and the charges are balanced. Like other types of balanced equations, half-reactions are balanced using the smallest possible whole-number coefficients. In the following equation, the atoms and charges are balanced, but the coefficients can all be divided by 2 to give the usual form of the half-reaction.

\[
2\text{Cu}^{2+}(aq) + 4e^- \rightarrow 2\text{Cu}(s)
\]
In most redox reactions, one substance is oxidized and a different substance is reduced. In a **disproportionation** reaction, however, a single element undergoes both oxidation and reduction in the same reaction. For example, a copper(I) solution undergoes disproportionation in the following reaction.

$$2\text{Cu}^+_{(aq)} \rightarrow \text{Cu}_{(s)} + \text{Cu}^{2+}_{(aq)}$$

In this reaction, some copper(I) ions gain electrons, while other copper(I) ions lose electrons.

The two half-reactions are as follows.

Oxidation: $$\text{Cu}^+_{(aq)} \rightarrow \text{Cu}^{2+}_{(aq)} + 1\text{e}^-$$

Reduction: $$\text{Cu}^+_{(aq)} + 1\text{e}^- \rightarrow \text{Cu}_{(s)}$$

You have learned that half-reactions can be used to represent oxidation and reduction separately. Half-reactions always come in pairs: an oxidation half-reaction is always accompanied by a reduction half-reaction, and vice versa. Try writing and balancing half-reactions using the following practice problems.

### Practice Problems

5. Write balanced half-reactions from the net ionic equation for the reaction between solid aluminum and aqueous iron(III) sulfate. The sulfate ions are spectator ions, and are not included.

$$\text{Al}_{(s)} + \text{Fe}^{3+}_{(aq)} \rightarrow \text{Al}^{3+}_{(aq)} + \text{Fe}_{(s)}$$

6. Write balanced half-reactions from the following net ionic equations.

   (a) $$\text{Fe}_{(s)} + \text{Cu}^{2+}_{(aq)} \rightarrow \text{Fe}^{2+}_{(aq)} + \text{Cu}_{(s)}$$

   (b) $$\text{Cd}_{(s)} + 2\text{Ag}^+_{(aq)} \rightarrow \text{Cd}^{2+}_{(aq)} + 2\text{Ag}_{(s)}$$

7. Write balanced half-reactions for each of the following reactions.

   (a) $$\text{Sn}_{(s)} + \text{PbCl}_2_{(aq)} \rightarrow \text{SnCl}_2_{(aq)} + \text{Pb}_{(s)}$$

   (b) $$\text{Au(NO}_3)_3_{(aq)} + 3\text{Ag}_{(s)} \rightarrow 3\text{AgNO}_3_{(aq)} + \text{Au}_{(s)}$$

   (c) $$3\text{Zn}_{(s)} + 2\text{Fe}_2\text{(SO}_4)_3_{(aq)} \rightarrow 3\text{ZnSO}_4_{(aq)} + 2\text{Fe}_{(s)}$$

8. Write the net ionic equation and the half-reactions for the disproportionation of mercury(I) ions in aqueous solution to give liquid mercury and aqueous mercury(II) ions. Assume that mercury(I) ions exist in solution as $\text{Hg}^{2+}$.

You may already know that some metals are more reactive than others. For instance, magnesium combusts readily, while gold does not. The arrangement of metals according to their reactivity is called a **metal activity series**. In Investigation 18-A, you will discover how this series is related to oxidation and reduction. You will write chemical equations, ionic equations, and half-reactions for the single displacement reactions of several metals.
Aging: Is Oxidation a Factor?

Why do we grow old? Despite advances in molecular biology and medical research, the reasons for aging remain mysterious. One theory suggests that aging may be influenced by oxidizing agents, also known as oxidants.

Oxidants are present in the environment and in foods. Nitrogen oxides are oxidants present in cigarette smoke and urban smog. Other oxidants include the copper and iron salts in meat and some plants. Inhaling and ingesting oxidants such as these can increase the level of oxidants in our bodies.

Oxidants are also naturally present in the body, where they participate in important redox reactions. For example, mitochondria consume oxygen during aerobic respiration, and cells ingest and destroy bacteria. Both these processes involve oxidation and reduction.

As you have just seen, redox reactions are an essential part of your body’s processes. However, these reactions can produce free radicals, which are highly reactive atoms or molecules with one or more unpaired electrons. Because they are so reactive, free radicals can oxidize surrounding molecules by robbing them of electrons. This process can damage DNA, proteins, and other macromolecules. Such damage may contribute to aging, and to diseases that are common among the aging, such as cancer, cardiovascular disease, and cataracts.

The study of oxidative damage has sparked a debate about the role that antioxidants might play in illness and aging. Antioxidants are reducing agents. They donate electrons to substances that have been oxidized, decreasing the damage caused by free radicals. Dietary antioxidants include vitamins C and E, beta-carotene, and carotenoids.

Most medical researchers agree that people with diets rich in fruits and vegetables have a lower incidence of cardiovascular disease, certain cancers, and cataracts. Although fruits and vegetables are high in antioxidants, they also contain fibre and many different vitamins and plant chemicals. It is hard to disentangle the effects of antioxidants from the beneficial effects of these other substances.

As a result, the benefits of antioxidant dietary supplements are under debate. According to one study, vitamin E supplements may lower the risk of heart disease. Another study, however, concludes that taking beta-carotene supplements does not reduce the risk of certain cancers.

We can be sure that a balanced diet including fruits and vegetables is beneficial to human health. Whether antioxidants confer these benefits, and whether these benefits include longevity, remain to be seen.

Making Connections

1. Research vitamins C, E, alpha- and beta-carotenes, and folic acid. How do they affect our health? What fruits and vegetables contain these vitamins?

2. Lycopene is a carotenoid that has been linked to a decreased risk of pancreatic, cervical, and prostate cancer. Find out what fruits and vegetables contain lycopene. What colour are these fruits and vegetables?
Single Displacement Reactions

The metal activity series is shown in the table below. The more reactive metals are near the top of the series, and the less reactive metals are near the bottom. In this investigation, you will relate the activity series to the ease with which metals are oxidized and metal ions are reduced.

### Activity Series of Metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>Most Reactive</th>
</tr>
</thead>
<tbody>
<tr>
<td>lithium</td>
<td></td>
</tr>
<tr>
<td>potassium</td>
<td></td>
</tr>
<tr>
<td>barium</td>
<td></td>
</tr>
<tr>
<td>calcium</td>
<td></td>
</tr>
<tr>
<td>sodium</td>
<td></td>
</tr>
<tr>
<td>magnesium</td>
<td></td>
</tr>
<tr>
<td>aluminum</td>
<td></td>
</tr>
<tr>
<td>zinc</td>
<td></td>
</tr>
<tr>
<td>chromium</td>
<td></td>
</tr>
<tr>
<td>iron</td>
<td></td>
</tr>
<tr>
<td>cadmium</td>
<td></td>
</tr>
<tr>
<td>cobalt</td>
<td></td>
</tr>
<tr>
<td>nickel</td>
<td></td>
</tr>
<tr>
<td>tin</td>
<td></td>
</tr>
<tr>
<td>lead</td>
<td></td>
</tr>
<tr>
<td>copper</td>
<td></td>
</tr>
<tr>
<td>mercury</td>
<td></td>
</tr>
<tr>
<td>silver</td>
<td></td>
</tr>
<tr>
<td>platinum</td>
<td></td>
</tr>
<tr>
<td>gold</td>
<td>Least Reactive</td>
</tr>
</tbody>
</table>

### Predictions

Predict the relative ease with which the metals aluminum, copper, iron, magnesium, and zinc can be oxidized. Predict the relative ease with which the ions of these same metals can be reduced. Explain your reasoning in both cases.

### Materials

- well plate
- test tube rack
- 4 small test tubes
- 4 small pieces of each of these metals: aluminum foil, thin copper wire or tiny copper beads, iron filings, magnesium, and zinc
- dropper bottles containing dilute solutions of aluminum sulfate, copper(II) sulfate, iron(II) sulfate, magnesium sulfate, and zinc nitrate

### Safety Precautions

- Wear goggles, gloves, and an apron for all parts of this investigation.

### Procedure

1. Place the well plate on a white piece of paper. Label it to match the table on the next page.
2. In each well plate, place a small piece of the appropriate metal, about the size of a grain of rice. Cover each piece with a few drops of the appropriate solution. Wait 3–5 min to observe if a reaction occurs.
3. Look for evidence of a chemical reaction in each mixture. Record the results, using “y” for a reaction, or “n” for no reaction. If you are unsure, repeat the process on a larger scale in a small test tube.
4. Discard the mixtures in the waste beaker supplied by your teacher. Do not pour anything down the drain.

**Analysis**

1. For each single displacement reaction you observed, write
   (a) a balanced chemical equation
   (b) a total ionic equation
   (c) a net ionic equation

2. Write an oxidation half-reaction and a reduction half-reaction for each net ionic equation you wrote in question 1. Use the smallest possible whole-number coefficients in each half-reaction.

3. Look at each balanced net ionic equation. Compare the total number of electrons lost by the reducing agent with the total number of electrons gained by the oxidizing agent.

4. List the different oxidation half-reactions. Start with the half-reaction for the most easily oxidized metal, and end with the half-reaction for the least easily oxidized metal. Explain your reasoning. Compare your list with your first prediction from the beginning of this investigation.

5. List the different reduction half-reactions. Start with the half-reaction for the most easily reduced metal ion, and end with the half-reaction for the least easily reduced metal ion. Explain your reasoning. Compare your list with your second prediction from the beginning of this investigation.

**Conclusions**

6. Which list from questions 4 and 5 puts the metals in the same order as they appear in the activity series?

7. How is the order of the metals in the activity series related to the ease with which metals are oxidized and metal ions are reduced?

**Applications**

8. Use the activity series to choose a reducing agent that will reduce aqueous nickel(II) ions to metallic nickel. Explain your reasoning.

9. Use the activity series to choose an oxidizing agent that will oxidize metallic cobalt to form aqueous cobalt(II) ions. Explain your reasoning.
Section Summary

In this section, you learned to define and recognize redox reactions, and to write oxidation and reduction half-reactions. In Investigation 18-A, you observed the connection between the metal activity series and redox reactions. However, thus far, you have only worked with redox reactions that involve atoms and ions as reactants or products. In the next section, you will learn about redox reactions that involve covalent reactants or products.

Predict whether each of the following single displacement reactions will occur. If so, write a balanced chemical equation, a balanced net ionic equation, and two balanced half-reactions. Include the physical states of the reactants and products in each case.

(a) aqueous silver nitrate and metallic cadmium
(b) gold and aqueous copper(II) sulfate
(c) aluminum and aqueous mercury(II) chloride

(a) On which side of an oxidation half-reaction are the electrons? Why?
(b) On which side of a reduction half-reaction are the electrons? Why?

Explain why, in a redox reaction, the oxidizing agent undergoes reduction.

In a combination reaction, does metallic lithium act as an oxidizing agent or a reducing agent? Explain.

Write a net ionic equation for a reaction in which
(a) $\text{Fe}^{2+}$ acts as an oxidizing agent
(b) $\text{Al}$ acts as a reducing agent
(c) $\text{Au}^{3+}$ acts as an oxidizing agent
(d) $\text{Cu}$ acts as a reducing agent
(e) $\text{Sn}^{2+}$ acts as an oxidizing agent and as a reducing agent

The element potassium is made industrially by the single displacement reaction of molten sodium with molten potassium chloride.

(a) Write a net ionic equation for the reaction, assuming that all reactants and products are in the liquid state.
(b) Identify the oxidizing agent and the reducing agent in the reaction.
(c) Explain why the reaction is carried out in the liquid state and not in aqueous solution.
In this section, you will describe oxidation and reduction in terms of changes in oxidation number. You will assign oxidation numbers to elements in covalent molecules and polyatomic ions. You will identify the species oxidized, the species reduced, the oxidizing agent, and the reducing agent in simple redox reactions. You will compare redox reactions with other kinds of reactions. You will communicate your understanding of the terms oxidation numbers, oxidation, reduction.

Redox reactions are very common. Some of them produce light in a process known as chemiluminescence. In living things, the production of light in redox reactions is known as bioluminescence. You can actually see the light from redox reactions occurring in some organisms, such as glowworms and fireflies, as shown in Figure 18.3.

Not all redox reactions give off light, however. How can you recognize a redox reaction, and how can you identify the oxidizing and reducing agents? In section 18.1, you saw net ionic equations with monatomic elements, such as Cu and Zn, and with ions containing a single element, such as Cu\(^{2+}\) and Zn\(^{2+}\). In these cases, you could use ionic charges to describe the transfer of electrons. However, many redox reactions involve reactants or products with covalent bonds, including elements that exist as covalent molecules, such as oxygen, \(O_2\); covalent compounds, such as water, \(H_2O\); or polyatomic ions that are not spectator ions, such as permanganate, \(MnO_4^-\). For reactions involving covalent reactants and products, you cannot use ionic charges to describe the transfer of electrons.

Oxidation numbers are actual or hypothetical charges, assigned using a set of rules. They are used to describe redox reactions with covalent reactants or products. They are also used to identify redox reactions, and to identify oxidizing and reducing agents. In this section, you will see how oxidation numbers were developed from Lewis structures, and then learn the rules to assign oxidation numbers.

### Oxidation Numbers from Lewis Structures

You are probably familiar with the Lewis structure of water, shown in Figure 18.4A. From the electronegativities on the periodic table in Figure 18.5, on the next page, you can see that oxygen (electronegativity 3.44) is more electronegative than hydrogen (electronegativity 2.20). The electronegativity difference is less than 1.7, so the two hydrogen-oxygen bonds are polar covalent, not ionic. In each bond, the electrons are more strongly attracted to the oxygen atom than to the hydrogen atom.

![Lewis structure of water](image)

**Figure 18.4** (A) The Lewis structure of water; (B) The formal counting of electrons with the more electronegative element assigned a negative charge.

Oxidation numbers are just a bookkeeping method used to keep track of electron transfers. In a covalent molecule or a polyatomic ion, the oxidation number of each element does not represent an ionic charge, because the elements are not present as ions. However, to assign oxidation numbers to the elements in a covalent molecule or polyatomic ion, you can pretend the bonds are ionic.
To assign oxidation numbers to the atoms in a water molecule, you can consider all the bonding electrons to be “owned” by the more electronegative oxygen atom, as shown in Figure 18.4B. Thus, each hydrogen atom in a water molecule is considered to have no electrons, as hydrogen would in a hydrogen ion, H⁺. Therefore, the element hydrogen is assigned an oxidation number of +1 in water. On the other hand, the oxygen atom in a water molecule is considered to have a filled octet of electrons, as oxygen would in an oxide ion, O²⁻. Therefore, the element oxygen is assigned an oxidation number of −2 in water. (Note: These are not ionic charges, since water is a covalent molecule. Also, note that the plus or minus sign in an oxidation number, such as −2, is written before the number. The plus or minus sign in an ionic charge, such as 2−, is written after the number.)

In a chlorine molecule, Cl₂, each atom has the same electronegativity, so the bond is non-polar covalent. Because the electrons are equally shared, you can consider each chlorine atom to “own” one of the shared electrons, as shown in Figure 18.6. Thus, each chlorine atom in the molecule is considered to have the same number of electrons as a neutral chlorine atom. Each chlorine atom is therefore assigned an oxidation number of 0.

![The periodic table, showing electronegativity values](image)

**Figure 18.5** The periodic table, showing electronegativity values

In a chlorine molecule, Cl₂, each atom has the same electronegativity, so the bond is non-polar covalent. Because the electrons are equally shared, you can consider each chlorine atom to “own” one of the shared electrons, as shown in Figure 18.6. Thus, each chlorine atom in the molecule is considered to have the same number of electrons as a neutral chlorine atom. Each chlorine atom is therefore assigned an oxidation number of 0.

![The Lewis structure of a chlorine molecule](image)

![The formal counting of electrons in a chlorine molecule for oxidation number purposes](image)

**Figure 18.6** (A) The Lewis structure of a chlorine molecule; (B) The formal counting of electrons in a chlorine molecule for oxidation number purposes
Figure 18.7 shows how oxidation numbers are assigned for the polyatomic cyanide ion, CN\(^-\). The electronegativity of nitrogen (3.04) is greater than the electronegativity of carbon (2.55). Thus, the three shared pairs of electrons are all considered to belong to the nitrogen atom. As a result, the carbon atom is considered to have two valence electrons, which is two electrons less than the four valence electrons of a neutral carbon atom. Therefore, the carbon atom in CN\(^-\) is assigned an oxidation number of +2. The nitrogen atom is considered to have eight valence electrons, which is three electrons more than the five valence electrons of a neutral nitrogen atom. Therefore, the nitrogen atom in CN\(^-\) is assigned an oxidation number of −3.

![Lewis structure](image)

**Figure 18.7** (A) The Lewis structure of a cyanide ion; (B) The formal counting of electrons in a cyanide ion for oxidation number purposes

You have seen examples of how Lewis structures can be used to assign oxidation numbers for polar molecules such as water, non-polar molecules such as chlorine, and polar polyatomic ions such as the cyanide ion. In the following ThoughtLab, you will use Lewis structures to assign oxidation number values, and then look for patterns in your results.

### ThoughtLab Finding Rules for Oxidation Numbers

#### Procedure
1. Use Lewis structures to assign an oxidation number to each element in the following covalent molecules.
   - (a) HI
   - (b) O\(_2\)
   - (c) PCl\(_5\)
   - (d) BBr\(_3\)
2. Use Lewis structures to assign an oxidation number to each element in the following polyatomic ions.
   - (a) OH\(^-\)
   - (b) NH\(_4^+\)
   - (c) CO\(_3^{2-}\)
3. Assign an oxidation number to each of the following atoms or monatomic ions. Explain your reasoning.
   - (a) Ne
   - (b) K
   - (c) I\(^-\)
   - (d) Mg\(^{2+}\)

#### Analysis
1. For each molecule in question 1 of the procedure, find the sum of the oxidation numbers of all the atoms present. What do you notice? Explain why the observed sum must be true for a neutral molecule.
2. For each polyatomic ion in question 2 of the procedure, find the sum of the oxidation numbers of all the atoms present. Describe and explain any pattern you see.

#### Extension
3. Predict the sum of the oxidation numbers of the atoms in the hypochlorite ion, OCI\(^-\).
4. Test your prediction from question 3.
Using Rules to Find Oxidation Numbers

Drawing Lewis structures to assign oxidation numbers can be a very time-consuming process for large molecules or large polyatomic ions. Instead, the results from Lewis structures have been summarized to produce a more convenient set of rules, which can be applied more quickly. Table 18.1 summarizes the rules used to assign oxidation numbers. You may have discovered some of these rules for yourself in the ThoughtLab you just completed.

Table 18.1 Oxidation Number Rules

<table>
<thead>
<tr>
<th>Rules</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. A pure element has an oxidation number of 0.</td>
<td>Na in Na(s), Br in Br₂(l), and P in P₄(s) all have an oxidation number of 0.</td>
</tr>
<tr>
<td>2. The oxidation number of an element in a monatomic ion equals the charge of the ion.</td>
<td>The oxidation number of Al in Al³⁺ is +3. The oxidation number of Se in Se²⁻ is −2.</td>
</tr>
<tr>
<td>3. The oxidation number of hydrogen in its compounds is +1, except in metal hydrides, where the oxidation number of hydrogen is −1.</td>
<td>The oxidation number of H in H₂S or CH₄ is +1. The oxidation number of H in NaH or in CaH₂ is −1.</td>
</tr>
<tr>
<td>4. The oxidation number of oxygen in its compounds is usually −2, but there are exceptions. These include peroxides, such as H₂O₂, and the compound OF₂.</td>
<td>The oxidation number of O in Li₂O or in KNO₃ is −2.</td>
</tr>
<tr>
<td>5. In covalent compounds that do not contain hydrogen or oxygen, the more electronegative element is assigned an oxidation number that equals the negative charge it usually has in its ionic compounds.</td>
<td>The oxidation number of Cl in PCl₃ is −1. The oxidation number of S in CS₂ is −2.</td>
</tr>
<tr>
<td>6. The sum of the oxidation numbers of all the elements in a compound is 0.</td>
<td>In CF₄, the oxidation number of F is −1, and the oxidation number of C is +4. ((+4) + 4(-1) = 0)</td>
</tr>
<tr>
<td>7. The sum of the oxidation numbers of all the elements in a polyatomic ion equals the charge on the ion.</td>
<td>In NO₂⁻, the oxidation number of O is −2, and the oxidation number of N is +3. ((+3) + 2(-2) = -1)</td>
</tr>
</tbody>
</table>

Some oxidation numbers found using these rules are not integers. For example, an important iron ore called magnetite has the formula Fe₃O₄. Using the oxidation number rules, you can assign oxygen an oxidation number of −2, and calculate an oxidation number of \(+\frac{8}{3}\) for iron. However, magnetite contains no iron atoms with this oxidation number. It actually contains iron(III) ions and iron(II) ions in a 2:1 ratio. The formula of magnetite is sometimes written as Fe₉O₈ • FeO to indicate that there are two different oxidation numbers. The value \(+\frac{8}{3}\) for the oxidation number of iron is an average value.

\[
\frac{2(+3) + (+2)}{3} = +\frac{8}{3}
\]

Even though some oxidation numbers found using these rules are averages, the rules are still useful for monitoring electron transfers in redox reactions.
In the following Sample Problem, you will find out how to apply these rules to covalent molecules and polyatomic ions.

**Sample Problem**

**Assigning Oxidation Numbers**

**Problem**
Assign an oxidation number to each element.
(a) SiBr$_4$  (b) HClO$_4$  (c) Cr$_2$O$_7^{2-}$

**Solution**
(a) • Because the compound SiBr$_4$ does not contain hydrogen or oxygen, rule 5 applies. Because SiBr$_4$ is a compound, rule 6 also applies.
  - Silicon has an electronegativity of 1.90. Bromine has an electronegativity of 2.96. From rule 5, therefore, you can assign bromine an oxidation number of $-1$.
  - The oxidation number of silicon is unknown, so let it be $x$. You know from rule 6 that the sum of the oxidation numbers is 0. Then,
    
    \[
    x + 4(-1) = 0 \\
    x - 4 = 0 \\
    x = 4
    \]

    The oxidation number of silicon is +4. The oxidation number of bromine is $-1$.

(b) • Because the compound HClO$_4$ contains hydrogen and oxygen, rules 3 and 4 apply. Because HClO$_4$ is a compound, rule 6 also applies.
  - Hydrogen has its usual oxidation number of +1. Oxygen has its usual oxidation number of $-2$. The oxidation number of chlorine is unknown, so let it be $x$. You know from rule 6 that the sum of the oxidation numbers is 0. Then,
    
    \[
    (+1) + x + 4(-2) = 0 \\
    x - 7 = 0 \\
    x = 7
    \]

    The oxidation number of hydrogen is +1. The oxidation number of chlorine is +7. The oxidation number of oxygen is $-2$.

(c) • Because the polyatomic ion Cr$_2$O$_7^{2-}$ contains oxygen, rule 4 applies. Because Cr$_2$O$_7^{2-}$ is a polyatomic ion, rule 7 also applies.
  - Oxygen has its usual oxidation number of $-2$.
  - The oxidation number of chromium is unknown, so let it be $x$. You know from rule 7 that the sum of the oxidation numbers is $-2$. Then,
    
    \[
    2x + 7(-2) = -2 \\
    2x - 14 = -2 \\
    2x = 12 \\
    x = 6
    \]

    The oxidation number of chromium is +6. The oxidation number of oxygen is $-2$. 

**PROBLEM TIP**

When finding the oxidation numbers of elements in ionic compounds, you can work with the ions separately. For example, Na$_2$Cr$_2$O$_7$ contains two Na$^+$ ions, and so sodium has an oxidation number of +1. The oxidation numbers of Cr and O can then be calculated as shown in part (c) of the Sample Problem.
Applying Oxidation Numbers to Redox Reactions

You have seen that the single displacement reaction of zinc with copper(II) sulfate is a redox reaction, represented by the following chemical equation and net ionic equation.

\[ \text{Zn}(s) + \text{CuSO}_4(aq) \rightarrow \text{Cu}(s) + \text{ZnSO}_4(aq) \]

Each atom or ion shown in the net ionic equation can be assigned an oxidation number. Zn has an oxidation number of 0; Cu\(^{2+}\) has an oxidation number of +2; Cu has an oxidation number of 0; and Zn\(^{2+}\) has an oxidation number of +2. Thus, there are changes in oxidation numbers in this reaction. The oxidation number of zinc increases, while the oxidation number of copper decreases.

\[
\begin{align*}
\text{oxidation number increases} & \quad \text{(loss of electrons)} \\
\text{Zn} + \text{Cu}^{2+} & \rightarrow \text{Zn}^{2+} + \text{Cu} \\
0 + 2 & \rightarrow 2 + 0
\end{align*}
\]

In the oxidation half-reaction, the element zinc undergoes an increase in its oxidation number from 0 to +2.

\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \]

\[ 0 \quad +2 \]

In the reduction half-reaction, the element copper undergoes a decrease in its oxidation number from +2 to 0.

\[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \]

\[ +2 \quad 0 \]

Practice Problems

9. Determine the oxidation number of the specified element in each of the following.
   (a) N in NF\(_3\)     (b) S in S\(_8\)     (c) Cr in CrO\(_4^{2-}\)  
   (d) P in P\(_2\)O\(_5\)    (e) C in C\(_{12}\)H\(_{22}\)O\(_{11}\)  
   (f) C in CHCl\(_3\)

10. Determine the oxidation number of each element in each of the following.
   (a) H\(_2\)SO\(_3\)     (b) OH\(^-\)     (c) HPO\(_4^{2-}\)

11. As stated in rule 4, oxygen does not always have its usual oxidation number of –2. Determine the oxidation number of oxygen in each of the following.
   (a) the compound oxygen difluoride, OF\(_2\)     (b) the peroxide ion, O\(_2^{2-}\)

12. Determine the oxidation number of each element in each of the following ionic compounds by considering the ions separately.
    **Hint:** One formula unit of the compound in part (c) contains two identical monatomic ions and one polyatomic ion.
    (a) Al(HCO\(_3\))\(_3\)     (b) (NH\(_4\))\(_3\)PO\(_4\)  
    (c) K\(_2\)H\(_3\)IO\(_6\)

Applying Oxidation Numbers to Redox Reactions

You have seen that the single displacement reaction of zinc with copper(II) sulfate is a redox reaction, represented by the following chemical equation and net ionic equation.

\[ \text{Zn}(s) + \text{CuSO}_4(aq) \rightarrow \text{Cu}(s) + \text{ZnSO}_4(aq) \]

Each atom or ion shown in the net ionic equation can be assigned an oxidation number. Zn has an oxidation number of 0; Cu\(^{2+}\) has an oxidation number of +2; Cu has an oxidation number of 0; and Zn\(^{2+}\) has an oxidation number of +2. Thus, there are changes in oxidation numbers in this reaction. The oxidation number of zinc increases, while the oxidation number of copper decreases.

\[
\begin{align*}
\text{oxidation number increases} & \quad \text{(loss of electrons)} \\
\text{Zn} + \text{Cu}^{2+} & \rightarrow \text{Zn}^{2+} + \text{Cu} \\
0 + 2 & \rightarrow 2 + 0
\end{align*}
\]

In the oxidation half-reaction, the element zinc undergoes an increase in its oxidation number from 0 to +2.

\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \]

\[ 0 \quad +2 \]

In the reduction half-reaction, the element copper undergoes a decrease in its oxidation number from +2 to 0.

\[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \]

\[ +2 \quad 0 \]
Therefore, you can describe oxidation and reduction as follows. (Also see Figure 18.8.)

- **Oxidation** is an increase in oxidation number.
- **Reduction** is a decrease in oxidation number.

You can also monitor changes in oxidation numbers in reactions that involve covalent molecules. For example, oxidation number changes occur in the reaction of hydrogen and oxygen to form water.

\[
2H_2(g) + O_2(g) \rightarrow 2H_2O(l)
\]

Because hydrogen combines with oxygen in this reaction, hydrogen undergoes oxidation, according to the historical definition given at the beginning of section 10.1. Hydrogen also undergoes oxidation according to the modern definition, because the oxidation number of hydrogen increases from 0 to +1. Hydrogen is the reducing agent in this reaction. The oxygen undergoes reduction, because its oxidation number decreases from 0 to −2. Oxygen is the oxidizing agent in this reaction.

The following Sample Problem illustrates how to use oxidation numbers to identify redox reactions, oxidizing agents, and reducing agents.

**Sample Problem**

**Identifying Redox Reactions**

**Problem**

Determine whether each of the following reactions is a redox reaction. If so, identify the oxidizing agent and the reducing agent.

(a) CH\(_4\)(g) + Cl\(_2\)(g) → CH\(_3\)Cl(g) + HCl(g)

(b) CaCO\(_3\)(s) + 2HCl(aq) → CaCl\(_2\)(aq) + H\(_2\)O(l) + CO\(_2\)(g)

**Solution**

Find the oxidation number of each element in the reactants and products. Identify any elements that undergo an increase or a decrease in oxidation number during the reaction.

(a) The oxidation number of each element in the reactants and products is as shown.

\[
\begin{array}{cccc}
\text{CH}_4(g) & \text{Cl}_2(g) & \text{CH}_3\text{Cl}(g) & \text{HCl}(g) \\
-4 & 0 & -1 & -1 \\
\end{array}
\]

- The oxidation number of hydrogen is +1 on both sides of the equation, so hydrogen is neither oxidized nor reduced.
- Both carbon and chlorine undergo changes in oxidation number, so the reaction is a redox reaction.
- The oxidation number of carbon increases from −4 to −2. The carbon atoms on the reactant side exist in methane molecules, CH\(_4\)(g), so methane is oxidized. Therefore, methane is the reducing agent.
- The oxidation number of chlorine decreases from 0 to −1, so elemental chlorine, Cl\(_2\)(g), is reduced. Therefore, elemental chlorine is the oxidizing agent.

(b) Because this reaction involves ions, write the equation in its total ionic form.

\[
\text{CaCO}_3(s) + 2\text{H}^+(aq) + 2\text{Cl}^-(aq) \rightarrow \text{Ca}^{2+}(aq) + 2\text{Cl}^-(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)
\]
In previous courses, you classified reactions into four main types: synthesis, decomposition, single displacement, and double displacement. You also learned to recognize combustion reactions and neutralization reactions. You have now learned to classify redox reactions. In addition, you have also learned about a special type of redox reaction known as a disproportionation reaction.

1. **Concept Check**

   In this section, you extended your knowledge of redox reactions to include covalent reactants and products. You did this by learning how to assign oxidation numbers and how to use them to recognize redox reactions, oxidizing agents, and reducing agents. In the next section, you will extend your knowledge further by learning how to write balanced equations that represent redox reactions.

   **Practice Problems**

   13. Determine whether each reaction is a redox reaction.
      
      (a) \( \text{H}_2\text{O}_2 + 2\text{Fe(OH)}_2 \rightarrow 2\text{Fe(OH)}_3 \)
      (b) \( \text{PCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4 + 3\text{HCl} \)

   14. Identify the oxidizing agent and the reducing agent for the redox reaction(s) in the previous question.

   15. For the following balanced net ionic equation, identify the reactant that undergoes oxidation and the reactant that undergoes reduction.
      
      \[ \text{Br}_2 + 2\text{ClO}_2^- \rightarrow 2\text{Br}^- + 2\text{ClO}_2 \]

   16. Nickel and copper are two metals that have played a role in the economy of Newfoundland and Labrador. Nickel and copper ores usually contain the metals as sulfides, such as NiS and CuS. Do the extractions of these pure elemental metals from their ores involve redox reactions? Explain your reasoning.

   **Section Review**

   1. At the beginning of section 18.1, it was stated that oxidation originally meant “to combine with oxygen.” Explain why a metal that combines with the element oxygen undergoes oxidation as we now define it. What happens to the oxygen in this reaction? Write a balanced chemical equation for a reaction that illustrates your answer.

   2. Determine whether each of the following reactions is a redox reaction.
      
      (a) \( \text{H}_2 + \text{I}_2 \rightarrow 2\text{HI} \)
      (b) \( 2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \)
      (c) \( 2\text{HBr} + \text{Ca(OH)}_2 \rightarrow \text{CaBr}_2 + 2\text{H}_2\text{O} \)
      (d) \( \text{PCl}_5 \rightarrow \text{PCl}_3 + \text{Cl}_2 \)
Write three different definitions for a redox reaction.

Explain why fluorine has an oxidation number of $-1$ in all its compounds.

When an element combines with another element, is the reaction a redox reaction? Explain your answer.

(a) Use the oxidation number rules to find the oxidation number of sulfur in a thiosulfate ion, $S_2O_3^{2-}$.

(b) The Lewis structure of a thiosulfate ion is given here. Use the Lewis structure to find the oxidation number of each sulfur atom.

\[
\begin{array}{c}
\cdot \cdot \cdot : O : \\
\cdot \cdot \cdot : S : S : \\
\cdot \cdot \cdot : O : 
\end{array}
\]

(c) Compare your results from parts (a) and (b) and explain any differences.

(d) What are the advantages and disadvantages of using Lewis structures to assign oxidation numbers?

(e) What are the advantages and disadvantages of using the oxidation number rules to assign oxidation numbers?

(a) The Haber Process for the production of ammonia from nitrogen and hydrogen is a very important industrial process. Write a balanced chemical equation for the reaction. Use oxidation numbers to identify the oxidizing agent and the reducing agent.

(b) When ammonia is reacted with nitric acid to make the common fertilizer ammonium nitrate, is the reaction a redox reaction? Explain. (Hint: Consider the two polyatomic ions in the product separately.)

Historically, the extraction of a metal from its ore was known as reduction. One way to reduce iron ore on an industrial scale is to use a huge reaction vessel, 30 m to 40 m high, called a blast furnace. The reactants in a blast furnace are an impure iron ore, such as $Fe_2O_3$, mixed with limestone, $CaCO_3$, and coke, C, which is made from coal. The solid mixture is fed into the top of the blast furnace. A blast of very hot air, at about 900˚C, is blown in near the bottom of the furnace. The following reactions occur.

\[
\begin{align*}
2C + O_2 & \rightarrow 2CO \\
Fe_2O_3 + 3CO & \rightarrow 2Fe + 3CO_2 \\
CaCO_3 & \rightarrow CaO + CO_2 \\
CaO + SiO_2 & \rightarrow CaSiO_3 
\end{align*}
\]

(a) Which of the four reactions above are redox reactions?

(b) For each redox reaction that you identified in part (a), name the oxidizing agent and the reducing agent.
18.3 The Half-Reaction Method for Balancing Equations

Did you know that redox reactions are an important part of CD manufacturing? The CDs you buy at a music store are made of Lexan®, the same plastic used for riot shields and bulletproof windows. The CDs are coated with a thin aluminum film. They are copies of a single master disc, which is made of glass coated with silver, as seen in Figure 18.9. Silver is deposited on a glass disc by the reduction of silver ions with methanal, HCHO, also known as formaldehyde. In the same reaction, formaldehyde is oxidized to methanoic acid, HCOOH, also known as formic acid. The redox reaction occurs under acidic conditions.

You have seen many balanced chemical equations and net ionic equations that represent redox reactions. There are specific techniques for balancing these equations. These techniques are especially useful for reactions that take place under acidic or basic conditions, such as the acidic conditions used in coating a master CD with silver.

In section 18.1, you learned to divide the balanced equations for some redox reactions into separate oxidation and reduction half-reactions. You will now use the reverse approach, and discover how to write a balanced equation by combining two half-reactions. To do this, you must first understand how to write a wide range of half-reactions.
Balancing Half-Reactions

In the synthesis of potassium chloride from its elements, metallic potassium is oxidized to form potassium ions, and gaseous chlorine is reduced to form chloride ions. This reaction is shown in Figure 18.10. Each half-reaction can be balanced by writing the correct formulas for the reactant and product, balancing the numbers of atoms, and then adding the correct number of electrons to balance the charges. For the oxidation half-reaction,

\[ K \rightarrow K^+ + e^- \]

The atoms are balanced. The net charge on each side is 0. For the reduction half-reaction,

\[ Cl_2 + 2e^- \rightarrow 2Cl^- \]

The atoms are balanced. The net charge on each side is −2.

Figure 18.10  Grey potassium metal, which is stored under oil, reacts very vigorously with greenish-yellow chlorine gas to form white potassium chloride. The changes in oxidation numbers show that this synthesis reaction is also a redox reaction.

Redox reactions do not always take place under neutral conditions. Balancing half-reactions is more complicated for reactions that take place in acidic or basic solutions. When an acid or base is present, $H^+$ or $OH^-$ ions must also be considered. However, the overall approach is similar. This approach involves writing the correct formulas for the reactants and products, balancing the atoms, and adding the appropriate number of electrons to one side of the half-reaction to balance the charges.
Balancing Half-Reactions for Acidic Solutions
The following steps are used to balance a half-reaction for an acidic solution. The Sample Problem that follows applies these steps.

Step 1  Write an unbalanced half-reaction that shows the formulas of the given reactant(s) and product(s).
Step 2  Balance any atoms other than oxygen and hydrogen first.
Step 3  Balance any oxygen atoms by adding water molecules.
Step 4  Balance any hydrogen atoms by adding hydrogen ions.
Step 5  Balance the charges by adding electrons.

Sample Problem
Balancing a Half-Reaction in Acidic Solution

Problem
Write a balanced half-reaction that shows the reduction of permanganate ions, MnO₄⁻, to manganese(II) ions in an acidic solution.

Solution
Step 1  Represent the given reactant and product with correct formulas.
MnO₄⁻ → Mn²⁺
Step 2  Balance the atoms, starting with the manganese atoms. Here, the manganese atoms are already balanced.
Step 3  The reduction occurs in aqueous solution, so add water molecules to balance the oxygen atoms.
MnO₄⁻ → Mn²⁺ + 4H₂O
Step 4  The reaction occurs in acidic solution, so add hydrogen ions to balance the hydrogen atoms.
MnO₄⁻ + 8H⁺ → Mn²⁺ + 4H₂O
Step 5  The atoms are now balanced, but the net charge on the left side is 7⁺, whereas the net charge on the right side is 2⁺. Add five electrons to the left side to balance the charges.
MnO₄⁻ + 8H⁺ + 5e⁻ → Mn²⁺ + 4H₂O

Practice Problems

17. Write a balanced half-reaction for the reduction of cerium(IV) ions to cerium(III) ions.
18. Write a balanced half-reaction for the oxidation of bromide ions to bromine.
19. Balance each of the following half-reactions under acidic conditions.
   (a) O₂ → H₂O₂      (b) H₂O → O₂      (c) NO₃⁻ → N₂
20. Balance each of the following half-reactions under acidic conditions.
   (a) ClO₃⁻ → Cl⁻      (b) NO → NO₃⁻     (c) Cr₂O₇²⁻ → Cr³⁺
Balancing Half-Reactions for Basic Solutions

The following steps are used to balance a half-reaction for a basic solution. The Sample Problem that follows applies these steps.

**Step 1** Write an unbalanced half-reaction that shows the formulas of the given reactant(s) and product(s).

**Step 2** Balance any atoms other than oxygen and hydrogen first.

**Step 3** Balance any oxygen and hydrogen atoms as if the conditions are acidic.

**Step 4** Adjust for basic conditions by adding to both sides the same number of hydroxide ions as the number of hydrogen ions already present.

**Step 5** Simplify the half-reaction by combining the hydrogen ions and hydroxide ions on the same side of the equation into water molecules.

**Step 6** Remove any water molecules present on both sides of the half-reaction.

**Step 7** Balance the charges by adding electrons.

---

Sample Problem

**Balancing a Half-Reaction in Basic Solution**

**Problem**

Write a balanced half-reaction that shows the oxidation of thiosulfate ions, \( S_2O_3^{2−} \), to sulfite ions, \( SO_3^{2−} \), in a basic solution.

**Solution**

**Step 1** Represent the given reactant and product with correct formulas.

\[
S_2O_3^{2−} \rightarrow SO_3^{2−}
\]

**Step 2** Balance the atoms, beginning with the sulfur atoms.

\[
S_2O_3^{2−} \rightarrow 2SO_3^{2−}
\]

**Step 3** Balance the oxygen and hydrogen atoms as if the solution is acidic.

\[
S_2O_3^{2−} + 3H_2O \rightarrow 2SO_3^{2−} \quad \text{and} \quad S_2O_3^{2−} + 3H_2O \rightarrow 2SO_3^{2−} + 6H^+
\]

**Step 4** There are six hydrogen ions present, so adjust for basic conditions by adding six hydroxide ions to each side.

\[
S_2O_3^{2−} + 3H_2O + 6OH^- \rightarrow 2SO_3^{2−} + 6H^+ + 6OH^-
\]

**Step 5** Combine the hydrogen ions and hydroxide ions on the right side into water molecules.

\[
S_2O_3^{2−} + 3H_2O + 6OH^- \rightarrow 2SO_3^{2−} + 6H_2O
\]

**Step 6** Remove three water molecules from each side.

\[
S_2O_3^{2−} + 6OH^- \rightarrow 2SO_3^{2−} + 3H_2O
\]

**Step 7** The atoms are now balanced, but the net charge on the left side is \( 8− \), whereas the net charge on the right side is \( 4− \). Add four electrons to the right side to balance the charges.

\[
S_2O_3^{2−} + 6OH^- \rightarrow 2SO_3^{2−} + 3H_2O + 4e^-
\]
Half-Reaction Method for Balancing Redox Reactions

Recall that, if you consider a redox reaction as two half-reactions, electrons are lost in the oxidation half-reaction, and electrons are gained in the reduction half-reaction. For example, you know the reaction of zinc with aqueous copper(II) sulfate.

\[ \text{Zn(s)} + \text{Cu}^{2+} \rightarrow \text{Cu(s)} + \text{Zn}^{2+} \]

Removing the spectator ions leaves the following net ionic equation.

\[ \text{Zn(s)} + \text{Cu}^{2+} \rightarrow \text{Cu(s)} + \text{Zn}^{2+} \]

You can break the net ionic equation into two half-reactions:

Oxidation half-reaction: \( \text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^- \)

Reduction half-reaction: \( \text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu} \)

You can also start with the half-reactions and use them to produce a net ionic equation. If you add the two half-reactions, the result is as follows.

\[ \text{Zn} + \text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu} + \text{Zn}^{2+} + 2\text{e}^- \]

Removing the two electrons from each side results in the original net ionic equation.

As shown above, you can use half-reactions to write balanced net ionic equations for redox reactions. In doing so, you use the fact that no electrons are created or destroyed in a redox reaction. Electrons are transferred from one reactant (the reducing agent) to another (the oxidizing agent).

Balancing a Net Ionic Equation

You know from Investigation 18-A that magnesium metal, \( \text{Mg(s)} \), displaces aluminum from an aqueous solution of one of its compounds, such as aluminum nitrate, \( \text{Al(NO}_3\text{)}_3\text{(aq)} \). To obtain a balanced net ionic equation for this reaction, you can start by looking at the half-reactions. Magnesium atoms undergo oxidation to form magnesium ions, which have a 2+ charge. The oxidation half-reaction is as follows.

\[ \text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^- \]

Aluminum ions, which have a 3+ charge, undergo reduction to form aluminum atoms. The reduction half-reaction is as follows.

\[ \text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al} \]

Practice Problems

21. Write a balanced half-reaction for the oxidation of chromium(II) ions to chromium(III) ions.

22. Write a balanced half-reaction for the reduction of oxygen to oxide ions.

23. Balance each of the following half-reactions under basic conditions.
   (a) \( \text{Al} \rightarrow \text{Al(OH)}_4^- \)
   (b) \( \text{CN}^- \rightarrow \text{CNO}^- \)
   (c) \( \text{MnO}_4^- \rightarrow \text{MnO}_2 \)
   (d) \( \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr(OH)}_3 \)
   (e) \( \text{CO}_2\text{O}_4^{2-} \rightarrow \text{C}_2\text{O}_4^{2-} \)

24. Balance each of the following half-reactions.
   (a) \( \text{FeO}_4^{2-} \rightarrow \text{Fe}^{3+} \) (acidic conditions)
   (b) \( \text{ClO}_2^- \rightarrow \text{Cl}^- \) (basic conditions)
To balance the net ionic equation for this redox reaction, you can combine the two half-reactions in such a way that the number of electrons lost through oxidation equals the number of electrons gained through reduction. In other words, you can model the transfer of a certain number of electrons from the reducing agent to the oxidizing agent.

For the reaction of magnesium metal with aluminum ions, the two balanced half-reactions include different numbers of electrons, 2 and 3. The least common multiple of 2 and 3 is 6. To combine the half-reactions and give a balanced net ionic equation, multiply the balanced half-reactions by different numbers so that the results both include six electrons, as shown below.

- Multiply the oxidation half-reaction by 3. Multiply the reduction half-reaction by 2.
  
  $3\text{Mg} \rightarrow 3\text{Mg}^{2+} + 6\text{e}^-$
  
  $2\text{Al}^{3+} + 6\text{e}^- \rightarrow 2\text{Al}$

- Add the results.
  
  $3\text{Mg} + 2\text{Al}^{3+} + 6\text{e}^- \rightarrow 3\text{Mg}^{2+} + 2\text{Al} + 6\text{e}^-$

- Remove $6\text{e}^-$ from each side to obtain the balanced net ionic equation.
  
  $3\text{Mg} + 2\text{Al}^{3+} \rightarrow 3\text{Mg}^{2+} + 2\text{Al}$

To produce the balanced chemical equation, you can include the spectator ions, which are nitrate ions in this example. Include the states, if necessary. The balanced chemical equation is:

$3\text{Mg}(s) + 2\text{Al(NO}_3)_3(aq) \rightarrow 3\text{Mg(NO}_3)_2(aq) + 2\text{Al}(s)$

**Steps for Balancing by the Half-Reaction Method**

You could balance the chemical equation for the reaction of magnesium with aluminum nitrate by inspection, instead of writing half-reactions. However, many redox equations are difficult to balance by the inspection method. In general, you can balance the net ionic equation for a redox reaction by a process known as the half-reaction method. The preceding example of the reaction of magnesium with aluminum nitrate illustrates this method. Specific steps for following the half-reaction method are given below.

**Step 1** Write an unbalanced net ionic equation, if it is not already given.

**Step 2** Divide the unbalanced net ionic equation into an oxidation half-reaction and a reduction half-reaction. To do this, you may need to assign oxidation numbers to all the elements in the net ionic equation to determine what is oxidized and what is reduced.

**Step 3** Balance the oxidation half-reaction and the reduction half-reaction independently.

**Step 4** Determine the least common multiple (LCM) of the numbers of electrons in the oxidation half-reaction and the reduction half-reaction.

Continued on the next page
When using the half-reaction method, keep in mind that, in a redox reaction, the number of electrons lost through oxidation must equal the number of electrons gained through reduction. Figure 10.11 provides another example.

Balancing Redox Reactions in Acidic and Basic Solutions

The half-reaction method of balancing equations can be more complicated for reactions that take place under acidic or basic conditions. The overall approach, however, is the same. You need to balance the two half-reactions, find the LCM of the numbers of electrons, and then multiply by coefficients to equate the number of electrons lost and gained. Finally, add the half-reactions and simplify to give a balanced net ionic equation for the reaction. The ten steps listed above show this process in more detail.

The Sample Problem on the next page illustrates the use of these steps for an acidic solution. To balance a net ionic equation for basic conditions by the half-reaction method, balance each half-reaction for acidic conditions, adjust for basic conditions, and then combine the half-reactions to obtain the balanced net ionic equation. The following Concept Organizer summarizes how to use the half-reaction method in both acidic and basic conditions.
Sample Problem

Balancing a Redox Equation in Acidic Solution

Problem
Write a balanced net ionic equation to show the reaction of perchlorate ions, ClO₄⁻, and nitrogen dioxide in acidic solution to produce chloride ions and nitrate ions.

What Is Required?
You need to write a balanced net ionic equation for the given reaction.

What Is Given?
You know the identities of two reactants and two products, and that the reaction takes place in acidic solution.

Plan Your Strategy
• Write an unbalanced ionic equation.
• Determine whether the reaction is a redox reaction.
• If it is not a redox reaction, balance by inspection.
• If it is a redox reaction, follow the steps for balancing by the half-reaction method.

Act on Your Strategy
• The unbalanced ionic equation is: ClO₄⁻ + NO₂ → Cl⁻ + NO₃⁻
• Assign oxidation numbers to all the elements to determine which reactant, if any, is oxidized or reduced.

ClO₄⁻ + NO₂ → Cl⁻ + NO₃⁻
\(+7\) \(-2\) \(+4\) \(-2\) \(-1\) \(+5\) \(-2\)
The oxidation number of chlorine decreases, so perchlorate ions are reduced to chloride ions.

The oxidation number of nitrogen increases, so nitrogen dioxide is oxidized to nitrate ions.

- This is a redox reaction. Use the half-reaction method to balance the equation.

**Step 1** The unbalanced net ionic equation is already written.

\[ \text{ClO}_4^- + \text{NO}_2 \rightarrow \text{Cl}^- + \text{NO}_3^- \]

**Step 2** Write two unbalanced half-reactions.

- **Oxidation:** \( \text{NO}_2 \rightarrow \text{NO}_3^- \)
- **Reduction:** \( \text{ClO}_4^- \rightarrow \text{Cl}^- \)

**Step 3** Balance the two half-reactions for acidic conditions.

<table>
<thead>
<tr>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NO}_2 \rightarrow \text{NO}_3^- )</td>
<td>( \text{ClO}_4^- \rightarrow \text{Cl}^- + 4\text{H}_2\text{O} )</td>
</tr>
<tr>
<td>( \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + 2\text{H}^+ )</td>
<td>( \text{ClO}_4^- + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{Cl}^- + 4\text{H}_2\text{O} )</td>
</tr>
</tbody>
</table>

**Step 4** The LCM of 1 and 8 is 8.

**Step 5** Multiply the oxidation half-reaction by 8, so that equal numbers of electrons are lost and gained.

\[ 8\text{NO}_2 + 8\text{H}_2\text{O} \rightarrow 8\text{NO}_3^- + 16\text{H}^+ + 8\text{e}^- \]

**Step 6** Add the half reactions.

\[ 8\text{NO}_2 + 8\text{H}_2\text{O} + \text{ClO}_4^- + 8\text{H}^+ + 8\text{e}^- \rightarrow 8\text{NO}_3^- + 16\text{H}^+ + 8\text{e}^- + \text{Cl}^- + 4\text{H}_2\text{O} \]

**Step 7** Simplify by removing 8 electrons from both sides.

\[ 8\text{NO}_2 + 8\text{H}_2\text{O} + \text{ClO}_4^- + 8\text{H}^+ \rightarrow 8\text{NO}_3^- + 16\text{H}^+ + \text{Cl}^- + 4\text{H}_2\text{O} \]

**Step 8** Simplify by removing 4 water molecules, and 8 hydrogen ions from each side.

\[ 8\text{NO}_2 + \text{ClO}_4^- + 4\text{H}_2\text{O} \rightarrow 8\text{NO}_3^- + 8\text{H}^+ + \text{Cl}^- \]

(Steps 9 and 10 are not required for this problem.)

**Check Your Solution**

- The atoms are balanced.
- The charges are balanced.

**Practice Problems**

25. Balance each of the following redox equations by inspection. Write the balanced half-reactions in each case.

(a) \( \text{Na} + \text{F}_2 \rightarrow \text{NaF} \)

(b) \( \text{Mg} + \text{N}_2 \rightarrow \text{Mg}_3\text{N}_2 \)

(c) \( \text{HgO} \rightarrow \text{Hg} + \text{O}_2 \)

26. Balance the following equation by the half-reaction method.

\( \text{Cu}^{2+} + \text{I}^- \rightarrow \text{CuI} + \text{I}_3^- \)
27. Balance each of the following ionic equations for acidic conditions. Identify the oxidizing agent and the reducing agent in each case.

(a) \( \text{MnO}_4^- + \text{Ag} \rightarrow \text{Mn}^{2+} + \text{Ag}^+ \)
(b) \( \text{Hg} + \text{NO}_3^- + \text{Cl}^- \rightarrow \text{HgCl}_4^{2-} + \text{NO}_2 \)
(c) \( \text{AsH}_3 + \text{Zn}^{2+} \rightarrow \text{H}_3\text{AsO}_4 + \text{Zn} \)
(d) \( \text{I}_3^- \rightarrow \text{I}^- + \text{IO}_3^- \)

28. Balance each of the following ionic equations for basic conditions. Identify the oxidizing agent and the reducing agent in each case.

(a) \( \text{CN}^- + \text{MnO}_4^- \rightarrow \text{CNO}^- + \text{MnO}_2 \)
(b) \( \text{H}_2\text{O}_2 + \text{ClO}_2 \rightarrow \text{ClO}_2^- + \text{O}_2 \)
(c) \( \text{ClO}^- + \text{CrO}_2^- \rightarrow \text{CrO}_4^{2-} + \text{Cl}_2 \)
(d) \( \text{Al} + \text{NO}_2^- \rightarrow \text{NH}_3 + \text{AlO}_2^- \)

In the next investigation, you will carry out several redox reactions, including reactions of acids with metals, and the combustion of hydrocarbons.

**Tools & Techniques**

**The Breathalyzer Test: A Redox Reaction**

The police may pull over a driver weaving erratically on the highway on suspicion of drunk driving. A police officer must confirm this suspicion by assessing whether the driver has a blood alcohol concentration over the “legal limit.” The “Breathalyzer” test checks a person’s breath using a redox reaction to determine blood alcohol concentration. This test was invented in 1953 by Robert Borkenstein, a former member of the Indiana State Police, and a professor of forensic studies.

What does a person’s breath have to do with the alcohol in his or her blood? In fact, there is a direct correlation between the concentration of alcohol in an exhaled breath and the concentration of alcohol in the blood.

As blood moves through the lungs, it comes in close contact with inhaled gases. If the blood contains alcohol, the concentration of alcohol in the blood quickly reaches equilibrium with the concentration of alcohol in each inhaled breath. Thus, the alcohol content in an exhaled breath is a measure of the alcohol concentration in the blood itself. For example, if a person has been drinking alcohol, every 2100 mL of air exhaled contains about the same amount of alcohol as 1 mL of blood.

In the Breathalyzer test, the subject blows into a tube connected to a vial. The exhaled air collects in the vial, which already contains a mixture of sulfuric acid, potassium dichromate, water, and the catalyst silver nitrate. The alcohol reacts with the dichromate ion in the following redox reaction.

\[
16\text{H}^+ + 2\text{Cr}_2\text{O}_7^{2-} + 3\text{C}_2\text{H}_5\text{OH} \rightarrow (\text{orange})
\]

\[4\text{Cr}^{3+} + 3\text{C}_2\text{H}_5\text{O}_2^- + 11\text{H}_2\text{O} \rightarrow (\text{green})
\]

This reaction is accompanied by a visible colour change, as orange dichromate ions become green chromium(III) ions. The concentration of alcohol in the blood is determined by measuring the intensity of the final colour.

A recent modification of the Breathalyzer test prevents drivers from starting their cars if they have been drinking. Alcohol ignition locks involve a type of Breathalyzer test that is linked to the car’s ignition system. Until the driver passes the test, the car will not start. This test is useful in regulating the driving habits of people who have been previously convicted of drinking and driving.
Redox Reactions and Balanced Equations

A redox reaction involves the transfer of electrons between reactants. A reactant that loses electrons is oxidized and acts as a reducing agent. A reactant that gains electrons is reduced and acts as an oxidizing agent. Redox reactions can be represented by balanced equations.

Questions
How can you tell if a redox reaction occurs when reactants are mixed? Can you observe the transfer of electrons in the mixture?

Predictions
• Predict which of the metals magnesium, zinc, copper, and aluminum can be oxidized by aqueous hydrogen ions. Explain your reasoning.
• Predict whether metals that cannot be oxidized by hydrogen ions can dissolve in acids. Explain your reasoning.
• Predict whether the combustion of a hydrocarbon is a redox reaction. What assumptions have you made about the products?

Materials
well plate
4 small test tubes
test tube rack
small pieces of each of the metals magnesium, zinc, copper, and aluminum
dilute hydrochloric acid (1 mol/L)
dilute sulfuric acid (1 mol/L)
Bunsen burner
candle

Safety Precautions
• The acid solutions are corrosive. Handle them with care.

Procedure
Part 1 Reactions of Acids
1. Place a small piece of each metal on the well plate. Add a few drops of hydrochloric acid to each metal. Record your observations. If you are unsure of your observations, repeat the procedure on a larger scale in a small test tube.

2. Place another small piece of each metal on clean sections of the well plate. Add a few drops of sulfuric acid to each metal. Record your observations. If you are unsure of your observations, repeat the procedure on a larger scale in a small test tube.

3. Dispose of the mixtures in the beaker supplied by your teacher.

Part 2 Combustion of Hydrocarbons
4. Observe the combustion of natural gas in a Bunsen burner. Adjust the colour of the flame by varying the quantity of oxygen admitted to the burner. How does the colour depend on the quantity of oxygen?

5. Observe the combustion of a candle. Compare the colour of the flame with the colour of the Bunsen burner flame. Which adjustment of the burner makes the colours of the two flames most similar?
Analysis

Part 1 Reactions of Acids

1. Write a balanced chemical equation for each of the reactions of an acid with a metal.

2. Write each equation from question 1 in net ionic form.

3. Determine which of the reactions from question 1 are redox reactions.

4. Write each redox reaction from question 3 as two half-reactions.

5. Explain any similarities in your answers to question 4.

6. In the reactions you observed, are the hydrogen ions acting as an oxidizing agent, a reducing agent, or neither?

7. In the neutralization reaction of hydrochloric acid and sodium hydroxide, do the hydrogen ions behave in the same way as you found in question 6? Explain.

8. Your teacher may demonstrate the reaction of copper with concentrated nitric acid to produce copper(II) ions and brown, toxic nitrogen dioxide gas. Write a balanced net ionic equation for this reaction. Do the hydrogen ions behave in the same way as you found in question 6? Identify the oxidizing agent and the reducing agent in this reaction.

9. From your observations of copper with hydrochloric acid and nitric acid, can you tell whether hydrogen ions or nitrate ions are the better oxidizing agent? Explain.

Part 2 Combustion of Hydrocarbons

10. The main component of natural gas is methane, CH₄. The products of the combustion of this gas in a Bunsen burner depend on how the burner is adjusted. A blue flame indicates complete combustion. What are the products in this case? Write a balanced chemical equation for this reaction.

11. A yellow or orange flame from a Bunsen burner indicates incomplete combustion and the presence of carbon in the flame. Write a balanced chemical equation for this reaction.

12. Name another possible carbon-containing product from the incomplete combustion of methane. Write a balanced chemical equation for this reaction.

13. The fuel in a burning candle is paraffin wax, C₂₅H₅₂. Write a balanced chemical equation for the complete combustion of paraffin wax.

14. Write two balanced equations that represent the incomplete combustion of paraffin wax.

15. How do you know that at least one of the incomplete combustion reactions is taking place when a candle burns?

16. Are combustion reactions also redox reactions? Does your answer depend on whether the combustion is complete or incomplete? Explain.

Conclusion

17. How could you tell if a redox reaction occurred when reactants were mixed? Could you observe the transfer of electrons in the mixture?

Applications

18. Gold is very unreactive and does not dissolve in most acids. However, it does dissolve in aqua regia (Latin for “royal water”), which is a mixture of concentrated hydrochloric and nitric acids. The unbalanced ionic equation for the reaction is as follows.

\[ \text{Au} + \text{NO}_3^- + \text{Cl}^- \rightarrow \text{AuCl}_4^- + \text{NO}_2 \]

Balance the equation, and identify the oxidizing agent and reducing agent.

19. Natural gas is burned in gas furnaces. Give at least three reasons why this combustion reaction should be as complete as possible. How would you try to ensure complete combustion?
Stoichiometry and Redox Titrations

Redox titrations are an important application of redox chemistry and stoichiometry. In an acid-base titration, a base is used to find the concentration of an acid, or vice versa. Similarly, in a redox titration, a known concentration of an oxidizing agent can be used to find the unknown concentration of a reducing agent, or vice versa. Redox titrations are used in a wide range of situations, including measuring the iron content in drinking water and the vitamin C content in foods or vitamin supplements.

The permanganate ion, MnO$_4^-$, is commonly used as an oxidizing agent in redox titrations. It is particularly useful because it has a strong purple colour, meaning that no additional indicator is needed to determine the endpoint of the titration. Figure 18.X shows the titration of a solution of sodium oxalate, Na$_2$C$_2$O$_4$(aq), with a solution of potassium permanganate, KMnO$_4$(aq).

As long as there are oxalate ions present in solution, they reduce the manganese with oxidation number $+7$ present in purple permanganate ions to nearly colourless manganese(II) ions, Mn$^{2+}$, where the oxidation number is $+2$). Once all oxalate ions have been oxidized, the next drop of potassium permanganate solution turns the solution faint purple. This purple colour signals the endpoint of the titration.

The permanganate ion may also be used to oxidize hydrogen peroxide, H$_2$O$_2$. The following equation shows the redox reaction in acidic conditions.

$$5\text{H}_2\text{O}_2(\text{aq}) + 2\text{MnO}_4^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 5\text{O}_2(g) + 2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O}(\ell)$$

Aqueous solutions of hydrogen peroxide sold in pharmacies are often about 3% H$_2$O$_2$ by mass. In solution, however, hydrogen peroxide decomposes steadily to form water and oxygen.

Suppose that you need to use hydrogen peroxide solution with a concentration of at least 2.5% by mass for a certain experiment. Your 3% H$_2$O$_2$ is not fresh, so it may have decomposed significantly. How do you find out if your H$_2$O$_2$ solution is concentrated enough? The following Sample Problem shows how to solve this problem using data from the titration of the hydrogen peroxide solution with a solution of potassium permanganate.
Problem
You are using 0.01143 mol/L KMnO₄(aq) to determine the percentage by mass of an aqueous solution of H₂O₂. You know that the solution is about 3% H₂O₂ by mass.

You prepare the sample by adding 1.423 g of the hydrogen peroxide solution to an Erlenmeyer flask. You add about 75 mL of water to dilute the solution. You also add some dilute sulfuric acid to acidify the solution. You reach the purple-coloured endpoint of the titration when you have added 40.22 mL of the KMnO₄(aq) solution.

What is Required?
You need to determine the mass of H₂O₂ in the sample. You need to express your result as a mass percent.

What is Given?
Concentration of KMnO₄(aq) = 0.01143 mol/L
Volume of KMnO₄(aq) = 40.22 mL
Mass of 3% H₂O₂ solution = 1.423 g

Plan Your Strategy
Step 1 Write the balanced chemical equation for the reaction.
Step 2 Calculate the amount (in mol) of permanganate ion added, based on the volume and concentration of the potassium permanganate solution.
Step 3 Determine the amount (in mol) of hydrogen peroxide needed to reduce the permanganate ions.
Step 4 Determine the mass of hydrogen peroxide, based on the molar mass of hydrogen peroxide. Finally, express your answer as a mass percent of the hydrogen peroxide solution, as the question directs.

Act on Your Strategy
Step 1 The redox equation was provided on the previous page. It is already balanced.

5H₂O₂ + 2MnO₄⁻ + 6H⁺ → 5O₂ + 2Mn²⁺ + 8H₂O

Step 2 The concentration of MnO₄⁻(aq) is the same as the concentration of KMnO₄(aq).

\[ n = C \times V \]
\[ = 0.01143 \text{ mol/L} \times 0.04022 \text{ L} \]
\[ = 4.597 \times 10^{-4} \text{ mol} \]

Step 3 Permanganate ion reacts with hydrogen peroxide in a 2:5 ratio.

Amount (in mol)H₂O₂ = \( \frac{5 \text{ mol H}_{2}\text{O}_{2}}{2 \text{ mol MnO}_4^-} \times 4.597 \times 10^{-4} \text{ mol MnO}_4^- \)
\[ = 1.149 \times 10^{-3} \text{ mol H}_2\text{O}_2 \]

Step 4

Mass (in g) H₂O₂ = 1.149 \times 10^{-3} \text{ mol} \times 34.02 \text{ g/mol}
\[ = 0.03909 \text{ g} \]
Mass percent $\text{H}_2\text{O}_2$ in solution = $0.03909 \text{ g}/1.423 \text{ g}$

$= 2.747\%$

**Check Your Solution**
The units are correct. The value for the mass of pure $\text{H}_2\text{O}_2$ that you obtained is less than the mass of the $\text{H}_2\text{O}_2(\text{aq})$ sample solution, as you would expect. The mass percent you obtained for the solution is close to the expected value. It makes sense that the value is somewhat less than 3%, since $\text{H}_2\text{O}_2$ decomposes in solution, forming water and oxygen.

**Practice Problems**

29. An analyst uses 0.02045 mol/L $\text{KMnO}_4$ to titrate a sample solution of $\text{H}_2\text{O}_2$. The analyst knows that the sample solution is about 6% $\text{H}_2\text{O}_2$ by mass. The analyst places 1.284 g of $\text{H}_2\text{O}_2$ solution in a flask, dilutes it with water, and adds a small amount of sulfuric acid to acidify it. It takes 38.95 mL of $\text{KMnO}_4$ solution to reach the endpoint. What mass of pure $\text{H}_2\text{O}_2$ was present? What is the mass percent of pure $\text{H}_2\text{O}_2$ in the original sample solution?

30. A forensic chemist wants to determine the level of alcohol in a sample of blood plasma. The chemist titrates the plasma with a solution of potassium dichromate. The balanced equation is:

$$16\text{H}^+ + 2\text{Cr}_2\text{O}_7^{2-} + \text{C}_2\text{H}_5\text{OH} \rightarrow 4\text{Cr}^{3+} + 2\text{CO}_2 + 11\text{H}_2\text{O}$$

If 32.35 mL of 0.05023 mol/L $\text{Cr}_2\text{O}_7^{2-}$ is required to titrate 27.00 g plasma, what is the mass percent of alcohol in the plasma?

31. An analyst titrates an acidified solution containing 0.153 g of purified sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$, with a potassium permanganate solution, $\text{KMnO}_4(\text{aq})$. The purple endpoint is reached when the chemist has added 41.45 mL of potassium permanganate solution. What is the molar concentration of the potassium permanganate solution? The balanced equation is:

$$2\text{MnO}_4^- + 5\text{H}_2\text{C}_2\text{O}_4 + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$$

32. 25.00 mL of a solution containing iron(II) ions was titrated with a 0.02043 mol/L potassium dichromate solution. The endpoint was reached when 35.55 mL of potassium dichromate solution had been added. What was the molar concentration of iron(II) ions in the original, acidic solution? The unbalanced equation is:

$$\text{Cr}_2\text{O}_7^{2-} + \text{Fe}^{2+} \rightarrow \text{Cr}^{3+} + \text{Fe}^{3+}$$

**PROBLEM TIP**

In question 32, you will need to balance the redox equation before solving the problem.
Section Summary

In this section, you learned the half-reaction method for balancing equations for redox reactions. You investigated the redox reactions of metals with acids, and the combustion of two hydrocarbons. You also learned how known concentrations of oxidizing agents can be used to find the unknown concentrations of reducing agents, or vice versa, in redox titrations.

Section Review

1. Balance each half-reaction. Identify it as an oxidation or reduction half-reaction.
   - (a) C → C_2^2-
   - (b) S_2O_3^{2-} → S_4O_6^{2-}
   - (c) AsO_4^{3-} → As_4O_6 (acidic conditions)
   - (d) Br_2 → BrO_3^- (basic conditions)

2. Balance each equation.
   - (a) Co^{3+} + Au → Co^{2+} + Au^{3+}
   - (b) Cu + NO_3^- → Cu^{2+} + NO (acidic conditions)
   - (c) NO_3^- + Al → NH_3 + AlO_2^- (basic conditions)

3. This section began with a description of the use of a redox reaction to make the master disc in the production of CDs. Write a balanced net ionic equation for the reaction of silver ions with methanal under acidic conditions to form metallic silver and methanoic acid.

4. In basic solution, ammonia, NH₃, can be oxidized to dinitrogen monoxide, N₂O.
   - (a) Try to balance the half-reaction by adding water molecules, hydroxide ions, and electrons, without first assuming acidic conditions. Describe any difficulties you encounter.
   - (b) Balance the half-reaction by first assuming acidic conditions and then adjusting to introduce the hydroxide ions. Compare your findings with those from part (a).

5. A mixture of liquid hydrazine, N₂H₄, and liquid dinitrogen tetroxide can be used as a rocket fuel. The products of the reaction are nitrogen gas and water vapour.
   - (a) Write a balanced chemical equation for the reaction by inspection.
   - (b) Identify the oxidizing agent and the reducing agent.
   - (c) Hydrazine is made in the Raschig Process. In this process, ammonia reacts with hypochlorite ions in a basic solution to form hydrazine and chloride ions. Write the balanced net ionic equation.

6. Ben and Larissa were working together to balance the following equation for a redox reaction.
   \[ \text{Zn} + \text{SO}_4^{2-} + \text{H}^+ \rightarrow \text{Zn}^{2+} + \text{S} + \text{H}_2\text{O} \]
   Ben suggested balancing by inspection, with the following result.
   \[ \text{Zn} + \text{SO}_4^{2-} + 8\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{S} + 4\text{H}_2\text{O} \]
   Larissa said: “That’s not balanced.”
   - (a) Was Larissa right? Explain.
   - (b) How would you balance the equation, and what would the result be?
Oxygen and other oxidizing agents can react harmfully with your body. Vitamin C acts as an antioxidant. It is very easily oxidized, so it reacts with oxidizing agents, preventing them from reacting with other important molecules in the body. Vitamin C is relatively stable when oxidized. Therefore, it does not propagate a harmful series of oxidation reactions. One way to determine the vitamin C content of a sample is to titrate it with an iodine/iodine solution. The diagram below shows the reaction involved.

In the iodine solution, iodine, \( I_2 \), and iodide, \( I^- \), ions are in equilibrium with triiodide, as shown below.

\[
I_2 + I^- \rightleftharpoons I_3^-
\]

Molecular iodine is a deep violet-red colour. Iodine ions are colourless. Thus, when an antioxidant reduces the iodine molecules in a solution, the iodine colour disappears completely.

(a) In storage, the concentration of iodine in solution decreases fairly quickly over time. Why do you think this happens?

(b) Because the iodine solution’s concentration is not stable, it should be standardized frequently. To standardize an iodine solution, use it to titrate a solution that contains a known quantity of vitamin C. Explain how you would standardize a solution of iodine using vitamin C tablets from a pharmacy.

(c) To standardize iodine using vitamin C tablets, you should use fresh tablets. Explain why.

If you titrate orange juice that has been exposed to the air for a week, will the vitamin C concentration be different from the vitamin C concentration in fresh juice? If so, will it decrease or increase? Explain your prediction, in terms of redox reactions.

A chemist adds a few drops of deep violet-red iodine to a vitamin C tablet. The iodine solution quickly becomes colourless. Then the chemist adds a solution that contains chlorine, \( Cl_2 \). The chemist observes that the violet-red colour of the iodine reappears. Explain the chemist’s observations, in terms of redox reactions.
In this section, you will write balanced equations for redox reactions using the oxidation number method.

In section 18.2, you learned that a redox reaction involves changes in oxidation numbers. If an element undergoes oxidation, its oxidation number increases. If an element undergoes reduction, its oxidation number decreases. When balancing equations by the half-reaction method in section 18.3, you sometimes used oxidation numbers to determine the reactant(s) and product(s) in each half-reaction.

In fact, you can use oxidation numbers to balance a chemical equation by a new method. The oxidation number method is a method of balancing redox equations by ensuring that the total increase in the oxidation numbers of the oxidized element(s) equals the total decrease in the oxidation numbers of the reduced element(s).

For example, the combustion of ammonia in oxygen produces nitrogen dioxide and water.

\[
\text{NH}_3 + \text{O}_2 \rightarrow \text{NO}_2 + \text{H}_2\text{O}
\]

The oxidation number of nitrogen increases from $-3$ to $+4$, an increase of 7. The oxidation number of oxygen decreases from 0 to $-2$, a decrease of 2. The least common multiple of 7 and 2 is 14. In this case, two nitrogen atoms must react for every seven oxygen atoms so that the total increase and decrease in oxidation numbers both equal 14.

\[
2\text{NH}_3 + \frac{7}{2}\text{O}_2 \rightarrow \text{NO}_2 + \text{H}_2\text{O}
\]

Complete the equation by inspection. If necessary, eliminate the fraction.

\[
2\text{NH}_3 + \frac{7}{2}\text{O}_2 \rightarrow 2\text{NO}_2 + 3\text{H}_2\text{O}
\]

\[
4\text{NH}_3 + 7\text{O}_2 \rightarrow 4\text{NO}_2 + 6\text{H}_2\text{O}
\]

A summary of the steps of the oxidation number method is given below. The following Sample Problem shows how these steps are applied.

**Step 1** Write an unbalanced equation, if it is not given.

**Step 2** Determine whether the reaction is a redox reaction by assigning an oxidation number to each element wherever it appears in the equation.

**Step 3** If the reaction is a redox reaction, identify the element(s) that undergo an increase in oxidation number and the element(s) that undergo a decrease in oxidation number.

**Step 4** Find the numerical values of the increase and the decrease in oxidation numbers.

**Step 5** Determine the smallest whole-number ratio of the oxidized and reduced elements so that the total increase in oxidation numbers equals the total decrease in oxidation numbers.

**Step 6** Use the smallest whole-number ratio to balance the numbers of atoms of the element(s) oxidized and the element(s) reduced.

*continued on the next page*
Step 7  Balance the other elements by inspection, if possible.

Step 8  For reactions that occur in acidic or basic solutions, include water molecules, hydrogen ions, or hydroxide ions as needed to balance the equation.

Sample Problem

Balancing a Redox Equation in Basic Solution

Problem
Write a balanced net ionic equation to show the formation of iodine by bubbling oxygen gas through a basic solution that contains iodide ions.

Solution
Step 1  Write an unbalanced equation from the given information.
\[ \text{O}_2 + \text{I}^- \rightarrow \text{I}_2 \]

Step 2  Assign oxidation numbers to see if it is a redox reaction.
\[ \begin{array}{c|c}
\text{O}_2 & \text{I}^- & \text{I}_2 \\
0 & 0 & 0
\end{array} \]
Because iodide is oxidized to iodine, the reaction is a redox reaction. Though the product that contains oxygen is unknown at this stage, oxygen must be reduced.

Step 3  Iodine is the element that undergoes an increase in oxidation number. Oxygen is the element that undergoes a decrease in oxidation number.

Step 4  Iodine undergoes an increase in its oxidation number from \(-1\) to 0, an increase of 1. Assume that the oxidation number of oxygen after reduction is its normal value, that is, \(-2\). Thus, oxygen undergoes a decrease in its oxidation number from 0 to \(-2\), a decrease of 2.

Step 5  A 2:1 ratio of iodine atoms to oxygen atoms ensures that the total increase in oxidation numbers and the total decrease in oxidation numbers are both equal to 2. This is the smallest whole-number ratio.

Step 6  Use the ratio to balance the numbers of atoms of iodine and oxygen. Make sure there are two iodine atoms for every oxygen atom.
\[ \text{O}_2 + 4\text{I}^- \rightarrow 2\text{I}_2 \]

Step 7  No other reactants or products can be balanced by inspection.

Step 8  The reaction occurs in basic solution. As you learned in section 10.3, for basic conditions, start by assuming that the conditions are acidic. Add water molecules and hydrogen ions as necessary to balance the atoms.
\[ \text{O}_2 + 4\text{I}^- + 4\text{H}^+ \rightarrow 2\text{I}_2 + 2\text{H}_2\text{O} \]

Add hydroxide ions to adjust for basic conditions. Simplify the resulting equation.
\[ \text{O}_2 + 4\text{I}^- + 4\text{H}_2\text{O} \rightarrow 2\text{I}_2 + 2\text{H}_2\text{O} + 4\text{OH}^- \]
\[ \text{O}_2 + 4\text{I}^- + 2\text{H}_2\text{O} \rightarrow 2\text{I}_2 + 4\text{OH}^- \]
33. Use the oxidation number method to balance the following equation for the combustion of carbon disulfide.

\[ \text{CS}_2 + \text{O}_2 \rightarrow \text{CO}_2 + \text{SO}_2 \]

34. Use the oxidation number method to balance the following equations.

(a) \[ \text{B}_2\text{O}_3 + \text{Mg} \rightarrow \text{MgO} + \text{Mg}_3\text{B}_2 \]
(b) \[ \text{H}_2\text{S} + \text{H}_2\text{O}_2 \rightarrow \text{S}_8 + \text{H}_2\text{O} \]

35. Use the oxidation number method to balance each ionic equation in acidic solution.

(a) \[ \text{Cr}_2\text{O}_7^{2-} + \text{Fe}^{2+} \rightarrow \text{Cr}^{3+} + \text{Fe}^{3+} \]
(b) \[ \text{I}_2 + \text{NO}_3^- \rightarrow \text{IO}_3^- + \text{NO}_2 \]
(c) \[ \text{PbSO}_4 \rightarrow \text{Pb} + \text{PbO}_2 + \text{SO}_4^{2-} \]

36. Use the oxidation number method to balance each ionic equation in basic solution.

(a) \[ \text{Cl}^- + \text{CrO}_4^{2-} \rightarrow \text{ClO}^- + \text{CrO}_2^- \]
(b) \[ \text{Ni} + \text{MnO}_4^- \rightarrow \text{NiO} + \text{MnO}_2 \]
(c) \[ \text{I}^- + \text{Ce}^{4+} \rightarrow \text{IO}_3^- + \text{Ce}^{3+} \]
Section Summary

In this section, you learned how to use the oxidation number method to balance redox equations. You now know various techniques for recognizing and representing redox reactions. In Chapter 19, you will use these techniques to examine specific applications of redox reactions in the business world and in your daily life.

Section Review

1. Is it possible to use the half-reaction method or the oxidation number method to balance the following equation? Explain your answer.
   \[ \text{Al}_2\text{S}_3 + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \text{H}_2\text{S} \]

2. Balance each equation by the method of your choice. Explain your choice of method in each case.
   (a) \[ \text{CH}_3\text{COOH} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]
   (b) \[ \text{O}_2 + \text{H}_2\text{SO}_3 \rightarrow \text{HSO}_4^- \text{ (acidic conditions)} \]

3. Use the oxidation number method to balance the following equations.
   (a) \[ \text{NH}_3 + \text{Cl}_2 \rightarrow \text{NH}_4\text{Cl} + \text{N}_2 \]
   (b) \[ \text{Mn}_3\text{O}_4 + \text{Al} \rightarrow \text{Al}_2\text{O}_3 + \text{Mn} \]

4. Explain why, in redox reactions, the total increase in the oxidation numbers of the oxidized elements must equal the total decrease in the oxidation numbers of the reduced elements.

5. The combustion of ammonia in oxygen to form nitrogen dioxide and water vapour involves covalent molecules in the gas phase. The oxidation number method for balancing the equation was shown in an example in this section. Devise a half-reaction method for balancing the equation. Describe the assumptions you made in order to balance the equation. Also, describe why these assumptions did not affect the final result.
Reflecting on Chapter 18
Summarize this chapter in the format of your choice. Here are a few ideas to use as guidelines:
• Give two different definitions for the term oxidation.
• Give two different definitions for the term reduction.
• Define a half-reaction. Give an example of an oxidation half-reaction and a reduction half-reaction.
• Practise balancing equations using the half-reaction method.
• Write an example of a balanced chemical equation for a redox reaction. Assign oxidation numbers to each element in the equation, then explain how you know it is a redox reaction.

Reviewing Key Terms
For each of the following terms, write a sentence that shows your understanding of its meaning.
- ore oxidation
- reduction oxidation-reduction
- redox reaction reaction
- oxidizing agent reducing agent
- half-reaction disproportionation
- oxidation numbers

Knowledge/Understanding
1. For each reaction below, write a balanced chemical equation by inspection.
   (a) zinc metal with aqueous silver nitrate
   (b) aqueous cobalt(II) bromide with aluminum metal
   (c) metallic cadmium with aqueous tin(II) chloride

2. For each reaction in question 1, write the total ionic and net ionic equations.

3. For each reaction in question 1, identify the oxidizing agent and reducing agent.

4. For each reaction in question 1, write the two half-reactions.

5. When a metallic element reacts with a non-metallic element, which reactant is (a) oxidized? (b) reduced? (c) the oxidizing agent? (d) the reducing agent?

6. Use a Lewis structure to assign an oxidation number to each element in the following compounds.
   (a) BaCl₂
   (b) CS₂
   (c) XeF₄

7. Determine the oxidation number of each element present in the following substances.
   (a) BaH₂
   (b) Al₄C₃
   (c) KCN
   (d) LiNO₂
   (e) (NH₄)₂C₂O₄
   (f) S₈
   (g) AsO₃³⁻
   (h) VO₂⁺
   (i) XeO₃F⁻
   (j) S₂O₆²⁻

8. Identify a polyatomic ion in which chlorine has an oxidation number of +3.

9. Determine which of the following balanced chemical equations represent redox reactions. For each redox reaction, identify the oxidizing agent and the reducing agent.
   (a) 2C₆H₆ + 15O₂ → 12CO₂ + 6H₂O
   (b) CaO + SO₂ → CaSO₃
   (c) H₂ + I₂ → 2HI
   (d) KMnO₄ + 5CuCl + 8HCl → KCl + MnCl₂ + 5CuCl₂ + 4H₂O

10. Determine which of the following balanced net ionic equations represent redox reactions. For each redox reaction, identify the reactant that undergoes oxidation and the reactant that undergoes reduction.
    (a) 2Ag⁺(aq) + Cu(s) → 2Ag(s) + Cu²⁺(aq)
    (b) Pb²⁺(aq) + S²⁻(aq) → PbS(s)
    (c) 2Mn²⁺ + 5BiO₃⁻ + 14H⁺ → 2MnO₄⁻ + 5Bi³⁺ + 7H₂O

Answers to questions highlighted in red type are provided in Appendix A.
11. (a) Examples of molecules and ions composed only of vanadium and oxygen are listed below. In this list, identify molecules and ions in which the oxidation number of vanadium is the same.

\[ \begin{align*}
V_2O_5 \\
V_2O_4 \\
VO \\
VO_2^+ \\
VO_3^- \\
VO_4^{3-} \\
V_3O_8^{3-}
\end{align*} \]

(b) Is the following reaction a redox reaction?

\[ 2NH_4VO_3 \rightarrow V_2O_5 + 2NH_3 + H_2O \]

12. The method used to manufacture nitric acid involves the following three steps.

\[ \text{Step 1} \quad 4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g) \]

\[ \text{Step 2} \quad 2NO(g) + O_2(g) \rightarrow 2NO_2(g) \]

\[ \text{Step 3} \quad 3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g) \]

(a) Which of these steps are redox reactions?

(b) Identify the oxidizing agent and the reducing agent in each redox reaction.

13. In a synthesis reaction involving elements A and B, the oxidation number of element A increases. What happens to the oxidation number of element B? How do you know?

14. Balance each of the following half-reactions.

(a) The reduction of iodine to iodide ions

(b) The oxidation of lead to lead(IV) ions

(c) The reduction of tetrachlorogold(III) ions, \( \text{AuCl}_4^- \), to chloride ions and metallic gold

(d) \( \text{C}_2\text{H}_3\text{OH} \rightarrow \text{CH}_3\text{COOH} \) (acidic conditions)

(e) \( \text{S}_8 \rightarrow \text{H}_2\text{S} \) (acidic conditions)

(f) \( \text{AsO}_2^- \rightarrow \text{AsO}_4^{3-} \) (basic conditions)

15. Use the half-reaction method to balance each of the following equations.

(a) \( \text{MnO}_2 + \text{Cl}^- \rightarrow \text{Mn}^{2+} + \text{Cl}_2 \) (acidic conditions)

(b) \( \text{NO} + \text{Sn} \rightarrow \text{NH}_2\text{OH} + \text{Sn}^{2+} \) (acidic conditions)

(c) \( \text{Cd}^{2+} + \text{V}^{2+} \rightarrow \text{Cd} + \text{VO}_3^- \) (acidic conditions)

(d) \( \text{Cr} \rightarrow \text{Cr(OH)}_4^- + \text{H}_2 \) (basic conditions)

(e) \( \text{S}_2\text{O}_3^{2-} + \text{NiO}_2 \rightarrow \text{Ni(OH)}_2 + \text{SO}_3^{2-} \) (basic conditions)

(f) \( \text{Sn}^{2+} + \text{O}_2 \rightarrow \text{Sn}^{4+} \) (basic conditions)

16. Use the oxidation number method to balance each of the following equations.

(a) \( \text{SiCl}_4 + \text{Al} \rightarrow \text{Si} + \text{AlCl}_3 \)

(b) \( \text{PH}_3 + \text{O}_2 \rightarrow \text{P}_4\text{O}_{10} + \text{H}_2\text{O} \)

(c) \( \text{I}_2\text{O}_5 + \text{CO} \rightarrow \text{I}_2 + \text{CO}_2 \)

(d) \( \text{SO}_3^{3-} + \text{O}_2 \rightarrow \text{SO}_4^{2-} \)

17. Complete and balance a net ionic equation for each of the following disproportionation reactions.

(a) \( \text{NO}_2 \rightarrow \text{NO}_2^- + \text{NO}_3^- \) (acidic conditions), which is one of the reactions involved in acid rain formation

(b) \( \text{Cl}_2 \rightarrow \text{ClO}^- + \text{Cl}^- \) (basic conditions), which is one of the reactions involved in the bleaching action of chlorine in basic solution

18. Balance each of the following net ionic equations. Then include the named spectator ions to write a balanced chemical equation. Include the states.

(a) \( \text{Co}^{3+} + \text{Cd} \rightarrow \text{Co}^{2+} + \text{Cd}^{2+} \) (spectator ions \( \text{NO}_3^- \))

(b) \( \text{Ag}^+ + \text{SO}_4^{2-} \rightarrow \text{Ag} + \text{SO}_4^{2-} \) (acidic conditions; spectator ions \( \text{NO}_3^- \))

(c) \( \text{Al} + \text{CrO}_4^{2-} \rightarrow \text{Al(OH)}_3 + \text{Cr(OH)}_3 \) (basic conditions; spectator ions Na\(^+ \))

19. If possible, give an example for each.

(a) a synthesis reaction that is a redox reaction

(b) a synthesis reaction that is not a redox reaction

(c) a decomposition reaction that is a redox reaction

(d) a decomposition reaction that is not a redox reaction

(e) a double displacement reaction that is a redox reaction

(f) a double displacement reaction that is not a redox reaction

20. Give an example of a reaction in which sulfur behaves as

(a) an oxidizing agent

(b) a reducing agent

21. Write a balanced equation for a synthesis reaction in which elemental oxygen acts as a reducing agent.
22. Phosphorus, \( P_4(\text{s}) \), reacts with hot water to form phosphine, \( \text{PH}_3(\text{g}) \), and phosphoric acid.
   (a) Write a balanced chemical equation for this reaction.
   (b) Is the phosphorus oxidized or reduced? Explain your answer.

23. The thermite reaction, which is highly exothermic, can be used to weld metals. In the thermite reaction, aluminum reacts with iron(III) oxide to form iron and aluminum oxide. The temperature becomes so high that the iron is formed as a liquid.
   (a) Write a balanced chemical equation for the reaction.
   (b) Is the reaction a redox reaction? If so, identify the oxidizing agent and the reducing agent.

Inquiry

24. Iodine reacts with concentrated nitric acid to form iodic acid, gaseous nitrogen dioxide, and water.
   (a) Write the balanced chemical equation.
   (b) Calculate the mass of iodine needed to produce 28.0 L of nitrogen dioxide at STP.

25. Describe a laboratory investigation you could perform to decide whether tin or nickel is the better reducing agent. Include in your description all the materials and equipment you would need, and the procedure you would follow.

26. The following table shows the average composition, by volume, of the air we inhale and exhale, as part of a biochemical process called respiration. (The values are rounded.)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Inhaled Air (% by volume)</th>
<th>Exhaled Air (% by volume)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>21</td>
<td>16</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.04</td>
<td>4</td>
</tr>
<tr>
<td>Nitrogen and other gases</td>
<td>79</td>
<td>80</td>
</tr>
</tbody>
</table>

How do the data indicate that at least one redox reaction is involved in respiration?

27. Highly toxic phosphine gas, \( \text{PH}_3 \), is used in industry to produce flame retardants. One way to make phosphine on a large scale is by heating elemental phosphorus with a strong base.
   (a) Balance the following net ionic equation for the reaction under basic conditions.
       \[ \text{P}_4 + \text{H}_2\text{PO}_2^- + \text{PH}_3 \rightarrow \text{H}_3\text{PO}_4 \]
   (b) Show that the reaction in part (a) is a disproportionation reaction.
   (c) Calculate the mass of phosphine that can theoretically be made from 10.0 kg of phosphorus by this method.

Communication

28. Explain why, in a redox reaction, the reducing agent undergoes oxidation.

29. Explain why you would not expect sulfide ions to act as an oxidizing agent.

30. Why can’t the oxidation number of an element in a compound be greater than the number of valence electrons in one atom of that element?

31. Explain why the historical use of the word “reduction,” that is, the production of a metal from its ore, is consistent with the modern definitions of reduction.

32. Organic chemists sometimes describe redox reactions in terms of the loss or gain of pairs of hydrogen atoms. Examples include the addition of hydrogen to ethene to form ethane, and the elimination of hydrogen from ethanol to form ethanal.
   (a) Write a balanced equation for each reaction.
   (b) Determine whether the organic reactant is oxidized or reduced in each reaction.
   (c) Write a definition of oxidation and a definition of reduction based on an organic reactant losing or gaining hydrogen.
   (d) Would your definitions be valid for the synthesis and decomposition of a metal hydride? Explain your answer.
Making Connections

33. The compound NaAl(OH)$_2$CO$_3$ is a component of some common stomach acid remedies.
   (a) Determine the oxidation number of each element in the compound.
   (b) Predict the products of the reaction of the compound with stomach acid (hydrochloric acid), and write a balanced chemical equation for the reaction.
   (c) Were the oxidation numbers from part (a) useful in part (b)? Explain your answer.
   (d) What type of reaction is this?
   (e) Check your medicine cabinet at home for stomach acid remedies. If possible, identify the active ingredient in each remedy.

34. Two of the substances on the head of a safety match are potassium chlorate and sulfur. When the match is struck, the potassium chlorate decomposes to give potassium chloride and oxygen. The sulfur then burns in the oxygen and ignites the wood of the match.
   (a) Write balanced chemical equations for the decomposition of potassium chlorate and for the burning of sulfur in oxygen.
   (b) Identify the oxidizing agent and the reducing agent in each reaction in part (a).
   (c) Does any element in potassium chlorate undergo disproportionation in the reaction? Explain your answer.
   (d) Research the history of the safety match to determine when it was invented, why it was invented, and what it replaced.

35. Ammonium ions, from fertilizers or animal waste, are oxidized by atmospheric oxygen. The reaction results in the acidification of soil on farms and the pollution of ground water with nitrate ions.
   (a) Write a balanced net ionic equation for this reaction.
   (b) Why do farmers use fertilizers? What alternative farming methods have you heard of? Which farming method(s) do you support, and why?

36. One of the most important discoveries in the history of the Canadian chemical industry was accidental. Thomas “Carbide” Willson (1860–1915) was trying to make the element calcium from lime, CaO, by heating the lime with coal tar. Instead, he made the compound calcium carbide, CaC$_2$. This compound reacts with water to form a precipitate of calcium hydroxide and gaseous ethyne (acetylene). Willson’s discovery led to the large-scale use of ethyne in numerous applications.
   (a) Was Willson trying to perform a redox reaction? How do you know? Why do you not need to know the substances in coal tar to answer this question?
   (b) Write a balanced chemical equation for the reaction of calcium carbide with water. Is this reaction a redox reaction?
   (c) An early use of Willson’s discovery was in car headlights. Inside a headlight, the reaction of calcium carbide and water produced ethyne, which was burned to produce light and heat. Write a balanced chemical equation for the complete combustion of ethyne. Is this reaction a redox reaction?
   (d) Research the impact of Willson’s discovery on society, from his lifetime to the present day.

Answers to Practice Problems and Short Answers to Section Review Questions

Practice Problems:
1. Zn(s) + Fe$^{2+}$(aq) → Zn$^{2+}$(aq) + Fe(s)
2.(a) 3Mg(s) + 2Al$^{3+}$(aq) → 3Mg$^{2+}$(aq) + 2Al(s)
   (b) 2Ag$^{+}$(aq) + Cd(s) → 2Ag(s) + Cd$^{2+}$(aq)
3.(a) Mg oxidized, Al$^{3+}$ reduced
   (b) Cd oxidized, Ag$^{+}$ reduced
4.(a) Al$^{3+}$ oxidizing agent, Mg reducing agent
   (b) Ag$^{+}$ oxidizing agent, Cd reducing agent
5. Al(s) → Al$^{3+}$(aq) + 3e$^-$, Fe$^{3+}$(aq) + 3e$^-$ → Fe(s)
6.(a) Fe(s) → Fe$^{2+}$(aq) + 2e$^-$, Cu$^{2+}$(aq) + 2e$^-$ → Cu(s)
   (b) Cd(s) → Cd$^{2+}$(aq) + 2e$^-$, Ag$^{+}$(aq) + e$^-$ → Ag(s)
7.(a) Sn(s) → Sn$^{2+}$(aq) + 2e$^-$, Pb$^{2+}$(aq) + 2e$^-$ → Pb(s)
   (b) Ag(s) → Ag$^{+}$ + e$^-$, Au$^{3+}$(aq) + 3e$^-$ → Au(s)
   (c) Zn(s) → Zn$^{2+}$(aq) + 2e$^-$, Fe$^{3+}$(aq) + 3e$^-$ → Fe(s)
8. Hg$^{2+}$(aq) → Hg(s) + Hg$^{2+}$(aq), Hg$^{2+}$(aq) + 2e$^-$ → Hg(s), Hg$^{2+}$(aq) + 2e$^-$ → 2Hg(s)
9.(a) +3 (b) 0 (c) +6 (d) +5 (e) 0 (f) +2
10. (a) H, +1; S, +4; O, −2
(b) H, +1; O, −2; (2) H, +1; P, +5; O, −2
11. (a) +2 (b) −1
12. (a) Al, +3; H, +1; C, +4; O, −2
13. (a) yes (b) no
14. (a) H₂O₂ oxidizing agent, Fe³⁺ reducing agent
15. ClO₂⁻ oxidized, Br⁻ reduced
16. yes
17. Ce⁴⁺ + e⁻ → Ce³⁺
18. Br⁻ → Br₂ + 2e⁻
19. (a) O₂ + 2H₂ → H₂O (b) 2H₂O → O₂ + 4H⁺ + 4e⁻
(c) 2NO₃⁻ + 12H⁺ + 10e⁻ → N₂ + 6H₂O
20. (a) ClO₃⁻ + 6H⁺ + 6e⁻ → Cl⁻ + 3H₂O
(b) NO + 2H₂O → NO₃⁻ + 4H⁺ + 3e⁻
(c) Cr₂O₇²⁻ + 14H⁺ + 6e⁻ → 2Cr³⁺ + 7H₂O
21. Cr⁺³ → Cr³⁺ + e⁻
22. O₂ + 4e⁻ → 2O²⁻
23. (a) Al + 4OH⁻ → Al(OH)₄ + 3e⁻
(b) CN⁻ + 2OH⁻ → CNO⁻ + H₂O + 2e⁻
(c) MnO₂ + 2H₂O + 3e⁻ → Mn₂O₄ + 4OH⁻
(d) CrO₃²⁻ + 4H₂O + 3e⁻ → Cr(OH)₃ + 5OH⁻
(e) 2CO₂⁺ + 2H₂O + 2e⁻ → CO₃²⁻ + 4OH⁻
24. (a) FeO₂⁺ + 8H⁺ + 3e⁻ → Fe³⁺ + 4H₂O
(b) ClO₃⁻ + 2H₂O + 4e⁻ → Cl⁻ + 4OH⁻
25. (a) 2Na + F₂ → 2NaF
(b) 3Mg + N₂ → Mg₂N₂
26. Cu²⁺ + 5I⁻ → 2CuI + 3I⁻
27. (a) MnO₄⁻ + 5Ag + 8H⁺ → Mn²⁺ + 5Ag⁺ + 4H₂O
(b) Hg + 2NO₃⁻ + 4Cl⁻ + 4H⁺ → HgCl₂ + 2NO₂ + 2H₂O
(c) Hg²⁺ + NO₃⁻ + 2H₂O → Hg₂O₂ + 2OH⁻
(d) Zn²⁺ + 2NO₂⁻ + 4H⁺ → Zn²⁺ + 2NO₂⁻ + 4H⁺
28. (a) 3CN⁻ + 2MnO₂⁻ + H₂O → 3CNO⁻ + 2MnO₂ + 2OH⁻
(b) H₂O₂ + 2ClO₂⁻ → H₂O + 2ClO₂⁻ + 2H⁺
(c) 6ClO₂⁻ + 2Cl⁻ + 2H₂O → 3Cl₂ + 2CrO₂₅²⁻ + 4OH⁻
(d) 2AI + NO₂⁻ + H₂O + OH⁻ → NH₄⁺ + 2AlO₂⁻
29. 0.06774 g; 5.276%
30. 0.1387%
Batteries come in a wide range of sizes and shapes, from the tiny button battery in a watch, to a large and heavy car battery. Although you probably use batteries every day, they may still surprise you. For example, did you know that you could make a battery from a lemon and two pieces of metal? To make a lemon battery, you could insert two different electrodes, such as copper and zinc strips, into a lemon. The battery can provide electricity for a practical use. For example, the battery can power a small light bulb, or turn a small motor.

For obvious reasons, lemon batteries are not a convenient way to power a portable device, such as a cell phone. Scientists and inventors have worked to develop a variety of batteries that are inexpensive, compact, and easy to store and to carry. Our society uses vast numbers of batteries.

What exactly is a battery, and how does it work? What is the relationship between batteries and the redox reactions studied in Chapter 18? You will find out the answers to these questions in this chapter.
Galvanic Cells

You know that redox reactions involve the transfer of electrons from one reactant to another. You may also recall that an electric current is a flow of electrons in a circuit. These two concepts form the basis of electrochemistry, which is the study of the processes involved in converting chemical energy to electrical energy, and in converting electrical energy to chemical energy.

As you learned in Chapter 18, a zinc strip reacts with a solution containing copper(II) ions, forming zinc ions and metallic copper. The reaction is spontaneous (a spontaneous reaction is a reaction that occurs by itself; that is, without an ongoing input of energy). It releases energy in the form of heat; in other words, this reaction is exothermic.

\[ \text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s) \]

This reaction occurs on the surface of the zinc strip, where electrons are transferred from zinc atoms to copper(II) ions when these atoms and ions are in direct contact. A common technological invention called a galvanic cell uses redox reactions, such as the one described above, to release energy in the form of electricity.

The Galvanic Cell

A galvanic cell, also called a voltaic cell, is a device that converts chemical energy to electrical energy. The key to this invention is to prevent the reactants in a redox reaction from coming into direct contact with each other. Instead, electrons flow from one reactant to the other through an external circuit, which is a circuit outside the reaction vessel. This flow of electrons through the external circuit is an electric current.

An Example of a Galvanic Cell: The Daniell Cell

Figure 19.1 shows one example of a galvanic cell, called the Daniell cell. One half of the cell consists of a piece of zinc placed in a zinc sulfate solution. The other half of the cell consists of a piece of copper placed in a copper(II) sulfate solution. A porous barrier, sometimes called a semi-permeable membrane, separates these two half-cells. It stops the copper(II) ions from coming into direct contact with the zinc electrode.

Figure 19.1 The Daniell cell is named after its inventor, the English chemist John Frederic Daniell (1790–1845). In the photograph shown here, the zinc sulfate solution is placed inside a porous cup, which is placed in a larger container of copper sulfate solution. The cup acts as the porous barrier.
In a Daniell cell, the pieces of metallic zinc and copper act as electrical conductors. The conductors that carry electrons into and out of a cell are named electrodes. The zinc sulfate and copper(II) sulfate act as electrolytes. Electrolytes are substances that conduct electricity when dissolved in water. (The fact that a solution of an electrolyte conducts electricity does not mean that free electrons travel through the solution. An electrolyte solution conducts electricity because of ion movements, and the loss and gain of electrons at the electrodes.) The terms electrode and electrolyte were invented by the leading pioneer of electrochemistry, Michael Faraday (1791–1867).

The redox reaction takes place in a galvanic cell when an external circuit, such as a metal wire, connects the electrodes. The oxidation half-reaction occurs in one half-cell, and the reduction half-reaction occurs in the other half-cell. For the Daniell cell:

Oxidation (loss of electrons): \( \text{Zn}^{(s)} \rightarrow \text{Zn}^{2+}^{(aq)} + 2\text{e}^- \)

Reduction (gain of electrons): \( \text{Cu}^{2+}^{(aq)} + 2\text{e}^- \rightarrow \text{Cu}^{(s)} \)

The electrode at which oxidation occurs is named the anode. In this example, zinc atoms undergo oxidation at the zinc electrode. Thus, the zinc electrode is the anode of the Daniell cell. The electrode at which reduction occurs is named the cathode. Here, copper(II) ions undergo reduction at the copper electrode. Thus, the copper electrode is the cathode of the Daniell cell.

Free electrons cannot travel through the solution. Instead, the external circuit conducts electrons from the anode to the cathode of a galvanic cell. Figure 19.2 gives a diagram of a typical galvanic cell.

At the anode of a galvanic cell, electrons are released by oxidation. For example, at the zinc anode of the Daniell cell, zinc atoms release electrons to become positive zinc ions. Thus, the anode of a galvanic cell is negatively charged. Relative to the anode, the cathode of a galvanic cell is positively charged. In galvanic cells, electrons flow through the external circuit from the negative electrode to the positive electrode. These electrode polarities may already be familiar to you. An example is shown in Figure 19.3.

Each half-cell contains a solution of a neutral compound. In a Daniell cell, these solutions are aqueous zinc sulfate and aqueous copper(II) sulfate. How can these electrolyte solutions remain neutral when electrons are leaving the anode of one half-cell and arriving at the cathode of the other half-cell? To maintain electrical neutrality in each half-cell, some ions migrate through the porous barrier, as shown in Figure 11.4, on the next page. Negative ions (anions) migrate toward the anode, and positive ions (cations) migrate toward the cathode.
The separator between the half-cells does not need to be a porous barrier. Figure 19.5 shows an alternative device. This device, called a salt bridge, contains an electrolyte solution that does not interfere in the reaction. The open ends of the salt bridge are plugged with a porous material, such as glass wool, to stop the electrolyte from leaking out quickly. The plugs allow ion migration to maintain electrical neutrality.

Suppose the salt bridge of a Daniell cell contains ammonium chloride solution, $\text{NH}_4\text{Cl(aq)}$. As positive zinc ions are produced at the anode, negative chloride ions migrate from the salt bridge into the half-cell that contains the anode. As positive copper(II) ions are removed from solution at the cathode, positive ammonium ions migrate from the salt bridge into the half-cell that contains the cathode.

Other electrolytes, such as sodium sulfate or potassium nitrate, could be chosen for the salt bridge. Neither of these electrolytes interferes in the cell reaction. Silver nitrate, $\text{AgNO}_3(aq)$, would be a poor choice for the salt bridge, however. Positive silver ions would migrate into the half-cell that contains the cathode. Zinc displaces both copper and silver from solution, so both copper(II) ions and silver ions would be reduced at the cathode. The copper produced would be contaminated with silver.
Galvanic Cell Notation

A convenient shorthand method exists for representing galvanic cells. The shorthand representation of a Daniell cell is as follows.

\[ \text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu} \]

The phases or states may be included.

\[ \text{Zn}_{(s)} \mid \text{Zn}^{2+}_{(aq)} \parallel \text{Cu}^{2+}_{(aq)} \mid \text{Cu}_{(s)} \]

As you saw in Figure 11.4 and Figure 11.5, the anode may appear on the left or on the right of a diagram. In the shorthand representation, however, the anode is always shown on the left and the cathode on the right. Each single vertical line, |, represents a phase boundary between the electrode and the solution in a half-cell. For example, the first single vertical line shows that the solid zinc and aqueous zinc ions are in different phases or states. The double vertical line, ||, represents the porous barrier or salt bridge between the half-cells. Spectator ions are usually omitted.

Inert Electrodes

The zinc anode and copper cathode of a Daniell cell are both metals, and can act as electrical conductors. However, some redox reactions involve substances that cannot act as electrodes, such as gases or dissolved electrolytes. Galvanic cells that involve such redox reactions use inert electrodes. An inert electrode is an electrode made from a material that is neither a reactant nor a product of the cell reaction. Figure 19.6 shows a cell that contains one inert electrode. The chemical equation, net ionic equation, and half-reactions for this cell are given below.

Chemical equation: \( \text{Pb}_{(s)} + 2\text{FeCl}_3(aq) \rightarrow 2\text{FeCl}_2(aq) + \text{PbCl}_2(aq) \)

Net ionic equation: \( \text{Pb}_{(s)} + 2\text{Fe}^{3+}(aq) \rightarrow 2\text{Fe}^{2+}(aq) + \text{Pb}^{2+}(aq) \)

Oxidation half-reaction: \( \text{Pb}_{(s)} \rightarrow \text{Pb}^{2+}(aq) + 2\text{e}^- \)

Reduction half-reaction: \( \text{Fe}^{3+}(aq) + \text{e}^- \rightarrow \text{Fe}^{2+}(aq) \)

The reduction half-reaction does not include a solid conductor of electrons, so an inert platinum electrode is used in this half-cell. The platinum electrode is chemically unchanged, so it does not appear in the chemical equation or half-reactions. However, it is included in the shorthand representation of the cell.

\[ \text{Pb} \mid \text{Pb}^{2+} \parallel \text{Fe}^{3+}, \text{Fe}^{2+} \mid \text{Pt} \]

A comma separates the formulas \( \text{Fe}^{3+} \) and \( \text{Fe}^{2+} \) for the ions involved in the reduction half-reaction. The formulas are not separated by a vertical line, because there is no phase boundary between these ions. The \( \text{Fe}^{3+} \) and \( \text{Fe}^{2+} \) ions exist in the same aqueous solution.
1. (a) If the reaction of zinc with copper(II) ions is carried out in a test tube, what is the oxidizing agent and what is the reducing agent?
(b) In a Daniell cell, what is the oxidizing agent and what is the reducing agent? Explain your answer.

2. Write the oxidation half-reaction, the reduction half-reaction, and the overall cell reaction for each of the following galvanic cells. Identify the anode and the cathode in each case. In part (b), platinum is present as an inert electrode.
(a) Sn(s) | Sn^{2+}(aq) || Tl^{+}(aq) | Tl(s)
(b) Cd(s) | Cd^{2+}(aq) || H^{+}(aq) | H_{2}(g) | Pt(s)

3. A galvanic cell involves the overall reaction of iodide ions with acidified permanganate ions to form manganese(II) ions and iodine. The salt bridge contains potassium nitrate.
(a) Write the half-reactions, and the overall cell reaction.
(b) Identify the oxidizing agent and the reducing agent.
(c) The inert anode and cathode are both made of graphite. Solid iodine forms on one of them. Which one?

4. As you saw earlier, pushing a zinc electrode and a copper electrode into a lemon makes a “lemon cell”. In the following representation of the cell, C_{6}H_{8}O_{7} is the formula of citric acid. Explain why the representation does not include a double vertical line.
Zn(s) | C_{6}H_{8}O_{7}(aq) | Cu(s)

### Introducing Cell Potentials

You know that water spontaneously flows from a higher position to a lower position. In other words, water flows from a state of higher gravitational potential energy to a state of lower gravitational potential energy. As water flows downhill, it can do work, such as turning a water wheel or a turbine. The chemical changes that take place in galvanic cells are also accompanied by changes in potential energy. Electrons spontaneously flow from a position of higher potential energy at the anode to a position of lower potential energy at the cathode. The moving electrons can do work, such as lighting a bulb or turning a motor.

The difference between the potential energy at the anode and the potential energy at the cathode is the **electric potential**, \( E \), of a cell. The unit used to measure electric potential is called the **volt**, with symbol V. Because of the name of this unit, electric potential is more commonly known as **cell voltage**. Another name for it is **cell potential**. A cell potential can be measured using an electrical device called a voltmeter.

A cell potential of 0 V means that the cell has no electric potential, and no electrons will flow. You know that you can generate electricity by connecting a zinc electrode and a copper electrode that have been inserted into a lemon. However, you cannot generate electricity by connecting two copper electrodes that have been inserted into the lemon. The two copper electrodes are the same and are in contact with the same electrolyte. There is no potential difference between the two electrodes.

Electric potentials vary from one cell to another, depending on various factors. You will examine some of these factors in the next investigation.

### Concept Check

The cell voltage is sometimes called the **electromotive force**, abbreviated emf. However, this term can be misleading. A cell voltage is a potential difference, not a force. The unit of cell voltage, the volt, is not a unit of force.
Measuring Cell Potentials of Galvanic Cells

In this investigation, you will build some galvanic cells and measure their cell potentials.

**Question**
What factors affect the cell potential of a galvanic cell?

**Prediction**
Predict whether the cell potentials of galvanic cells depend on the electrodes and electrolytes in the half-cells. Give reasons for your prediction.

**Materials**
- 25 cm clear aquarium rubber tubing (Tygon®), internal diameter 4–6 mm
- 1 Styrofoam or clear plastic egg carton with 12 wells
- 5 cm strip of Mg ribbon
- 1 cm × 5 cm strips of Cu, Al, Ni, Sn, Fe, and Ag
- 5 cm of thick graphite pencil lead or a graphite rod
- 5 mL of 0.1 mol/L solutions of each of the following: Mg(NO₃)₂, Cu(NO₃)₂, Al(NO₃)₃, Ni(NO₃)₂, Zn(NO₃)₂, SnSO₄, Fe(NO₃)₃, AgNO₃, HNO₃
- 15 mL of 1.0 mol/L KNO₃
- 5 mL of saturated NaCl solution
- disposable pipette
cotton batting
sandpaper
black and red electrical leads with alligator clips
voltmeter set to a scale of 0 V to 20 V
paper towel

**Safety Precautions**

Handle the nitric acid solution with care. It is an irritant. Wash any spills on your skin with copious amounts of water, and inform your teacher.

**Procedure**

1. Use tape or a permanent marker to label the outside of nine wells of your egg carton with the nine different half-cells. Each well should correspond to one of the eight different metal/metal ion pairs: Mg/Mg²⁺, Cu/Cu²⁺, Al/Al³⁺, Ni/Ni²⁺, Zn/Zn²⁺, Sn/Sn²⁺, Fe/Fe³⁺, and Ag/Ag⁺. Label the ninth well H⁺/H₂.

2. Prepare a 9 × 9 grid in your notebook. Label the nine columns to match the nine half-cells. Label the nine rows in the same way. You will use this chart to mark the positive cell potentials you obtain when you connect two half-cells to build a galvanic cell. You will also record the anode and the cathode for each galvanic cell you build. (You may not need to fill out the entire chart.)

3. Sand each of the metals to remove any oxides.

4. Pour 5 mL of each metal salt solution into the appropriate well of the egg carton. Pour 5 mL of the nitric acid into the well labelled H⁺/H₂.

5. Prepare your salt bridge as follows.
   (a) Roll a small piece of cotton batting so that it forms a plug about the size of a grain of rice. Place the plug in one end of your aquarium tubing, but leave a small amount of the cotton hanging out, so you can remove the plug later.
   (b) Fill a disposable pipette as full as possible with the 1 mol/L KNO₃ electrolyte solution. Fit the tip of the pipette firmly into the open end of the tubing. Slowly inject the electrolyte solution into the tubing. Fill the tubing completely, so that the cotton on the other side becomes wet.
   (c) With the tubing completely full, insert another cotton plug into the other end. There should be no air bubbles. (You may have to repeat this step from the beginning if you have air bubbles.)
6. Insert each metal strip into the corresponding well. Place the graphite rod in the well with the nitric acid. The metal strips and the graphite rod are your electrodes.

7. Attach the alligator clip on the red lead to the red probe of the voltmeter. Attach the black lead to the black probe.

8. Choose two wells to test. Insert one end of the salt bridge into the solution in the first well. Insert the other end of the salt bridge into the solution in the second well. Attach a free alligator clip to the electrode in each well. (Note: The graphite electrode is very fragile. Be gentle when using it.) You have built a galvanic cell.

9. If you get a negative reading, switch the alligator clips. Once you obtain a positive value, record it in your chart. The black lead should be attached to the anode (electrons flowing into the voltmeter). Record which metal is acting as the anode and which is acting as the cathode in this galvanic cell.

10. Remove the salt bridge and wipe any excess salt solution off the outside of the tubing. Remove the alligator clips from the electrodes.

11. Repeat steps 8 to 10 for all other combinations of electrodes. Record your results.

12. Reattach the leads to the silver and magnesium electrodes, and insert your salt bridge back into the two appropriate wells. While observing the reading on the voltmeter, slowly add 5 mL of saturated NaCl solution to the Ag/Ag⁺ well to precipitate AgCl. Record any changes in the voltmeter reading. Observe the Ag/Ag⁺ well.

13. Rinse off the metals and the graphite rod with water. Dispose of the salt solutions into the heavy metal salts container your teacher has set aside. Rinse out your egg carton. Remove and discard the plugs of the salt bridge, and dispose of the KNO₃ solution as directed by your teacher. Return all your materials to their appropriate locations.

Analysis

1. For each cell in which you measured a cell potential, identify
   (a) the anode and the cathode
   (b) the positive and negative electrodes

2. For each cell in which you measured a cell potential, write a balanced equation for the reduction half-reaction, the oxidation half-reaction, and the overall cell reaction.

3. For any one cell in which you measured a cell potential, describe
   (a) the direction in which electrons flow through the external circuit
   (b) the movements of ions in the cell

4. Use your observations to decide which of the metals used as electrodes is the most effective reducing agent. Explain your reasoning.

5. List all the reduction half-reactions you wrote in question 2 so that the metallic elements in the half-reactions appear in order of their ability as reducing agents. Put the least effective reducing agent at the top of the list and the most effective reducing agent at the bottom.

6. In which part of your list from question 5 are the metal ions that are the best oxidizing agents? Explain.

7. (a) When saturated sodium chloride solution was added to the silver nitrate solution, what reaction took place? Explain.
   (b) Does the concentration of an electrolyte affect the cell potential of a galvanic cell? How do you know?

Conclusion

8. Identify factors that affect the cell potential of a galvanic cell.

Applications

9. Predict any other factors that you think might affect the voltage of a galvanic cell. Describe an investigation you could complete to test your prediction.
Disposable Batteries

The Daniell cell is fairly large and full of liquid. Realistically, you could not use this type of cell to power a wristwatch, a remote control, or a flashlight. Galvanic cells have been modified, however, to make them more useful.

The Dry Cell Battery

A dry cell is a galvanic cell with the electrolyte contained in a paste thickened with starch. This cell is much more portable than the Daniell cell. The first dry cell, invented by the French chemist Georges Leclanché in 1866, was called the Leclanché cell.

Modern dry cells are closely modelled on the Leclanché cell, and also contain electrolyte pastes. You have probably used dry cells in all kinds of applications, such as lighting a flashlight, powering a remote control, or ringing a doorbell. Dry cells are inexpensive. The cheapest AAA-, AA-, C-, and D-size 1.5-V batteries are dry cells.

A battery is defined as a set of galvanic cells connected in series. The negative electrode of one cell is connected to the positive electrode of the next cell in the set. The voltage of a set of cells connected in series is the sum of the voltages of the individual cells. Thus, a 9-V battery contains six 1.5-V dry cells connected in series. Often, the term “battery” is also used to describe a single cell. For example, a 1.5-V dry cell battery contains only a single cell.

A dry cell battery stops producing electricity when the reactants are used up. This type of battery is disposable after it has run down completely. A disposable battery is known as a primary battery. Some other batteries are rechargeable. A rechargeable battery is known as a secondary battery. The rest of this section will deal with primary batteries. You will learn about secondary batteries in section 11.3.

A dry cell contains a zinc anode and an inert graphite cathode, as shown in Figure 19.7. The electrolyte is a moist paste of manganese(IV) oxide, MnO₂, zinc chloride, ZnCl₂, ammonium chloride, NH₄Cl, and “carbon black,” C(s), also known as soot.

The oxidation half-reaction at the zinc anode is already familiar to you.

\[ \text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^- \]

The reduction half-reaction at the cathode is more complicated. An approximation is given here.

\[ 2\text{MnO}_2(s) + \text{H}_2\text{O}(l) + 2e^- \rightarrow \text{Mn}_2\text{O}_3(aq) + 2\text{OH}^-(aq) \]

Therefore, an approximation of the overall cell reaction is:

\[ 2\text{MnO}_2(s) + \text{Zn}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Mn}_2\text{O}_3(aq) + \text{Zn}^{2+}(aq) + 2\text{OH}^-(aq) \]
The Alkaline Cell Battery

The more expensive alkaline cell, shown in Figure 19.8, is an improved, longer-lasting version of the dry cell.

![Figure 19.8](image)

**Figure 19.8** The structure of an alkaline cell is similar to the structure of a dry cell. Each type has a voltage of 1.5 V.

Billions of alkaline batteries, each containing a single alkaline cell, are made every year. The ammonium chloride and zinc chloride used in a dry cell are replaced by strongly alkaline (basic) potassium hydroxide, KOH.

The half-reactions and the overall reaction in an alkaline cell are given here.

**Oxidation (at the anode):** \( \text{Zn}(s) + 2\text{OH}^- \rightarrow \text{ZnO}(s) + \text{H}_2\text{O}(l) + 2e^- \)

**Reduction (at the cathode):** \( \text{MnO}_2(s) + 2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{Mn(OH)}_2(s) + 2\text{OH}^- \)

**Overall cell reaction:** \( \text{Zn}(s) + \text{MnO}_2(s) + 2\text{H}_2\text{O}(l) \rightarrow \text{ZnO}(s) + \text{Mn(OH)}_2(s) \)

The Button Cell Battery

A button battery is much smaller than an alkaline battery. Button batteries are commonly used in watches, as shown in Figure 19.9. Because of its small size, the button battery is also used for hearing aids, pacemakers, and some calculators and cameras. The development of smaller batteries has had an enormous impact on portable devices, as shown in Figure 19.10.

Two common types of button batteries both use a zinc container, which acts as the anode, and an inert stainless steel cathode, as shown in Figure 11.11 on the next page. In the mercury button battery, the alkaline electrolyte paste contains mercury(II) oxide, HgO. In the silver button battery, the electrolyte paste contains silver oxide, Ag_2O. The batteries have similar voltages: about 1.3 V for the mercury cell, and about 1.6 V for the silver cell.

The reaction products in a mercury button battery are solid zinc oxide and liquid mercury. The two half-reactions and the overall equation are as follows.

**Oxidation half-reaction:** \( \text{Zn}(s) + 2\text{OH}^- \rightarrow \text{ZnO}(s) + \text{H}_2\text{O}(l) + 2e^- \)

**Reduction half-reaction:** \( \text{HgO}(s) + \text{H}_2\text{O}(l) + 2e^- \rightarrow \text{Hg}(l) + 2\text{OH}^- \)

**Overall reaction:** \( \text{Zn}(s) + \text{HgO}(s) \rightarrow \text{ZnO}(s) + \text{Hg}(l) \)
A common type of button battery, shown here, contains silver oxide or mercury(II) oxide. Mercury is cheaper than silver, but discarded mercury batteries release toxic mercury metal into the environment.

Figure 19.11 Careers in Chemistry

Explosives Chemist
Fortunato Villamagna works as the vice-president of technology for an Australian-owned company with offices worldwide, including Canada. Villamagna’s job has given him the opportunity to invent new products, build chemical plants, and conduct projects in Africa and Australia.

Born in Italy, Villamagna moved to Canada when he was eight. He grew up in Montréal, where his interest in chemistry was sparked by a Grade 10 teacher.

At university, Villamagna gained a greater understanding of the value of chemistry research. “Research creates new technologies and concepts, results in new products and services, creates jobs and prosperity, and in the end improves people’s lives,” he says. Villamagna decided to pursue graduate studies. He obtained a Masters of Science in physical chemistry at Concordia University, and a Ph.D. in physical chemistry at McGill University. Today, Villamagna leads a team of researchers responsible for developing new products and techniques involving explosives.

Redox reactions play an important role in industrial safety. Explosives are used in controlled ways in the mining, highway, and construction industries. The use of explosives allows modern workers to break up bedrock and carry out necessary demolitions from a safe distance. Chemists are involved in the development and production of explosives. They are also involved in making recommendations for the safe handling and disposal of explosives.

Many explosives are based on redox reactions. For example, the decomposition of nitroglycerin into nitrogen, carbon dioxide, water vapour, and oxygen is a redox reaction that results in a powerful explosion. The three nitrate groups of a nitroglycerin molecule act as powerful oxidizing agents, and the glycerol portion of the compound acts as a fuel. Fuels are very easily oxidized.

Nitroglycerin is highly unstable and can explode very easily. Therefore, it is difficult to manufacture and transport safely. Ammonium nitrate, an explosive that can act as both an oxidizing agent and a reducing agent, is often used to modify other explosives such as nitroglycerin. Ammonium nitrate is one of the products made by Villamagna’s company.

Making Career Connections
• The chemical formula of nitroglycerin is C₅O₉N₃H₅. Write the balanced chemical equation for the decomposition of nitroglycerin, as described in this feature.
• Find out which Canadian companies employ chemists who specialize in safe applications of explosives. Contact those companies for more information.
Section Summary

In this section, you learned how to identify the different components of a galvanic cell. Also, you found out how galvanic cells convert chemical energy into electrical energy. You were introduced to several common primary batteries that contain galvanic cells. In the next section, you will learn more about the cell potentials of galvanic cells.

Section Review

1. Identify the oxidizing agent and the reducing agent in a dry cell.

2. Explain why the top of a commercial 1.5-V dry cell battery is always marked with a plus sign.

3. The reaction products in a silver button battery are solid zinc oxide and solid silver.
   (a) Write the two half-reactions and the equation for the overall reaction in the battery.
   (b) Name the materials used to make the anode and the cathode.

4. If two 1.5-V D-size batteries power a flashlight, at what voltage is the flashlight operating? Explain.

5. How many dry cells are needed to make a 6-V dry cell battery? Explain.

6. Research the environmental impact of mercury pollution. Describe the main sources of mercury in the environment, the effects of mercury on human health, and at least one incident in which humans were harmed by mercury pollution.

7. When a dry cell produces electricity, what happens to the container? Explain.

8. Use the following shorthand representation to sketch a possible design of the cell. Include as much information as you can. Identify the anode and cathode, and write the half-reactions and the overall cell reaction.
   \[ \text{Fe}_\text{(s)} | \text{Fe}^{2+}_\text{(aq)} \ || \ \text{Ag}^{+}_\text{(aq)} | \text{Ag}_\text{(s)} \]
In section 19.1, you learned that a cell potential is the difference between the potential energies at the anode and the cathode of a cell. In other words, a cell potential is the difference between the potentials of two half-cells. You cannot measure the potential of one half-cell, because a single half-reaction cannot occur alone. However, you can use measured cell potentials to construct tables of half-cell potentials. A table of standard half-cell potentials allows you to calculate cell potentials, rather than building the cells and measuring their potentials. Table 19.1 includes a few standard half-cell potentials. A larger table of standard half-cell potentials is given in Appendix E.

### Table 19.1 Standard Half-Cell Potentials (298 K)

<table>
<thead>
<tr>
<th>Half-reaction</th>
<th>$E^\circ$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$</td>
<td>2.866</td>
</tr>
<tr>
<td>$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$</td>
<td>1.066</td>
</tr>
<tr>
<td>$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$</td>
<td>0.536</td>
</tr>
<tr>
<td>$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$</td>
<td>0.342</td>
</tr>
<tr>
<td>$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$</td>
<td>0.000</td>
</tr>
<tr>
<td>$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$</td>
<td>-0.447</td>
</tr>
<tr>
<td>$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$</td>
<td>-0.762</td>
</tr>
<tr>
<td>$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$</td>
<td>-1.662</td>
</tr>
<tr>
<td>$Na^+(aq) + e^- \rightleftharpoons Na(s)$</td>
<td>-2.711</td>
</tr>
</tbody>
</table>

Table 19.1 and the larger table in Appendix E are based on the following conventions.

- Each half-reaction is written as a reduction. The half-cell potential for a reduction half-reaction is called a **reduction potential**. Look at the molecules and ions on the left side of each half-reaction. The most easily reduced molecules and ions (best oxidizing agents), such as $F_2$, $MnO_4^-$, and $O_2$, are near the top of the list. The least easily reduced molecules and ions (worst oxidizing agents), such as $Na^+$, $Ca^{2+}$, and $H_2O$, are near the bottom of the list.

- The numerical values of cell potentials and half-cell potentials depend on various conditions, so tables of **standard** reduction potentials are true when ions and molecules are in their **standard states**. These standard states are the same as for tables of standard enthalpy changes. Aqueous molecules and ions have a standard concentration of 1 mol/L. Gases have a standard pressure of 101.3 kPa or 1 atm. The standard temperature is 25°C or 298 K. Standard reduction potentials are designated by the symbol $E^\circ$, where the superscript “ indicates standard states.

- Because you can measure potential differences, but not individual reduction potentials, all values in the table are relative. Each half-cell reduction potential is given relative to the reduction potential of the standard hydrogen electrode, which has been assigned a value of zero. The design of this electrode is shown in Figure 19.12.
In a standard hydrogen electrode, which is open to the atmosphere, hydrogen gas at 1 atm pressure bubbles over an inert platinum electrode. The electrode is immersed in a solution containing 1 mol/L $H^+$ ions.

Calculating Standard Cell Potentials

You can use Table 19.1 to calculate the standard cell potential of the familiar Daniell cell. This cell has its standard potential when the solution concentrations are 1 mol/L, as shown in the shorthand representation below.

$$\text{Zn} \mid \text{Zn}^{2+} \text{(1 mol/L)} \parallel \text{Cu}^{2+} \text{(1 mol/L)} \mid \text{Cu}$$

One method to calculate the standard cell potential is to subtract the standard reduction potential of the anode from the standard reduction potential of the cathode.

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

For a Daniell cell, you know that copper is the cathode and zinc is the anode. The relevant half-reactions and standard reduction potentials from Table 19.1 are as follows.

$$\text{Cu}^{2+} \text{(aq)} + 2e^- \rightleftharpoons \text{Cu(s)} \quad E^\circ = 0.342 \text{ V}$$
$$\text{Zn}^{2+} \text{(aq)} + 2e^- \rightleftharpoons \text{Zn(s)} \quad E^\circ = -0.762 \text{ V}$$

Use these values to calculate the cell potential.

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$$
$$= 0.342 \text{ V} - (-0.762 \text{ V})$$
$$= 0.342 \text{ V} + 0.762 \text{ V}$$
$$= 1.104 \text{ V}$$

Thus, the standard cell potential for a Daniell cell is 1.104 V. The standard cell potentials of all galvanic cells have positive values, as explained in Figure 19.13, on the following page. Figure 19.13 shows a “potential ladder” diagram. A “potential ladder” diagram models the potential difference. The rungs on the ladder correspond to the values of the reduction potentials.
This calculation of the standard cell potential for the Daniell cell used the mathematical concept that the subtraction of a negative number is equivalent to the addition of its positive value. You saw that

\[ 0.342 \text{ V} - (-0.762 \text{ V}) = 0.342 \text{ V} + 0.762 \text{ V} \]

In other words, the subtraction of the reduction potential for a half-reaction is equivalent to the addition of the potential for the reverse half-reaction. The reverse half-reaction of a reduction is an oxidation. The half-cell potential for an oxidation half-reaction is called an oxidation potential. If the reduction half-reaction is as follows,

\[ \text{Zn}^{2+} (\text{aq}) + 2e^- \rightleftharpoons \text{Zn} (s) \]

then the oxidation half-reaction is

\[ \text{Zn} (s) \rightleftharpoons \text{Zn}^{2+} (\text{aq}) + 2e^- \]

To summarize, the standard cell potential can also be calculated as the sum of a standard reduction potential and a standard oxidation potential.

\[ E_{\text{cell}} = E_{\text{red}} + E_{\text{ox}} \]

As shown above, you can obtain the standard oxidation potential from a table of standard reduction potentials by reversing the reduction half-reaction, and changing the sign of the relevant potential. The reduction and oxidation half-reactions for the previous example are as follows.

\[ \text{Cu}^{2+} (\text{aq}) + 2e^- \rightleftharpoons \text{Cu} (s) \]

\[ E_{\text{red}} = 0.342 \text{ V} \]

\[ \text{Zn} (s) \rightleftharpoons \text{Zn}^{2+} (\text{aq}) + 2e^- \]

\[ E_{\text{ox}} = +0.762 \text{ V} \]

The calculation of the standard cell potential using these standard half-reaction potentials is as follows.

\[ E_{\text{cell}} = E_{\text{red}} + E_{\text{ox}} \]

\[ = 0.342 \text{ V} + 0.762 \text{ V} \]

\[ = 1.104 \text{ V} \]

Finding the difference between two reduction potentials, and finding the sum of a reduction potential and an oxidation potential are exactly equivalent methods for finding a cell potential. Use whichever method you prefer. The first Sample Problem includes both methods for finding cell potentials. The second Sample Problem uses only the subtraction of two reduction potentials. Practice problems are included after the second Sample Problem.
Sample Problem
Calculating a Standard Cell Potential, Given a Net Ionic Equation

Problem
Calculate the standard cell potential for the galvanic cell in which the following reaction occurs.

\[ 2\Gamma_{(aq)} + \text{Br}_2(ℓ) \rightarrow I_2(s) + 2\text{Br}^-(aq) \]

What Is Required?
You need to find the standard cell potential for the given reaction.

What Is Given?
You have the balanced net ionic equation and a table of standard reduction potentials.

Plan Your Strategy
Method 1: Subtracting Two Reduction Potentials
Step 1 Write the oxidation and reduction half-reactions.
Step 2 Locate the relevant reduction potentials in a table of standard reduction potentials.
Step 3 Subtract the reduction potentials to find the cell potential, using

\[ E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \]

Method 2: Adding an Oxidation Potential and a Reduction Potential
Step 1 Write the oxidation and reduction half-reactions.
Step 2 Locate the relevant reduction potentials in a table of standard reduction potentials.
Step 3 Change the sign of the reduction potential for the oxidation half-reaction to find the oxidation potential.
Step 4 Add the reduction potential and the oxidation potential, using

\[ E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{ox}} \]

Act on Your Strategy
Method 1: Subtracting Two Reduction Potentials
Step 1 The oxidation and reduction half-reactions are as follows.
Oxidation half-reaction (occurs at the anode): \(2\Gamma_{(aq)} \rightarrow I_2(s) + 2e^-\)
Reduction half-reaction (occurs at the cathode): \(\text{Br}_2(ℓ) + 2e^- \rightarrow 2\text{Br}^-(aq)\)
Step 2 The relevant reduction potentials in the table of standard reduction potentials are:
\(I_2(s) + 2e^- \rightleftharpoons 2\Gamma_{(aq)} \quad E^\circ_{\text{anode}} = 0.536 \text{ V}\)
\(\text{Br}_2(ℓ) + 2e^- \rightleftharpoons 2\text{Br}^-(aq) \quad E^\circ_{\text{cathode}} = 1.066 \text{ V}\)
Step 3 Calculate the cell potential by subtraction.

\[ E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \]
\[ = 1.066 \text{ V} - 0.536 \text{ V} \]
\[ = 0.530 \text{ V} \]
Method 2: Adding an Oxidation Potential and a Reduction Potential

Step 1 The oxidation and reduction half-reactions are as follows.
Oxidation half-reaction (occurs at the anode): \( 2I^- \rightarrow I_2 + 2e^- \)
Reduction half-reaction (occurs at the cathode): \( Br_2 + 2e^- \rightarrow 2Br^- \)

Step 2 The relevant reduction potentials in the table of standard reduction potentials are:
- \( I_2 + 2e^- \rightleftharpoons 2I^- \) \( E_{\text{anode}}^{\circ} = 0.536 \text{ V} \)
- \( Br_2 + 2e^- \rightleftharpoons 2Br^- \) \( E_{\text{cathode}}^{\circ} = 1.066 \text{ V} \)

Step 3 The standard electrode potential for the reduction half-reaction is \( E_{\text{red}}^{\circ} = 1.066 \text{ V} \). Changing the sign of the potential for the oxidation half-reaction gives
- \( 2I^- \rightleftharpoons I_2 + 2e^- \) \( E_{\text{ox}}^{\circ} = -0.536 \text{ V} \)

Step 4 Calculate the cell potential by addition.
\[
E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} + E_{\text{ox}}^{\circ} = 1.066 \text{ V} + (-0.536 \text{ V}) = 0.530 \text{ V}
\]

Check Your Solution
Both methods give the same answer. The cell potential is positive, as expected for a galvanic cell.

A standard cell potential depends only on the identities of the reactants and products in their standard states. As you will see in the next Sample Problem, you do not need to consider the amounts of reactants or products present, or the reaction stoichiometry, when calculating a standard cell potential. Since you have just completed a similar Sample Problem, only a brief solution using the subtraction method is given here. Check that you can solve this problem by adding a reduction potential and an oxidation potential.

Sample Problem

Calculating a Standard Cell Potential, Given a Chemical Equation

Problem
Calculate the standard cell potential for the galvanic cell in which the following reaction occurs.
\[ 2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g) \]
**Solution**

**Step 1** Write the equation in ionic form to identify the half-reactions.

\[ 2\text{Na}(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{Na}^+(aq) + 2\text{OH}^-(aq) + \text{H}_2(g) \]

Write the oxidation and reduction half-reactions.

Oxidation half-reaction (occurs at the anode): \( \text{Na}(s) \rightarrow \text{Na}^+(aq) + e^- \)

Reduction half-reaction (occurs at the cathode): \( 2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq) \)

**Step 2** Locate the relevant reduction potentials in a table of standard reduction potentials.

\[
\begin{align*}
\text{Na}(s) + e^- &\leftrightarrow \text{Na}^+(aq) \quad E^\circ_{\text{anode}} = -2.711 \text{ V} \\
2\text{H}_2\text{O}(l) + 2e^- &\leftrightarrow \text{H}_2(g) + 2\text{OH}^-(aq) \quad E^\circ_{\text{cathode}} = -0.828 \text{ V}
\end{align*}
\]

**Step 3** Subtract the standard reduction potentials to calculate the cell potential.

\[
E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}
\]

\[
= -0.828 \text{ V} - (-2.711 \text{ V})
\]

\[
= 1.883 \text{ V}
\]

The standard cell potential is 1.883 V. The Problem Tip on this page illustrates this calculation.

---

**Practice Problems**

(\textbf{Note:} Obtain the necessary standard reduction potential values from the table in Appendix E.)

5. Write the two half-reactions for the following redox reaction. Subtract the two reduction potentials to find the standard cell potential for a galvanic cell in which this reaction occurs.

\[ \text{Cl}_2(g) + 2\text{Br}^-_{(aq)} \rightarrow 2\text{Cl}^-_{(aq)} + \text{Br}_2(l) \]

6. Write the two half-reactions for the following redox reaction. Add the reduction potential and the oxidation potential to find the standard cell potential for a galvanic cell in which this reaction occurs.

\[ 2\text{Cu}^+_{(aq)} + 2\text{H}^+_{(aq)} + \text{O}_2(g) \rightarrow 2\text{Cu}^{2+}_{(aq)} + \text{H}_2\text{O}(aq) \]

7. Write the two half-reactions for the following redox reaction. Subtract the two standard reduction potentials to find the standard cell potential for the reaction.

\[ \text{Sn}(s) + 2\text{HBr}_{(aq)} \rightarrow \text{SnBr}_2_{(aq)} + \text{H}_2(g) \]

8. Write the two half-reactions for the following redox reaction. Add the standard reduction potential and the standard oxidation potential to find the standard cell potential for the reaction.

\[ \text{Cr}(s) + 3\text{AgCl}(s) \rightarrow \text{CrCl}_3_{(aq)} + 3\text{Ag}(s) \]

You have learned that the standard hydrogen electrode has an assigned standard reduction potential of exactly 0 V, and is the reference for all half-cell standard reduction potentials. What would happen to cell potentials if a different reference were used? You will address this question in the following ThoughtLab.
Many scales of measurement have zero values that are arbitrary. For example, on Earth, average sea level is often assigned as the zero of altitude. In this ThoughtLab, you will investigate what happens to calculated cell potentials when the reference half-cell is changed.

**Procedure**

1. Copy the following table of reduction potentials into your notebook. Change the zero on the scale by adding 1.662 V to each value to create new, adjusted reduction potentials.

<table>
<thead>
<tr>
<th>Reduction half-reaction</th>
<th>$E^\circ$ (V)</th>
<th>$E^\circ + 1.662$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{F}<em>2(g) + 2e^- \rightleftharpoons 2\text{F}^-</em>{(aq)}$</td>
<td>2.866</td>
<td>4.528</td>
</tr>
<tr>
<td>$\text{Fe}^{3+}<em>{(aq)} + e^- \rightleftharpoons \text{Fe}^{2+}</em>{(aq)}$</td>
<td>0.771</td>
<td>2.433</td>
</tr>
<tr>
<td>$2\text{H}^+_{(aq)} + 2e^- \rightleftharpoons \text{H}_2(g)$</td>
<td>0.000</td>
<td>1.662</td>
</tr>
<tr>
<td>$\text{Al}^{3+}<em>{(aq)} + 3e^- \rightleftharpoons \text{Al}</em>{(s)}$</td>
<td>−1.662</td>
<td>0.000</td>
</tr>
<tr>
<td>$\text{Li}^+<em>{(aq)} + e^- \rightleftharpoons \text{Li}</em>{(s)}$</td>
<td>−3.040</td>
<td>−1.378</td>
</tr>
</tbody>
</table>

2. Use the given standard reduction potentials to calculate the standard cell potentials for the following redox reactions.
   
   (a) $2\text{Li}_{(s)} + 2\text{H}^+_{(aq)} \rightarrow 2\text{Li}^+_{(aq)} + \text{H}_2(g)$
   
   (b) $2\text{Al}_{(s)} + 3\text{F}_2(g) \rightarrow 2\text{Al}^{3+}_{(aq)} + 6\text{F}^-_{(aq)}$
   
   (c) $2\text{FeCl}_3_{(aq)} + \text{H}_2(g) \rightarrow 2\text{FeCl}_2_{(aq)} + 2\text{HCl}_{(aq)}$
   
   (d) $\text{Al(NO}_3)_3_{(aq)} + 3\text{Li}_{(s)} \rightarrow 3\text{LiNO}_3_{(aq)} + \text{Al}_{(s)}$

3. Repeat your calculations using the new, adjusted reduction potentials.

**Analysis**

1. Compare your calculations from questions 2 and 3 of the procedure. What effect does changing the zero on the scale of reduction potentials have on
   
   (a) reduction potentials?
   
   (b) cell potentials?

**Applications**

2. Find the difference between the temperatures at which water boils and freezes on the following scales. (Assume that a difference is positive, rather than negative.)
   
   (a) the Celsius temperature scale
   
   (b) the Kelvin temperature scale

3. What do your answers for the previous question tell you about these two temperature scales?

4. The zero on a scale of masses is not arbitrary. Why not?

**Section Summary**

In this section, you learned that you can calculate cell potentials by using tables of half-cell potentials. The half-cell potential for a reduction half-reaction is called a reduction potential. The half-cell potential for an oxidation half-reaction is called an oxidation potential. Standard half-cell potentials are written as reduction potentials. The values of standard reduction potentials for half-reactions are relative to the reduction potential of the standard hydrogen electrode. You used standard reduction potentials to calculate standard cell potentials for galvanic cells. You learned two methods of calculating standard cell potentials. One method is to subtract the standard reduction potential of the anode from the standard reduction potential of the cathode. The other method is to add the standard reduction potential of the cathode and the standard oxidation potential of the anode. In the next section, you will learn about a different type of cell, called an electrolytic cell.
1. Determine the standard cell potential for each of the following redox reactions.
   (a) \(3\text{Mg}(s) + 2\text{Al}^{3+}(aq) \rightarrow 3\text{Mg}^{2+}(aq) + 2\text{Al}(s)\)
   (b) \(2\text{K}(s) + \text{F}_2(g) \rightarrow 2\text{K}^+(aq) + 2\text{F}^-(aq)\)
   (c) \(\text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6\text{Ag}(s) \rightarrow 2\text{Cr}^{3+}(aq) + 6\text{Ag}^+(aq) + 7\text{H}_2\text{O}(l)\)

2. Determine the standard cell potential for each of the following redox reactions.
   (a) \(\text{CuSO}_4(aq) + \text{Ni}(s) \rightarrow \text{NiSO}_4(aq) + \text{Cu}(s)\)
   (b) \(4\text{Au(OH)}_3(aq) \rightarrow 4\text{Au}(s) + 6\text{H}_2\text{O}(l) + 3\text{O}_2(g)\)
   (c) \(\text{Fe}(s) + 4\text{HNO}_3(aq) \rightarrow \text{Fe(NO}_3)_3(aq) + \text{NO}(g) + 2\text{H}_2\text{O}(l)\)

3. For which half-cell are the values of the standard reduction potential and the standard oxidation potential equal?

4. Look at the half-cells in the table of standard reduction potentials in Appendix E. Could you use two of the standard half-cells to build a galvanic cell with a standard cell potential of 7 V? Explain your answer.

5. Compare the positions of metals in the metal activity series with their positions in the table of standard reduction potentials. Describe the similarities and differences.

6. The cell potential for the following galvanic cell is given.
   \(\text{Zn} \mid \text{Zn}^{2+} (1 \text{ mol/L}) \parallel \text{Pd}^{2+} (1 \text{ mol/L}) \mid \text{Pd} \quad E_{\text{cell}}^\circ = 1.750 \text{ V}\)
   Determine the standard reduction potential for the following half-reaction.
   \(\text{Pd}^{2+}(aq) + 2e^- \rightarrow \text{Pd}(s)\)

---

**Section Review**

Battery makers have been challenged to make batteries smaller, lighter, longer-lasting, and more powerful. In March, 2003, Dalhousie University established a Research Chair in Battery and Fuel Cell Materials. The university’s new laboratory is one of the few in the world equipped to use a new mode of research developed in 1995, called Combinatorial Materials Synthesis (CMS). CMS rapidly accelerates the time needed to test new combinations of materials by uncovering thousands of distinct compositions in a single experiment. Chief researcher Jeffery Dahn is applying CMS methods to improve the safety of lithium-ion batteries and produce cells large enough to power electric vehicles.

To research the history and latest developments in the field of battery technology, go to the web site above and click on Web Links.
In this section, you will

- identify the components of an electrolytic cell, and describe how they work
- describe electrolytic cells using oxidation and reduction half-cells
- determine oxidation and reduction half-cell reactions, direction of current flow, electrode polarity, cell potential, and ion movement in some electrolytic cells
- build and investigate an electrolytic cell in the laboratory
- predict whether or not redox reactions are spontaneous, using standard cell potentials
- compare galvanic and electrolytic cells in terms of energy efficiency, electron flow, and chemical change
- describe some common rechargeable batteries, and evaluate their impact on the environment and on society
- communicate your understanding of the following terms: electrolytic cell, electrolysis, overvoltage, electroplating

Section Preview/Outcomes

Electrolytic Cells

For a galvanic cell, you have learned that the overall reaction is spontaneous, and that the cell potential has a positive value. A galvanic cell converts chemical energy to electrical energy. Electrons flow from a higher potential energy to a lower potential energy. As described earlier, the flow of electrons in the external circuit of a galvanic cell can be compared to water flowing downhill.

Although water flows downhill spontaneously, you can also pump water uphill. This process requires energy because it moves water from a position of lower potential energy to a position of higher potential energy. You will now learn about a type of cell that uses energy to move electrons from lower potential energy to higher potential energy. This type of cell, called an electrolytic cell, is a device that converts electrical energy to chemical energy. The process that takes place in an electrolytic cell is called electrolysis. The overall reaction in an electrolytic cell is non-spontaneous, and requires energy to occur. This type of reaction is the reverse of a spontaneous reaction, which generates energy when it occurs.

Like a galvanic cell, an electrolytic cell includes electrodes, at least one electrolyte, and an external circuit. Unlike galvanic cells, electrolytic cells require an external source of electricity, sometimes called the external voltage. This is included in the external circuit. Except for the external source of electricity, an electrolytic cell may look just like a galvanic cell. Some electrolytic cells include a porous barrier or salt bridge. In other electrolytic cells, the two half-reactions are not separated, and take place in the same container.

Electrolysis of Molten Salts

The electrolytic cell shown in Figure 19.14 decomposes sodium chloride into its elements. The cell consists of a single container with two inert electrodes dipping into liquid sodium chloride. To melt the sodium chloride, the temperature must be above its melting point of about 800°C. As in an aqueous solution of sodium chloride, the ions in molten sodium chloride have some freedom of movement. In other words, molten sodium chloride is the electrolyte of this cell.

![Figure 19.14](molten-sodium-chloride-decomposes-into-sodium-and-chlorine-in-this-electrolytic-cell. The sodium chloride is said to undergo electrolysis, or to be electrolyzed.)
The external source of electricity forces electrons onto one electrode. As a result, this electrode becomes negative relative to the other electrode. The positive sodium ions move toward the negative electrode, where they gain electrons and are reduced to the element sodium. At this temperature, sodium metal is produced as a liquid. The negative chloride ions move toward the positive electrode, where they lose electrons and are oxidized to the element chlorine, a gas. *As in a galvanic cell, reduction occurs at the cathode, and oxidation occurs at the anode of an electrolytic cell.* The half-reactions for this electrolytic cell are as follows.

Reduction half-reaction (occurs at the cathode): \( \text{Na}^+ + e^- \rightarrow \text{Na} \)

Oxidation half-reaction (occurs at the anode): \( 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \)

Because of the external voltage of the electrolytic cell, the electrodes do not have the same polarities in electrolytic and galvanic cells. In a galvanic cell, the cathode is positive and the anode is negative. In an electrolytic cell, the anode is positive and the cathode is negative.

The electrolysis of molten sodium chloride is an important industrial reaction. Figure 19.15 shows the large electrolytic cell used in the industrial production of sodium and chlorine. You will meet other industrial electrolytic processes later in this chapter.

![Diagram of electrolytic cell](image)

**Check your understanding of the introduction to electrolytic cells by completing the following practice problems.**

**Practice Problems**

9. The electrolysis of molten calcium chloride produces calcium and chlorine. Write
   (a) the half-reaction that occurs at the anode
   (b) the half-reaction that occurs at the cathode
   (c) the chemical equation for the overall cell reaction

“Electrochemical cell” is a common term in electrochemistry. Some scientists include both galvanic cells and electrolytic cells as types of electrochemical cells. Other scientists consider galvanic cells, but not electrolytic cells, as electrochemical cells. If you meet the term “electrochemical cell,” always check its exact meaning.
10. For the electrolysis of molten lithium bromide, write
   (a) the half-reaction that occurs at the negative electrode
   (b) the half-reaction that occurs at the positive electrode
   (c) the net ionic equation for the overall cell reaction

11. A galvanic cell produces direct current, which flows in one direction.
    The mains supply at your home is a source of alternating current, which changes direction every fraction of a second. Explain why the external electrical supply for an electrolytic cell must be a source of direct current, rather than alternating current.

12. Suppose a battery is used as the external electrical supply for an electrolytic cell. Explain why the negative terminal of the battery must be connected to the cathode of the cell.

Electrolysis of Water

The electrolysis of aqueous solutions may not yield the desired products. Sir Humphry Davy (1778–1829) discovered the elements sodium and potassium by electrolyzing their molten salts. Before this discovery, Davy had electrolyzed aqueous solutions of sodium and potassium salts. He had not succeeded in reducing the metal ions to the pure metals at the cathode. Instead, his first experiments had produced hydrogen gas. Where did the hydrogen gas come from?

When electrolyzing an aqueous solution, there are two compounds present: water, and the dissolved electrolyte. Water may be electrolyzed as well as, or instead of, the electrolyte. The electrolysis of water produces oxygen gas and hydrogen gas, as shown in Figure 19.16.

![Figure 19.16](image-url) The electrolysis of water produces hydrogen gas at the cathode and oxygen gas at the anode. Explain why the volume of hydrogen gas is twice the volume of oxygen gas.
The half-reactions for the electrolysis of water are given below.

Oxidation half-reaction (occurs at the anode):
\[ 2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4\text{e}^- \]

Reduction half-reaction (occurs at the cathode):
\[ 2\text{H}_2\text{O}(l) + 2\text{e}^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq) \]

Because the number of electrons lost and gained must be equal, multiply the reduction half-reaction by 2. Then add and simplify to obtain the overall cell reaction.

Overall cell reaction: \[ 2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g) \]

The standard reduction potentials are as follows.
\[ \text{O}_2(g) + 4\text{H}^+(aq) + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(l) \quad E^\circ = 1.229 \text{ V} \]
\[ 2\text{H}_2\text{O}(l) + 2\text{e}^- \rightleftharpoons \text{H}_2(g) + 2\text{OH}^-(aq) \quad E^\circ = -0.828 \text{ V} \]

You can use these values to calculate the \( E^\circ_{\text{cell}} \) value for the decomposition of water.
\[
E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\
= -0.828 \text{ V} - 1.229 \text{ V} \\
= -2.057 \text{ V}
\]

Therefore, \[ 2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g) \quad E^\circ_{\text{cell}} = -2.057 \text{ V} \]

The negative cell potential shows that the reaction is not spontaneous. Electrolytic cells are used for non-spontaneous redox reactions, so all electrolytic cells have negative cell potentials.

The standard reduction potentials used to calculate \( E^\circ_{\text{cell}} \) for the decomposition of water apply only to reactants and products in their standard states. However, in pure water at 25°C, the hydrogen ions and hydroxide ions each have concentrations of \( 1 \times 10^{-7} \text{ mol/L} \). This is not the standard state value of 1 mol/L. The reduction potential values for the non-standard conditions in pure water are given below. The superscript zero is now omitted from the \( E \) symbol, because the values are no longer standard.

\[ \text{O}_2(g) + 4\text{H}^+(aq) + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(l) \quad E = 0.815 \text{ V} \]
\[ 2\text{H}_2\text{O}(l) + 2\text{e}^- \rightleftharpoons \text{H}_2(g) + 2\text{OH}^-(aq) \quad E = -0.414 \text{ V} \]

Using these new half-cell potentials, \( E_{\text{cell}} \) for the decomposition of pure water at 25°C by electrolysis has a calculated value of \(-1.229 \text{ V} \). Therefore, the calculated value of the external voltage needed is 1.229.

In practice, the external voltage needed for an electrolytic cell is always greater than the calculated value, especially for reactions involving gases. Therefore, the actual voltage needed to electrolyze pure water is greater than 1.229 V. The excess voltage required above the calculated value is called the overvoltage. Overvoltages depend on the gases involved and on the materials in the electrodes.

When electrolyzing water, there is another practical difficulty to consider. Pure water is a very poor electrical conductor. To increase the conductivity, an electrolyte that does not interfere in the reaction is added to the water.
Electrolysis of Aqueous Solutions

As stated previously, an electrolytic cell may have the same design as a galvanic cell, except for the external source of electricity. Consider, for example, the familiar Daniell cell. (This cell was described in section 19.1 and shown in Figure 19.5.) By adding an external electrical supply, with a voltage greater than the voltage of the Daniell cell, you can push electrons in the opposite direction. By pushing electrons in the opposite direction, you reverse the chemical reaction. Figure 19.17 shows both cells, while their properties are compared in Table 19.2.

![Figure 19.17 Adding an external voltage to reverse the electron flow converts a Daniell cell from a galvanic cell into an electrolytic cell. The result is to switch the anode and cathode.](image)

<table>
<thead>
<tr>
<th>Table 19.2 Cell Comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Galvanic Cell</strong></td>
</tr>
<tr>
<td>Spontaneous reaction</td>
</tr>
<tr>
<td>Converts chemical energy to electrical energy</td>
</tr>
<tr>
<td>Anode (negative): Zinc</td>
</tr>
<tr>
<td>Cathode (positive): Copper</td>
</tr>
<tr>
<td>Oxidation (at anode): ( \text{Zn}^{(s)} \rightarrow \text{Zn}^{2+}{}_{(aq)} + 2 \text{e}^- )</td>
</tr>
<tr>
<td>Reduction (at cathode): ( \text{Cu}^{2+}{}_{(aq)} + 2 \text{e}^- \rightarrow \text{Cu}^{(s)} )</td>
</tr>
<tr>
<td>Cell reaction: ( \text{Zn}^{(s)} + \text{Cu}^{2+}{}<em>{(aq)} \rightarrow \text{Zn}^{2+}{}</em>{(aq)} + \text{Cu}^{(s)} )</td>
</tr>
</tbody>
</table>

In the galvanic cell, the zinc anode gradually dissolves. The copper cathode grows as more copper is deposited onto it. In the electrolytic cell, the copper anode gradually dissolves. The zinc cathode grows as more zinc is deposited onto it. The process in which a metal is deposited, or plated, onto the cathode in an electrolytic cell is known as **electroplating**. Electroplating is very important in industry, as you will learn later in this chapter.
Predicting the Products of Electrolysis for an Aqueous Solution

The comparison of the Daniell cell with the electrolytic version of the cell appears straightforward. One reaction is the reverse of the other. However, you have just learned that the electrolysis of an aqueous solution may involve the electrolysis of water. How can you predict the actual products for this type of electrolysis reaction?

To predict the products of an electrolysis involving an aqueous solution, you must examine all possible half-reactions and their reduction potentials. Then, you must find the overall reaction that requires the lowest external voltage. That is, you must find the overall cell reaction with a negative cell potential that is closest to zero. The next Sample Problem shows you how to predict the products of the electrolysis of an aqueous solution.

In practice, reaction products are sometimes different from the products predicted, using the method described here. Predictions are least reliable when the reduction potentials are close together, especially when gaseous products are expected. However, there are many cases in which the predictions are correct.

Sample Problem

Electrolysis of an Aqueous Solution

Problem

Predict the products of the electrolysis of 1 mol/L LiBr\(_{\text{aq}}\).

What Is Required?

You need to predict the products of the electrolysis of 1 mol/L LiBr\(_{\text{aq}}\).

What Is Given?

This is an aqueous solution. You are given the formula and concentration of the electrolyte. You have a table of standard reduction potentials, and you know the non-standard reduction potentials for water.

Plan Your Strategy

Step 1 List the four relevant half-reactions and their reduction potentials.

Step 2 Predict the products by finding the cell reaction that requires the lowest external voltage.

Act on Your Strategy

Step 1 The Li\(^+\) and Br\(^-\) concentrations are 1 mol/L, so use the standard reduction potentials for the half-reactions that involve these ions. Use the non-standard values for water.

\[
\begin{align*}
\text{Br}_2(\ell) + 2e^- &\rightleftharpoons 2\text{Br}^-_{\text{aq}} \quad E^\circ = 1.066 \text{ V} \\
\text{O}_2(\ell) + 4\text{H}^+_{\text{aq}} + 4e^- &\rightleftharpoons 2\text{H}_2\text{O}(\ell) \quad E = 0.815 \text{ V} \\
2\text{H}_2\text{O}(\ell) + 2e^- &\rightleftharpoons \text{H}_2(\ell) + 2\text{OH}^-_{\text{aq}} \quad E = -0.414 \text{ V} \\
\text{Li}^+_{\text{aq}} + e^- &\rightleftharpoons \text{Li}(s) \quad E^\circ = -3.040 \text{ V}
\end{align*}
\]
There are two possible oxidation half-reactions at the anode: the oxidation of bromide ion in the electrolyte, or the oxidation of water.

\[
2\text{Br}^-_{(aq)} \rightarrow \text{Br}_2(l) + 2e^-
\]

\[
2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+_{(aq)} + 4e^-
\]

There are two possible reduction half-reactions at the cathode: the reduction of lithium ions in the electrolyte, or the reduction of water.

\[
\text{Li}^+_{(aq)} + e^- \rightarrow \text{Li}(s)
\]

\[
2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-_{(aq)}
\]

**Step 2** Combine pairs of half-reactions to produce four possible overall reactions. (You learned how to do this in Chapter 10.)

**Reaction 1:** the production of lithium and bromine

\[
2\text{Li}^+_{(aq)} + 2\text{Br}^-_{(aq)} \rightarrow 2\text{Li}(s) + \text{Br}_2(l)
\]

\[
E_{cell} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}
\]

\[
= -3.040 \text{ V} - 1.066 \text{ V}
\]

\[
= -4.106 \text{ V}
\]

**Reaction 2:** the production of hydrogen and oxygen

\[
2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g)
\]

\[
E_{cell} = E_{\text{cathode}} - E_{\text{anode}}
\]

\[
= -0.414 \text{ V} - 0.815 \text{ V}
\]

\[
= -1.229 \text{ V}
\]

**Reaction 3:** the production of lithium and oxygen

\[
4\text{Li}^+_{(aq)} + 2\text{H}_2\text{O}(l) \rightarrow 4\text{Li}(s) + \text{O}_2(g) + 4\text{H}^+_{(aq)}
\]

\[
E_{cell} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}
\]

\[
= -3.040 \text{ V} - 0.815 \text{ V}
\]

\[
= -3.855 \text{ V}
\]

**Reaction 4:** the production of hydrogen and bromine

\[
2\text{H}_2\text{O}(l) + 2\text{Br}^-_{(aq)} \rightarrow 2\text{H}_2(g) + 2\text{OH}^-_{(aq)} + \text{Br}_2(l)
\]

\[
E_{cell} = E_{\text{cathode}} - E^\circ_{\text{anode}}
\]

\[
= -0.414 \text{ V} - 1.066 \text{ V}
\]

\[
= -1.480 \text{ V}
\]

The electrolysis of water requires the lowest external voltage. Therefore, the predicted products of this electrolysis are hydrogen and oxygen.

**Check Your Solution**

Use a potential ladder diagram, such as the one on the next page, part A, to visualize the cell potentials. For an electrolytic cell, the half-reaction at the anode is always on the upper rung, and the subtraction \(E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}\) always gives a negative cell potential, as shown in part B.
13. Predict the products of the electrolysis of a 1 mol/L solution of sodium chloride.

14. Explain why calcium can be produced by the electrolysis of molten calcium chloride, but not by the electrolysis of aqueous calcium chloride.

15. One half-cell of a galvanic cell has a nickel electrode in a 1 mol/L nickel(II) chloride solution. The other half-cell has a cadmium electrode in a 1 mol/L cadmium chloride solution.

   (a) Find the cell potential.
   (b) Identify the anode and the cathode.
   (c) Write the oxidation half-reaction, the reduction half-reaction, and the overall cell reaction.

16. An external voltage is applied to change the galvanic cell in question 15 into an electrolytic cell. Repeat parts (a) to (c) for the electrolytic cell.

Practice Problems

In Investigation 19-B, you will build an electrolytic cell for the electrolysis of an aqueous solution of potassium iodide. You will predict the products of the electrolysis, and compare the observed products with your predictions.
Electrolysis of Aqueous Potassium Iodide

When an aqueous solution is electrolyzed, the electrolyte or water can undergo electrolysis. In this investigation, you will build an electrolytic cell, carry out the electrolysis of an aqueous solution, and identify the products.

Questions
What are the products from the electrolysis of a 1 mol/L aqueous solution of potassium iodide? Are the observed products the ones predicted using reduction potentials?

Predictions
Use the relevant standard reduction potentials from the table in Appendix E, and the non-standard reduction potentials you used previously for water, to predict the electrolysis products. Predict which product(s) are formed at the anode and which product(s) are formed at the cathode.

Materials
25 cm clear aquarium rubber tubing (Tygon®), internal diameter 4–6 mm
1 graphite pencil lead, 2 cm long
2 wire leads (black and red) with alligator clips
600 mL or 400 mL beaker
sheet of white paper
1 elastic band
3 toothpicks
3 disposable pipettes
2 cm piece of copper wire (20 gauge)
1 drop 1% starch solution
10 mL 1 mol/L KI
1 drop 1% phenolphthalein
9-V battery or variable power source set to 9 V

Safety Precautions
Make sure your lab bench is dry before carrying out this investigation.

Procedure
1. Fold a sheet of paper lengthwise. Curl the folded paper so that it fits inside the 600 mL beaker. Invert the beaker on your lab bench.
2. Use the elastic to strap the aquarium tubing to the side of the beaker in a U shape, as shown in the diagram.
3. Fill a pipette as completely as possible with 1 mol/L KI solution. Insert the tip of the pipette firmly into one end of the aquarium tubing. Slowly inject the solution into the U-tube until the level of the solution is within 1 cm to 2 cm from the top of both ends. If air bubbles are present, try to remove them by poking them with a toothpick. You may need to repeat this step from the beginning.

4. Attach the black lead to the 2 cm piece of wire. Insert the wire into one end of the U-tube. Attach the red electrical lead to the graphite. Insert the graphite into the other end of the U-tube.

5. Attach the leads to the 9-V battery or to a variable power source set to 9 V. Attach the black lead to the negative terminal, and the red lead to the positive terminal.

6. Let the reaction proceed for three minutes, while you examine the U-tube. Record your observations. Shut off the power source and remove the electrodes. Determine the product formed around the anode by adding a drop of starch solution to the end of the U-tube that contains the anode. Push the starch solution down with a toothpick if there is an air lock. Determine one of the products around the cathode by adding a drop of phenolphthalein to the appropriate end of the U-tube.

7. Dispose of your reactants and products as instructed by your teacher. Take your apparatus apart, rinse out the tubing, and rinse off the electrodes. Return your equipment to its appropriate location.

Analysis

1. Sketch the cell you made in this investigation. On your sketch, show
   (a) the direction of the electron flow in the external circuit
   (b) the anode and the cathode
   (c) the positive electrode and the negative electrode
   (d) the movement of ions in the cell

2. Use your observations to identify the product(s) formed at the anode and the product(s) formed at the cathode.

3. Write a balanced equation for the half-reaction that occurs at the anode.

4. Write a balanced equation for the half-reaction that occurs at the cathode.

5. Write a balanced equation for the overall cell reaction.

6. Calculate the external voltage required to carry out the electrolysis. Why was the external voltage used in the investigation significantly higher than the calculated value?

Conclusion

7. What are the products from the electrolysis of a 1 mol/L aqueous solution of potassium iodide? Are the observed products the same as the products predicted using reduction potentials?

Applications

8. If you repeated the electrolysis using aqueous sodium iodide instead of aqueous potassium iodide, would your observations change? Explain your answer.

9. To make potassium by electrolyzing potassium iodide, would you need to modify the procedure? Explain your answer.
Spontaneity of Reactions
You know that galvanic cells have positive standard cell potentials, and that these cells use spontaneous chemical reactions to produce electricity. You also know that electrolytic cells have negative standard cell potentials, and that these cells use electricity to perform non-spontaneous chemical reactions. Thus, you can use the sign of the standard cell potential to predict whether a reaction is spontaneous or not under standard conditions.

Sample Problem
Predicting Spontaneity

Problem
Predict whether each reaction is spontaneous or non-spontaneous under standard conditions.
(a) \( \text{Cd} (s) + \text{Cu}^{2+} (aq) \rightarrow \text{Cd}^{2+} (aq) + \text{Cu} (s) \)  
(b) \( \text{I}_2 (s) + 2\text{Cl}^- (aq) \rightarrow 2\text{I}^- (aq) + \text{Cl}_2 (g) \)

Solution
(a) The two half-reactions are as follows.
Oxidation (occurs at the anode): \( \text{Cd} (s) \rightarrow \text{Cd}^{2+} (aq) + 2e^- \)
Reduction (occurs at the cathode): \( \text{Cu}^{2+} (aq) + 2e^- \rightarrow \text{Cu} (s) \)
The relevant standard reduction potentials are:
\[ E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.342 \text{ V} \]
\[ E^\circ_{\text{Cd}^{2+}/\text{Cd}} = -0.403 \text{ V} \]
\[ E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \]
\[ = 0.342 \text{ V} - (-0.403 \text{ V}) \]
\[ = 0.745 \text{ V} \]
The standard cell potential is positive, so the reaction is spontaneous under standard conditions.

(b) The two half-reactions are as follows.
Oxidation (occurs at the anode): \( 2\text{Cl}^- (aq) \rightarrow \text{Cl}_2 (g) + 2e^- \)
Reduction (occurs at the cathode): \( \text{I}_2 (s) + 2e^- \rightarrow 2\text{I}^- (aq) \)
The relevant standard reduction potentials are:
\[ E^\circ_{\text{Cl}_2/2\text{Cl}^-} = 1.358 \text{ V} \]
\[ E^\circ_{\text{I}_2/2\text{I}^-} = 0.536 \text{ V} \]
\[ E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \]
\[ = 0.536 \text{ V} - 1.358 \text{ V} \]
\[ = -0.822 \text{ V} \]
The standard cell potential is negative, so the reaction is non-spontaneous under standard conditions.

Practice Problems
17. Look up the standard reduction potentials of the following half-reactions. Predict whether acidified nitrate ions will oxidize manganese(II) ions to manganese(IV) oxide under standard conditions.
\[ \text{MnO}_2 (s) + 4\text{H}^+ (aq) + 2e^- \rightarrow \text{Mn}^{2+} (aq) + 2\text{H}_2\text{O (l)} \]
\[ \text{NO}_3^- (aq) + 4\text{H}^+ (aq) + 3e^- \rightarrow \text{NO}_2 (g) + 2\text{H}_2\text{O (l)} \]
Rechargeable Batteries

In section 19.1, you learned about several primary (disposable) batteries that contain galvanic cells. One of the most common secondary (rechargeable) batteries is found in car engines. Most cars contain a lead-acid battery, shown in Figure 19.18. When you turn the ignition, a surge of electricity from the battery starts the motor.

When in use, a lead-acid battery partially discharges. In other words, the cells in the battery operate as galvanic cells, and produce electricity. The reaction in each cell proceeds spontaneously in one direction. To recharge the battery, a generator driven by the car engine supplies electricity to the battery. The external voltage of the generator reverses the reaction in the cells. The reaction in each cell now proceeds non-spontaneously, and the cells operate as electrolytic cells. All secondary batteries, including the lead-acid battery, operate some of the time as galvanic cells, and some of the time as electrolytic cells.

As the name suggests, the materials used in a lead-acid battery include lead and an acid. Figure 19.19 shows that the electrodes in each cell are constructed using lead grids. One electrode consists of powdered lead packed into one grid. The other electrode consists of powdered lead(IV) oxide packed into the other grid. The electrolyte solution is fairly concentrated sulfuric acid, at about 4.5 mol/L.

18. Predict whether each reaction is spontaneous or non-spontaneous under standard conditions.

(a) \(2Cr(s) + 3Cl_2(g) \rightarrow 2Cr^{3+}(aq) + 6Cl^-(aq)\)
(b) \(Zn^{2+}(aq) + Fe(s) \rightarrow Zn(s) + Fe^{2+}(aq)\)
(c) \(5Ag(s) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Ag^{+}(aq) + Mn^{2+}(aq) + 4H_2O(l)\)

19. Explain why an aqueous copper(I) compound disproportionates to form copper metal and an aqueous copper(II) compound under standard conditions. (You learned about disproportionation in Chapter 10.)

20. Predict whether each reaction is spontaneous or non-spontaneous under standard conditions in an acidic solution.

(a) \(H_2O_2(aq) \rightarrow H_2(g) + O_2(g)\)
(b) \(3H_2(g) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)\)
When the battery supplies electricity, the half-reactions and overall cell reaction are as follows.

**Oxidation (at the Pb anode):** \( \text{Pb}^{(s)} + \text{SO}_4^{2-\text{(aq)}} \rightarrow \text{PbSO}_4^{(s)} + 2e^- \)

**Reduction (at the PbO\(_2\) cathode):** \( \text{PbO}_2^{(s)} + 4\text{H}^+\text{(aq)} + \text{SO}_4^{2-\text{(aq)}} + 2e^- \rightarrow \text{PbSO}_4^{(s)} + 2\text{H}_2\text{O}(l) \)

**Overall cell reaction:** \( \text{Pb}^{(s)} + \text{PbO}_2^{(s)} + 4\text{H}^+\text{(aq)} + 2\text{SO}_4^{2-\text{(aq)}} \rightarrow 2\text{PbSO}_4^{(s)} + 2\text{H}_2\text{O}(l) \)

You can see that the reaction consumes some of the lead in the anode, some of the lead(IV) oxide in the cathode, and some of the sulfuric acid. A precipitate of lead(II) sulfate forms.

When the battery is recharged, the half-reactions and the overall cell reaction are reversed. In this reverse reaction, lead and lead(IV) oxide are redeposited in their original locations, and sulfuric acid is re-formed.

**Reduction (at the Pb cathode):** \( \text{PbSO}_4^{(s)} + 2e^- \rightarrow \text{Pb}^{(s)} + \text{SO}_4^{2-\text{(aq)}} \)

**Oxidation (at the PbO\(_2\) anode):** \( \text{PbSO}_4^{(s)} + 2\text{H}_2\text{O}(l) \rightarrow \text{PbO}_2^{(s)} + 4\text{H}^+\text{(aq)} + \text{SO}_4^{2-\text{(aq)}} + 2e^- \)

**Overall cell reaction:** \( 2\text{PbSO}_4^{(s)} + 2\text{H}_2\text{O}(l) \rightarrow \text{Pb}^{(s)} + \text{PbO}_2^{(s)} + 4\text{H}^+\text{(aq)} + 2\text{SO}_4^{2-\text{(aq)}} \)

In practice, this reversibility is not perfect. However, the battery can go through many charge/discharge cycles before it eventually wears out.

Many types of rechargeable batteries are much more portable than a car battery. For example, there is now a rechargeable version of the alkaline battery. Another example, shown in Figure 19.20, is the rechargeable nickel-cadmium (nicad) battery. Figure 19.21 shows a nickel-cadmium cell, which has a potential of about 1.4 V. A typical nicad battery contains three cells in series to produce a suitable voltage for electronic devices. When the cells in a nicad battery operate as galvanic cells, the half-reactions and the overall cell reaction are as follows.

**Oxidation (at the Cd anode):** \( \text{Cd}^{(s)} + 2\text{OH}^-\text{(aq)} \rightarrow \text{Cd(OH)}_2^{(s)} + 2e^- \)

**Reduction (at the NiO(OH) cathode):** \( \text{NiO(OH)}^{(s)} + \text{H}_2\text{O}(l) + e^- \rightarrow \text{Ni(OH)}_2^{(s)} + \text{OH}^-\text{(aq)} \)

**Overall cell reaction:** \( \text{Cd}^{(s)} + 2\text{NiO(OH)}^{(s)} + 2\text{H}_2\text{O}(l) \rightarrow \text{Cd(OH)}_2^{(s)} + 2\text{Ni(OH)}_2^{(s)} \)

Like many technological innovations, nickel-cadmium batteries carry risks as well as benefits. After being discharged repeatedly, they eventually wear out. In theory, worn-out nicad batteries should be recycled. In practice, however, many end up in garbage dumps. Over time, discarded nicad batteries release toxic cadmium. The toxicity of this substance makes it hazardous to the environment, as cadmium can enter the food chain. Long-term exposure to low levels of cadmium can have serious medical effects on humans, such as high blood pressure and heart disease.
Section Summary

In this section, you learned about electrolytic cells, which convert electrical energy into chemical energy. You compared the spontaneous reactions in galvanic cells, which have positive cell potentials, with the non-spontaneous reactions in electrolytic cells, which have negative cell potentials. You then considered cells that act as both galvanic cells and electrolytic cells in some common rechargeable batteries. These batteries are an important application of electrochemistry. In the next two sections, you will learn about many more electrochemical applications.

Section Review

1. Predict the products of the electrolysis of a 1 mol/L aqueous solution of copper(I) bromide.

2. In this section, you learned that an external electrical supply reverses the cell reaction in a Daniell cell so that the products are zinc atoms and copper(II) ions.
   (a) What are the predicted products of this electrolysis reaction?
   (b) Explain the observed products.

3. Predict whether each reaction is spontaneous or non-spontaneous under standard conditions.
   (a) \(2\text{FeI}_3(\text{aq}) \rightarrow 2\text{Fe(s)} + 3\text{I}_2(\text{s})\)
   (b) \(2\text{Ag}^+(\text{aq}) + \text{H}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}(\ell) \rightarrow 2\text{Ag(s)} + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq})\)

4. Write the two half-reactions and the overall cell reaction for the process that occurs when a nicad battery is being recharged.

5. What external voltage is required to recharge a lead-acid car battery?

6. The equation for the overall reaction in an electrolytic cell does not include any electrons. Why is an external source of electrons needed for the reaction to proceed?

7. (a) Predict whether aluminum will displace hydrogen from water.
   (b) Water boiling in an aluminum saucepan does not react with the aluminum. Give possible reasons why.

8. Research the impact of lead pollution on the environment. Do lead-acid batteries contribute significantly to lead pollution?

9. Lithium batteries are increasingly common. The lithium anode undergoes oxidation when the battery discharges. Various cathodes and electrolytes are used to make lithium batteries with different characteristics. Research lithium batteries. Prepare a report describing the designs, cell reactions, and uses of lithium batteries. Include a description of the advantages and disadvantages of these batteries.
Faraday’s Law

As mentioned earlier in this chapter, Michael Faraday (1791–1867) was the leading pioneer of electrochemistry. One of Faraday’s major contributions was to connect the concepts of stoichiometry and electrochemistry.

You know that a balanced equation represents relationships between the quantities of reactants and products. For a reaction that takes place in a cell, stoichiometric calculations can also include the quantity of electricity produced or consumed. Stoichiometric calculations in electrochemistry make use of a familiar unit—the mole.

As a first step, you need information about measurements in electricity. You know that the flow of electrons through an external circuit is called the electric current. It is measured in a unit called the ampere (symbol A), named after the French physicist André Ampère (1775–1836). The quantity of electricity, also known as the electric charge, is the product of the current flowing through a circuit and the time for which it flows. The quantity of electricity is measured in a unit called the coulomb (symbol C). This unit is named after another French physicist, Charles Coulomb (1736–1806). The ampere and the coulomb are related, in that one coulomb is the quantity of electricity that flows through a circuit in one second if the current is one ampere. This relationship can be written mathematically.

\[
\text{charge (in coulombs)} = \text{current (in amperes)} \times \text{time (in seconds)}
\]

For example, suppose a current of 2.00 A flows for 5.00 min. You can use this information to find the quantity of electricity, in coulombs.

\[
5.00 \text{ min} = 300 \text{ s} \\
2.00 \text{ A} \times 300 \text{ s} = 600 \text{ C}, \text{ or } 6.00 \times 10^2 \text{ C}
\]
For stoichiometric calculations, you also need to know the electric charge on a mole of electrons. This charge can be calculated by multiplying the charge on one electron and the number of electrons in one mole (Avogadro’s number). The charge on a mole of electrons is known as one faraday (1 F), named after Michael Faraday.

\[
\text{Charge on one mole of electrons} = \frac{1.602 \times 10^{-19} \text{ C}}{1 \text{ e}^-} \times 6.022 \times 10^{23} \text{ e}^- = 9.647 \times 10^4 \text{ C/mol}
\]

A rounded value of 96 500 C/mol is often used in calculations. Note that this rounded value has three significant digits.

The information you have just learned permits a very precise control of electrolysis. For example, suppose you modify a Daniell cell to operate as an electrolytic cell. You want to plate 0.1 mol of zinc onto the zinc electrode. The coefficients in the half-reaction for the reduction represent stoichiometric relationships. Figure 19.23 shows that two moles of electrons are needed for each mole of zinc deposited. Therefore, to deposit 0.1 mol of zinc, you need to use 0.2 mol of electrons.

\[
0.1 \text{ mol Zn} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Zn}} = 0.2 \text{ mol e}^-
\]

<table>
<thead>
<tr>
<th>( \text{Zn}^{2+} )</th>
<th>+</th>
<th>2e(^-)</th>
<th>→</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ion</td>
<td>2 electrons</td>
<td></td>
<td>1 atom</td>
<td></td>
</tr>
<tr>
<td>( 1 \times 6.02 \times 10^{23} ) ions</td>
<td>( 2 \times 6.02 \times 10^{23} ) electrons</td>
<td>( 1 \times 6.02 \times 10^{23} ) atoms</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 mol of ions</td>
<td>2 mol of electrons</td>
<td></td>
<td>1 mol of atoms</td>
<td></td>
</tr>
</tbody>
</table>

*Figure 19.23* A balanced half-reaction shows relationships between the amounts of reactants and products and the amount of electrons transferred.

In the next Sample Problem, you will learn to apply the relationship between the amount of electrons and the amount of an electrolysis product.

**Sample Problem**

**Calculating the Mass of an Electrolysis Product**

**Problem**

Calculate the mass of aluminum produced by the electrolysis of molten aluminum chloride, if a current of 500 mA passes for 1.50 h.

**What Is Required?**

You need to calculate the mass of aluminum produced.

**What Is Given?**

You know the name of the electrolyte, the current, and the time.

- Electrolyte: \( \text{AlCl}_3(\ell) \)
- Current: 500 mA
- Time: 1.50 h

From the previous calculation, you know the charge on one mole of electrons is 96 500 C/mol.

Considered by many the greatest experimental chemist ever, Michael Faraday did not receive any formal education beyond the primary grades. At the age of 14, Faraday worked as an apprentice at a book bindery in London, where he educated himself by reading many of the books brought there for binding, including the section on electricity in the *Encyclopaedia Britannica*. A client of the bookbindery gave Faraday tickets to lectures at the Royal Institution given by Sir Humphry Davy. Faraday eagerly attended the lectures, and afterwards presented his detailed and precise notes on them to Davy. Impressed by the young Faraday’s diligence, Davy hired him as his laboratory assistant in 1813, saying “his disposition is active and cheerful, his manner intelligent.” In 1825, Faraday took over from Davy directing the laboratory at the Royal Institution, and went on to contribute even more to the study of electricity and its applications than Davy, himself an eminent figure in the field, did.
Plan Your Strategy

**Step 1** Use the current and the time to find the quantity of electricity used.

**Step 2** From the quantity of electricity, find the amount of electrons that passed through the circuit.

**Step 3** Use the stoichiometry of the relevant half-reaction to relate the amount of electrons to the amount of aluminum produced.

**Step 4** Use the molar mass of aluminum to convert the amount of aluminum to a mass.

Act on Your Strategy

**Step 1** To calculate the quantity of electricity in coulombs, work in amperes and seconds.

\[
1000 \text{ mA} = 1 \text{ A}
\]

\[
500 \text{ mA} = 500 \text{ mA} \times \frac{1 \text{ A}}{1000 \text{ mA}} = 0.500 \text{ A}
\]

\[
1.50 \text{ h} = 1.50 \text{ h} \times \frac{60 \text{ min}}{1 \text{ h}} \times \frac{60 \text{ s}}{1 \text{ min}} = 5400 \text{ s}, \text{ or } 5.40 \times 10^3 \text{ s}
\]

Quantity of electricity = 0.500 A × 5400 s = 2700 C, or 2.70 × 10³ C

**Step 2** Find the amount of electrons. One mole of electrons has a charge of 96 500 C.

\[
\text{Amount of electrons} = 2700 \text{ C} \times \frac{1 \text{ mol e}^-}{96500 \text{ C}} = 0.0280 \text{ mol e}^-\]

**Step 3** The half-reaction for the reduction of aluminum ions to aluminum is \( \text{Al}^{3+} + 3e^- \rightarrow \text{Al} \).

\[
\text{Amount of aluminum formed} = 0.0280 \text{ mol e}^- \times \frac{1 \text{ mol Al}}{3 \text{ mol e}^-} = 0.00933 \text{ mol Al}
\]

**Step 4** Convert the amount of aluminum to a mass.

\[
\text{Mass of Al formed} = 0.00933 \text{ mol Al} \times \frac{27.0 \text{ g Al}}{1 \text{ mol Al}} = 0.252 \text{ g}
\]

Check Your Solution

The answer is expressed in units of mass. To check your answer, use estimation. If the current were 1 A, then 1 mol of electrons would pass in 96 500 s. In this example, the current is less than 1 A, and the time is much less than 96 500 s. Therefore, much less than 1 mol of electrons would be used, and much less than 1 mol (27 g) of aluminum would be formed.
Practice Problems

21. Calculate the mass of zinc plated onto the cathode of an electrolytic cell by a current of 750 mA in 3.25 h.

22. How many minutes does it take to plate 0.925 g of silver onto the cathode of an electrolytic cell using a current of 1.55 A?

23. The nickel anode in an electrolytic cell decreases in mass by 1.20 g in 35.5 min. The oxidation half-reaction converts nickel atoms to nickel(II) ions. What is the constant current?

24. The following two half-reactions take place in an electrolytic cell with an iron anode and a chromium cathode.

Oxidation: \( \text{Fe}_\text{(s)} \rightarrow \text{Fe}^{2+}_{\text{(aq)}} + 2e^- \)

Reduction: \( \text{Cr}^{3+}_{\text{(aq)}} + 3e^- \rightarrow \text{Cr}_\text{(s)} \)

During the process, the mass of the iron anode decreases by 1.75 g.

(a) Find the change in mass of the chromium cathode.

(b) Explain why you do not need to know the electric current or the time to complete part (a).

The preceding Sample Problem gave an example of the mathematical use of Faraday's law. **Faraday's law** states that the amount of a substance produced or consumed in an electrolysis reaction is directly proportional to the quantity of electricity that flows through the circuit.

To illustrate this statement, think about changing the quantity of electricity used in the Sample Problem. Suppose this quantity were doubled by using the same current, 500 mA, for twice the time, 3 h. As a result, the amount of electrons passing into the cell would also be doubled.

\[
\begin{align*}
500 \text{ mA} &= 0.500 \text{ A} \\
3 \text{ h} &= 2 \times 1.5 \text{ h} \\
&= 2 \times 5400 \text{ s} \\
\text{Quantity of electricity} &= 0.500 \text{ A} \times (2 \times 5400 \text{ s}) \\
&= 2 \times 2700 \text{ C} \\
&= 5400 \text{ C}, \text{ or } 5.40 \times 10^3 \text{ C} \\
\text{Amount of electrons} &= 5400 \text{ C} \times \frac{1 \text{ mol e}^-}{96 500 \text{ C}} \\
&= 0.0560 \text{ mol e}^- 
\end{align*}
\]

Then, as you can see from the relevant half-reaction, the mass of aluminum produced would be doubled. The mass of aluminum produced is clearly proportional to the quantity of electricity used.

In Investigation 19-C, you will apply Faraday's law to an electrolytic cell that you construct.
Electroplating

You have learned that electroplating is a process in which a metal is deposited, or plated, onto the cathode of an electrolytic cell. In this investigation, you will build an electrolytic cell and electrolyze a copper(II) sulfate solution to plate copper onto the cathode. You will use Faraday’s law to relate the mass of metal deposited to the quantity of electricity used.

**Question**
Does the measured mass of copper plated onto the cathode of an electrolytic cell agree with the mass calculated from Faraday’s law?

**Prediction**
Predict whether the measured mass of copper plated onto the cathode of an electrolytic cell will be greater than, equal to, or less than the mass calculated using Faraday’s law.

**Materials**
150 mL 1.0 mol/L HNO₃ in a 250 mL beaker
120 mL acidified 0.50 mol/L CuSO₄ solution
(with 5 mL of 6 mol/L H₂SO₄ and 3 mL of 0.1 mol/L HCl added)
drying oven, or acetone in a wash bottle
3 cm × 12 cm × 1 mm Cu strip
50 cm 16-gauge bare solid copper wire
250 mL beaker
adjustable D.C. power supply with ammeter
deionized water in a wash bottle
fine sandpaper
2 electrical leads with alligator clips
electronic balance

**Safety Precautions**
- Nitric acid is corrosive. Also, note that the CuSO₄ solution contains sulfuric acid and hydrochloric acid. Wash any spills on your skin with plenty of cold water. Inform your teacher immediately.
- Avoid touching the parts of the electrodes that have been washed with nitric acid.
- Acetone is flammable. Use acetone in the fume hood.
- Make sure your hands and your lab bench are dry before handling any electrical equipment.

**Procedure**
1. Clean off any tarnish on the copper strip by sanding it gently. Dip the bottom of the copper strip in the nitric acid for a few seconds, and then rinse off the strip carefully with deionized water. Avoid touching the section that has been cleaned by the acid.
2. Place the copper strip in the beaker, with the clean part of the strip at the bottom. Bend the top of the strip over the rim of the beaker so that the copper strip is secured in a vertical position. This copper strip will serve as the anode.
3. Wrap the copper wire around a pencil to make a closely spaced coil. Leave 10 cm of the wire unwrapped. Measure and record the mass of the wire. Dip the coil in the nitric acid, and rinse the coil with water. Use the 10 cm of uncoiled wire to secure the coil on the opposite side of the beaker from the anode, as shown in the diagram. This copper wire will serve as the cathode.
Pour 120 mL of the acidified CuSO$_4$ solution into the beaker. Attach the lead from the negative terminal of the power supply to the cathode. Attach the positive terminal to the anode.

Turn on the power supply and set the current to 1 A. Maintain this current for 20 min by adjusting the variable current knob as needed.

After 20 min, turn off the power. Remove the cathode and rinse it very gently with deionized water. Place the cathode in a drying oven for 20 min. Alternatively, rinse the cathode gently with acetone, and let the acetone evaporate in the fume hood for 5 min.

Measure and record the new mass of the cathode.

Dispose of all materials as instructed by your teacher.

---

**Analysis**

1. Write a balanced equation for the half-reaction that occurs at the cathode.

2. Use the measured current and the time for which the current passed to calculate the quantity of electricity used.

3. Use your answers to questions 1 and 2 to calculate the mass of copper plated onto the cathode.

4. Compare the calculated mass from question 3 with the measured increase in mass of the cathode. Give possible reasons for any difference between the two values.

**Conclusion**

5. How did the mass of copper electroplated onto the cathode of the electrolytic cell compare with the mass calculated using Faraday's law? Compare your answer with your prediction from the beginning of this investigation.

**Applications**

6. Suppose you repeated this investigation using iron electrodes, and 0.5 mol/L iron(II) sulfate solution as the electrolyte. If you used the same current for the same time, would you expect the increase in mass of the cathode to be greater than, less than, or equal to the increase in mass that you measured? Explain your answer.

7. Suppose you repeated the investigation with the copper(II) sulfate solution, but you passed the current for only half as long as before. How would the masses of copper plated onto the cathode compare in the two investigations? Explain your answer.

8. Could you build a galvanic cell without changing the electrodes or the electrolyte solution you used in this investigation? Explain your answer.
Industrial Extraction and Refining of Metals

Many metals, and their alloys, are widely used in modern society. The enormous variety of metal objects ranges from large vehicles, such as cars and aircraft, to small items, such as the pop cans shown in Figure 19.24.

**Extraction** is a process by which a metal is obtained from an ore. Some metals are extracted in electrolytic cells. In section 19.3, you saw the extraction of sodium from molten sodium chloride in a Downs cell. Other reactive metals, including lithium, beryllium, magnesium, calcium, and radium, are also extracted industrially by the electrolysis of their molten chlorides.

One of the most important electrolytic processes is the extraction of aluminum from an ore called bauxite. This ore is mainly composed of hydrated aluminum oxide, \( \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O} \). (The “\( x \)” in the formula indicates that the number of water molecules per formula unit is variable.) In industry, the scale of production of metals is huge. The electrolytic production of aluminum is over two million tonnes per year in Canada alone. As you know from Faraday’s law, the amount of a metal produced by electrolysis is directly proportional to the quantity of electricity used. Therefore, the industrial extraction of aluminum and other metals by electrolysis requires vast quantities of electricity. The availability and cost of electricity greatly influence the location of industrial plants.

In industry, the process of purifying a material is known as **refining**. After the extraction stage, some metals are refined in electrolytic cells. For example, copper is about 99% pure after extraction. This copper is pure enough for some uses, such as the manufacture of copper pipes for plumbing. However, the copper is not pure enough for one of its principal uses, electrical wiring. Therefore, some of the impure copper is refined electrolytically, as shown in Figure 19.25. Nickel can be refined electrolytically in a similar way. You refined copper on a small scale in Investigation 19-C.
Section Summary

In this section, you learned how stoichiometry relates the quantities of reactants and products to the quantity of electricity consumed in an electrolytic cell. You used Faraday's law to solve problems relating to electrolysis. You also learned that the extraction and refining of some metals are carried out electrolytically. In the next section, you will see several other important applications of electrochemistry to modern society.

Section Review

1. In Section 18.3, you learned about a redox reaction used in the production of compact discs. In another step of this production process, nickel is electroplated onto the silver-coated master disc. The nickel layer is removed and used to make pressings of the CD onto plastic discs. The plastic pressings are then coated with aluminum to make the finished CDs.

   (a) When nickel is plated onto the silver master disc, is the master disc the anode or the cathode of the cell? Explain.

   (b) Calculate the quantity of electricity needed to plate each gram of nickel onto the master disc. Assume that the plating process involves the reduction of nickel(II) ions.

2. Most industrial reactions take place on a much larger scale than reactions in a laboratory or classroom. The voltage used in a Downs cell for the industrial electrolysis of molten sodium chloride is not very high, about 7 V to 8 V. However, the current used is 25 000 A to 40 000 A. Assuming a current of $3.0 \times 10^4$ A, determine the mass of sodium and the mass of chlorine made in 24 h in one Downs cell. Express your answers in kilograms.

3. An industrial cell that purifies copper by electrolysis operates at $2.00 \times 10^2$ A. Calculate the mass, in tonnes, of pure copper produced if the cell is supplied with raw materials whenever necessary, and if it works continuously for a year that is not a leap year.

4. Canada is a major producer of aluminum by the electrolysis of bauxite. However, there are no bauxite mines in Canada, and all the ore must be imported. Explain why aluminum is produced in Canada.

5. Research the extraction of aluminum by the electrolysis of bauxite. Write a report on your findings. Include a description of the electrolytic cell and how it operates. Indicate where aluminum is produced in Canada. Also include any environmental concerns associated with aluminum production by electrolysis.

6. Nickel and copper are both very important to the Ontario economy. Before they can be refined by electrolysis, they must be extracted from their ores. Both metals can be extracted from a sulfide ore, NiS or Cu$_2$S. The sulfide is roasted to form an oxide, and then the oxide is reduced to the metal. Research the extraction processes for both nickel and copper, and write balanced equations for the redox reactions involved. One product of each extraction process is sulfur dioxide. Research the environmental effects of this compound. Describe any steps taken to decrease these effects.
You have probably seen many examples of rusty objects, such as the one in Figure 19.26. However, you may not realize that rusting costs many billions of dollars per year in prevention, maintenance, and replacement costs. You will now learn more about rusting and about other issues involving electrochemistry.

Rusting is an example of corrosion, which is a spontaneous redox reaction of materials with substances in their environment. Figure 19.27 shows an example of the hazards that result from corrosion.

Many metals are fairly easily oxidized. The atmosphere contains a powerful oxidizing agent: oxygen. Because metals are constantly in contact with oxygen, they are vulnerable to corrosion. In fact, the term “corrosion” is sometimes defined as the oxidation of metals exposed to the environment. In North America, about 20% to 25% of iron and steel production is used to replace objects that have been damaged or destroyed by corrosion. However, not all corrosion is harmful. For example, the green layer formed by the corrosion of a copper roof is considered attractive by many people.
Rust is a hydrated iron(III) oxide, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. The electrochemical formation of rust occurs in small galvanic cells on the surface of a piece of iron, as shown in Figure 19.28. In each small cell, iron acts as the anode. The cathode is inert, and may be an impurity that exists in the iron or is deposited onto it. For example, the cathode could be a piece of soot that has been deposited onto the iron surface from the air.

Water, in the form of rain, is needed for rusting to occur. Carbon dioxide in the air dissolves in water to form carbonic acid, $\text{H}_2\text{CO}_3(\text{aq})$. This weak acid partially dissociates into ions. Thus, the carbonic acid is an electrolyte for the corrosion process. Other electrolytes, such as road salt, may also be involved. The circuit is completed by the iron itself, which conducts electrons from the anode to the cathode.

![Figure 19.28](image)

**Figure 19.28** The rusting of iron involves the reaction of iron, oxygen, and water in a naturally occurring galvanic cell on the exposed surface of the metal. There may be many of these small cells on the surface of the same piece of iron.

The rusting process is complex, and the equations may be written in various ways. A simplified description of the half-reactions and the overall cell reaction is given here.

**Oxidation half-reaction (occurs at the anode):**

$$\text{Fe}(s) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2e^-$$

**Reduction half-reaction (occurs at the cathode):**

$$\text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- \rightarrow 4\text{OH}^- (\text{aq})$$

Multiply the oxidation half-reaction by two and add the half-reactions to obtain the overall cell reaction.

$$2\text{Fe}(s) + \text{O}_2(g) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{Fe}^{2+}(\text{aq}) + 4\text{OH}^- (\text{aq})$$

There is no barrier in the cell, so nothing stops the dissolved $\text{Fe}^{2+}$ and $\text{OH}^-$ ions from mixing. The iron(II) ions produced at the anode and the hydroxide ions produced at the cathode react to form a precipitate of iron(II) hydroxide, $\text{Fe(OH)}_2$. Therefore, the overall cell reaction could be written as follows.

$$2\text{Fe}(s) + \text{O}_2(g) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{Fe(OH)}_2(s)$$

The iron(II) hydroxide undergoes further oxidation by reaction with the oxygen in the air to form iron(III) hydroxide.

$$4\text{Fe(OH)}_2(s) + \text{O}_2(g) + 2\text{H}_2\text{O}(l) \rightarrow 4\text{Fe(OH)}_3(s)$$
Iron(III) hydroxide readily breaks down to form hydrated iron(III) oxide, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, more commonly known as rust. As noted earlier, the “$x$” signifies a variable number of water molecules per formula unit.

$$2\text{Fe(OH)}_3(\text{s}) \rightarrow \text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}(\text{s})$$

Both $\text{Fe(OH)}_3$ and $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ are reddish-brown, or “rust coloured.”

A rust deposit may contain a mixture of these compounds.

Fortunately, not all metals corrode to the same extent as iron. Many metals do corrode in air to form a surface coating of metal oxide. However, in many cases, the oxide layer adheres, or sticks firmly, to the metal surface. This layer protects the metal from further corrosion. For example, aluminum, chromium, and magnesium are readily oxidized in air to form their oxides, $\text{Al}_2\text{O}_3$, $\text{Cr}_2\text{O}_3$, and $\text{MgO}$. Unless the oxide layer is broken by a cut or a scratch, the layer prevents further corrosion. In contrast, rust easily flakes off from the surface of an iron object and provides little protection against further corrosion.

**Corrosion Prevention**

Corrosion, and especially the corrosion of iron, can be very destructive. For this reason, a great deal of effort goes into corrosion prevention. The simplest method of preventing corrosion is to paint an iron object. The protective coating of paint prevents air and water from reaching the metal surface. Other effective protective layers include grease, oil, plastic, or a metal that is more resistant to corrosion than iron. For example, a layer of chromium protects bumpers and metal trim on cars. An enamel coating is often used to protect metal plates, pots, and pans. *Enamel* is a shiny, hard, and very unreactive type of glass that can be melted onto a metal surface. A protective layer is effective as long as it completely covers the iron object. If a hole or scratch breaks the layer, the metal underneath can corrode.

It is also possible to protect iron against corrosion by forming an alloy with a different metal. *Stainless steel* is an alloy of iron that contains at least 10% chromium, by mass, in addition to small quantities of carbon and occasionally metals such as nickel. Stainless steel is much more resistant to corrosion than iron. Therefore, stainless steel is often used for cutlery, taps, and various other applications where rust-resistance is important. However, chromium is much more expensive than iron. As a result, stainless steel is too expensive for use in large-scale applications, such as building bridges.

*Galvanizing* is a process in which iron is covered with a protective layer of zinc. Galvanized iron is often used to make metal buckets and chain-link fences. Galvanizing protects iron in two ways. First, the zinc acts as a protective layer. If this layer is broken, the iron is exposed to air and water. When this happens, however, the iron is still protected. Zinc is more easily oxidized than iron. Therefore, zinc, not iron, becomes the anode in the galvanic cell. The zinc metal is oxidized to zinc ions. In this situation, zinc is known as a **sacrificial anode**, because it is destroyed (sacrificed) to protect the iron. Iron acts as the cathode when zinc is present. Thus, iron does not undergo oxidation until all the zinc has reacted.
Cathodic protection is another method of preventing rusting, as shown in Figure 19.29. As in galvanizing, a more reactive metal is attached to the iron object. This reactive metal acts as a sacrificial anode, and the iron becomes the cathode of a galvanic cell. Unlike galvanizing, the metal used in cathodic protection does not completely cover the iron. Because the sacrificial anode is slowly destroyed by oxidation, it must be replaced periodically.

If iron is covered with a protective layer of a metal that is less reactive than iron, there can be unfortunate results. A “tin” can is actually a steel can coated with a thin layer of tin. While the tin layer remains intact, it provides effective protection against rusting. If the tin layer is broken or scratched, however, the iron in the steel corrodes faster in contact with the tin than the iron would on its own. Since tin is less reactive than iron, tin acts as a cathode in each galvanic cell on the surface of the can. Therefore, the tin provides a large area of available cathodes for the small galvanic cells involved in the rusting process. Iron acts as the anode of each cell, which is its normal role when rusting.

Sometimes, the rusting of iron is promoted accidentally. For example, by connecting an iron pipe to a copper pipe in a plumbing system, an inexperienced plumber could accidentally speed up the corrosion of the iron pipe. Copper is less reactive than iron. Therefore, copper acts as the cathode and iron as the anode in numerous small galvanic cells at the intersection of the two pipes.

Build on your understanding of corrosion by completing the following practice problems.

### Practice Problems

25. (a) Use the two half-reactions for the rusting process, and a table of standard reduction potentials. Determine the standard cell potential for this reaction.

   (b) Do you think that your calculated value is the actual cell potential for each of the small galvanic cells on the surface of a rusting iron object? Explain.

26. Explain why aluminum provides cathodic protection to an iron object.

27. In the year 2000, Transport Canada reported that thousands of cars sold in the Atlantic Provinces between 1989 and 1999 had corroded engine cradle mounts. Failure of these mounts can cause the steering shaft to separate from the car. The manufacturer recalled the cars so that repairs could be made, where necessary. The same cars were sold across the country. Why do you think that the corrosion problems showed up in the Atlantic Provinces?

28. (a) Use a table of standard reduction potentials to determine whether elemental oxygen, $O_{2(g)}$, is a better oxidizing agent under acidic conditions or basic conditions.

   (b) From your answer to part (a), do you think that acid rain promotes or helps prevent the rusting of iron?
Automobile Engines

The internal combustion engine found in most automobiles uses gasoline as a fuel. Unfortunately, this type of engine produces pollutants, such as carbon dioxide (CO₂), nitrogen oxides (NOₓ), and volatile organic compounds (VOCs). These pollutants contribute to health and environmental problems, such as smog and the greenhouse effect. In addition, the internal combustion engine is very inefficient. It converts only about 25% of the chemical energy of the fuel into the kinetic energy of the car. Electric cars, such as those shown in Figure 19.30, may provide a more efficient and less harmful alternative.

Manufacturers and researchers have attempted to power electric cars with rechargeable batteries, such as modified lead-acid and nickel-cadmium batteries. However, rechargeable batteries run down fairly quickly. The distance driven before recharging a battery may be 250 km or less. The battery must then be recharged from an external electrical source. Recharging the lead-acid battery of an electric car takes several hours. Cars based on a version of the nickel-cadmium battery can be recharged in only fifteen minutes. However, recharging the batteries of an electric car is still inconvenient.

A new type of power supply for electric cars eliminates the need for recharging. A fuel cell is a battery that produces electricity while reactants are supplied continuously from an external source. Because reactants continuously flow into the cell, a fuel cell is also known as a flow battery. Unlike the fuel supply of a more conventional battery, the fuel supply in a fuel cell is unlimited. As in the combustion of gasoline in a conventional engine, the overall reaction in a fuel cell is the oxidation of a fuel by oxygen.

The space shuttle uses a fuel cell as a source of energy. This cell depends on the oxidation of hydrogen by oxygen to form water. The fuel cell operates under basic conditions, so it is sometimes referred to as an alkaline fuel cell. Figure 19.31, on the next page, shows the design of the cell. The half-reactions and the overall reaction are as follows.

Reduction (occurs at the cathode): \[ \text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- \rightarrow 4\text{OH}^-(aq) \]

Oxidation (occurs at the anode): \[ \text{H}_2(g) + 2\text{OH}^-(aq) \rightarrow 2\text{H}_2\text{O}(l) + 2e^- \]

Multiply the oxidation half-reaction by 2, add the two half-reactions, and simplify to obtain the overall cell reaction.

\[ 2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l) \]

Notice that the overall equation is the same as the equation for the combustion of hydrogen. The combustion of hydrogen is an exothermic reaction. In the fuel cell, this reaction produces energy in the form of electricity, rather than heat.
In an alkaline fuel cell, the half-reactions do not include solid conductors of electrons. Therefore, the cell has two inert electrodes.

The hydrogen fuel cell produces water vapour, which does not contribute to smog formation or to the greenhouse effect. This product makes the hydrogen fuel cell an attractive energy source for cars. Also, the hydrogen fuel cell is much more efficient than the internal combustion engine. A hydrogen fuel cell converts about 80% of the chemical energy of the fuel into the kinetic energy of the car.

There is a possible problem with the hydrogen fuel cell. The cell requires hydrogen fuel. Unfortunately, uncombined hydrogen is not found naturally on Earth. Most hydrogen is produced from hydrocarbon fuels, such as petroleum or methane. These manufacturing processes may contribute significantly to pollution problems. However, hydrogen can also be produced by the electrolysis of water. If a source such as solar energy or hydroelectricity is used to power the electrolysis, the overall quantity of pollution is low.

The following practice problems will allow you to test your understanding of fuel cells.

**Practice Problems**

29. Calculate $E_{\text{cell}}$ for a hydrogen fuel cell.

30. In one type of fuel cell, methane is oxidized by oxygen to form carbon dioxide and water.
   (a) Write the equation for the overall cell reaction.
   (b) Write the two half-reactions, assuming acidic conditions.

31. Reactions that occur in fuel cells can be thought of as being “flameless combustion reactions.” Explain why.

32. If a hydrogen fuel cell produces an electric current of 0.600 A for 120 min, what mass of hydrogen is consumed by the cell?
Water Treatment and the Chlor-Alkali Process

In many countries, water is not safe to drink. Untreated water is sometimes polluted with toxic chemicals. It may also carry numerous water-borne diseases, including typhoid fever, cholera, and dysentery. In Canada, the water that comes through your tap has been through an elaborate purification process. This process is designed to remove solid particles and toxic chemicals, and to reduce the number of bacteria to safe levels. Adding chlorine to water is the most common way to destroy bacteria.

You have already seen that chlorine gas can be made by the electrolysis of molten sodium chloride. In industry, some chlorine is produced in this way using the Downs cell described earlier. However, more chlorine is produced in Canada using a different method, called the chlor-alkali process. In this process, brine is electrolyzed in a cell like the one shown in Figure 19.32. Brine is a saturated solution of sodium chloride.

Canadians in Chemistry

Dr. Viola Birss

As a science student, Viola Birss decided to focus on chemistry. “I have always had a concern for the environment,” she says. “I am particularly interested in identifying new, non-polluting ways of converting, storing, and using energy.” Dr. Birss’s interest in non-polluting energy narrowed her field of interest to electrochemistry.

Today, Dr. Birss is a chemistry professor at the University of Calgary. Her research focuses on developing films to coat metal surfaces. Among other uses, these films can serve as protective barriers against corrosion, and as catalysts in fuel cells.

Magnesium alloys are very lightweight, and are being used in the aerospace industry. Because they are very reactive, these alloys need to be protected from corrosion. Dr. Birss holds a patent on a new approach to the electrochemical formation of protective oxide films on magnesium alloys. Dr. Birss also works on developing new catalysts for fuel cells, and studies the factors that lead to the breakdown of fuel cells.

After finishing an undergraduate degree at the University of Calgary, Dr. Birss went on to complete her doctoral degree as a Commonwealth Scholar at the University of Auckland in New Zealand. During her postdoctoral studies at the University of Ottawa, she worked with Dr. Brian Conway, a famous Canadian electrochemist. Dr. Conway’s work in electrochemistry has led to progress in a range of electrochemical devices including fuel cells, advanced batteries, and electrolytic cells.

Dr. Birss takes pride in her team of undergraduate, graduate, and post-doctoral students. She works hard to provide a creative and inspiring environment for them. Together, they go on wilderness hiking and cross country ski trips. In addition to creating a sense of community within her team, Birss feels that sports and nature help to recharge her internal “battery.” Dr. Birss comments, “These activities seem to provide me with mental and physical rest, so that my creativity and energy are catalyzed.”
The chlor-alkali cell in this diagram electrolyzes an aqueous solution of sodium chloride to produce chlorine gas, hydrogen gas, and aqueous sodium hydroxide. The asbestos diaphragm stops the chlorine gas produced at the anode from mixing with the hydrogen gas produced at the cathode. Sodium hydroxide solution is removed from the cell periodically, and fresh brine is added to the cell.

The half-reactions and the overall cell reaction in the chlor-alkali process are as follows.

**Oxidation:** \(2\text{Cl}^- \text{(aq)} \rightarrow \text{Cl}_2 \text{(g)} + 2\text{e}^-\)

**Reduction:** \(2\text{H}_2\text{O} \text{(l)} + 2\text{e}^- \rightarrow \text{H}_2 \text{(g)} + 2\text{OH}^- \text{(aq)}\)

**Overall:** \(2\text{Cl}^- \text{(aq)} + 2\text{H}_2\text{O} \text{(l)} \rightarrow \text{Cl}_2 \text{(g)} + \text{H}_2 \text{(g)} + 2\text{OH}^- \text{(aq)}\)

Note that the sodium ion is a spectator ion, and does not take part in this reaction. However, it combines with \(\text{OH}^-\) to produce sodium hydroxide, as shown by the balanced chemical equation below.

\[2\text{NaCl(aq)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Cl}_2 \text{(g)} + \text{H}_2 \text{(g)} + 2\text{NaOH(aq)}\]

The products of the chlor-alkali process are all useful. Sodium hydroxide is used to make soaps and detergents. It is widely used as a base in many other industrial chemical reactions, as well. The hydrogen produced by the chlor-alkali process is used as a fuel. Chlorine has many uses besides water treatment. For example, chlorine is used as a bleach in the pulp and paper industry. Chlorine is also used in the manufacture of chlorinated organic compounds, such as the common plastic polyvinyl chloride (PVC).

The chlorination of water is usually carried out by adding chlorine gas, sodium hypochlorite, or calcium hypochlorite to the water in low concentrations. The active antibacterial agent in each case is hypochlorous acid, \(\text{HClO(aq)}\). For example, when chlorine gas is added to water, hypochlorous acid is formed by the following reaction.

\[\text{Cl}_2 \text{(g)} + \text{H}_2\text{O(l)} \rightarrow \text{HClO(aq)} + \text{HCl(aq)}\]

Some people object to the chlorination of water, and prefer to drink bottled spring water. There is controversy over the level of risk associated with chlorination, and over the possible benefits of spring water. For example, hypochlorous acid reacts with traces of organic materials in the water supply. These reactions can produce toxic substances, such as chloroform. Supporters of chlorination believe that these substances are present at very low, safe levels, but opponents of chlorination disagree. Complete the following practice problems to help you decide on your own opinion of chlorination.
Section Summary

In this section, you learned about some important electrochemical processes. You had the opportunity to weigh some positive and negative effects of electrochemical technologies. The questions that follow in the section review and chapter review will encourage you to think further about the science of electrochemistry, and about its impact on society.

Section Review

1. Why does the use of road salt cause cars to rust faster than they otherwise would?

2. Aluminum is a more reactive metal than any of the metals present in steel. However, discarded steel cans disintegrate much more quickly than discarded aluminum cans when both are left open to the environment in the same location. Give an explanation.

3. Explain why zinc acts as a sacrificial anode in contact with iron.

4. (a) Identify two metals that do not corrode easily in the presence of oxygen and water. Explain why they do not corrode.
   (b) How are these metals useful? How do the uses of these metals depend on their resistance to corrosion?

5. A silver utensil is said to tarnish when its surface corrodes to form a brown or black layer of silver sulfide. Research and describe a chemical procedure that can be used to remove this layer. Write balanced half-reactions and a chemical equation for the process.

6. In a chlor-alkali cell, the current is very high. A typical current would be about 100 000 A. Calculate the mass of sodium hydroxide, in kilograms, that a cell using this current can produce in one minute.

7. Research the advances made in the development of fuel cells since this book was written. Describe how any new types of fuel cells operate. Evaluate their advantages and disadvantages, as compared to the internal combustion engine and other fuel cells.

Practice Problems

33. Show that the reaction of chlorine gas with water is a disproportionation reaction.

34. Would you predict the products of the chlor-alkali process to be hydrogen and chlorine? Explain.

35. Research and assess the most recent information you can find on the health and safety aspects of the chlorination of water. Are you in favour of chlorination, or opposed to it? Explain your answer.

36. Some municipalities use ozone gas rather than chlorine to kill bacteria in water. Research the advantages and disadvantages of using ozone in place of chlorine.

www.mcgrawhill.ca/links/atlchemistry
For more information about aspects of material covered in this section of the chapter, go to the website above, and click on Electronic Learning Partner.
Reflecting on Chapter 19

Summarize this chapter in the format of your choice. Here are a few ideas to use as guidelines:

- Represent one example of a galvanic cell, and one example of an electrolytic cell, using chemical equations, half-reactions, and diagrams.
- Calculate a standard cell potential using a table of standard reduction potentials.
- Compare primary and secondary batteries.
- Predict the products of the electrolysis of molten salts and aqueous solutions.
- Perform a sample stoichiometric calculation involving the quantity of electricity used in electrolytic processes.
- Describe some electrolytic processes involved in extracting and refining metals.
- Describe the process of corrosion. Explain some methods used to prevent it.
- Describe the design of fuel cells, and their potential use in automobiles.
- Describe the industrial production of chlorine, and its use in the purification of water.
- Give some examples of how electrochemistry affects the environment, human health, and safety.

Reviewing Key Terms

For each of the following terms, write a sentence that shows your understanding of its meaning.

- electric current
- galvanic cell
- spontaneous reaction
- external circuit
- electrolytes
- cathode
- inert electrode
- cell voltage
- dry cell
- primary battery
- reduction potential
- electrolytic cell
- overvoltage
- quantity of electricity
- Faraday’s law
- refining
- galvanizing
- cathodic protection
- fuel cell
- electrochemistry
- voltaic cell
- electrodes
- anode
- salt bridge
- electric potential
- cell potential
- battery
- secondary battery
- oxidation potential
- electrolysis
- electroplating
- electric charge
- extraction
- corrosion
- sacrificial anode
- chlor-alkali process

Knowledge/Understanding

1. Explain the function of the following parts of an electrolytic cell.
   - (a) electrodes  
   - (c) external voltage  
   - (b) electrolyte

2. In a galvanic cell, one half-cell has a cadmium electrode in a 1 mol/L solution of cadmium nitrate. The other half-cell has a magnesium electrode in a 1 mol/L solution of magnesium nitrate. Write the shorthand representation.

3. Write the oxidation half-reaction, the reduction half-reaction, and the overall cell reaction for the following galvanic cell.
   \[
   \text{Pt} \mid \text{NO}_2(g) \mid \text{NO}_3^-(aq), \text{H}^+(aq) \mid \mid \text{I}^-(aq) \mid \text{I}_2(s), \text{Pt}
   \]

4. What is the importance of the hydrogen electrode?

5. Lithium, sodium, beryllium, magnesium, calcium, and radium are all made industrially by the electrolysis of their molten chlorides. These salts are all soluble in water, but aqueous solutions are not used for the electrolytic process. Explain why.

6. Use the following two half-reactions to write balanced net ionic equations for one spontaneous reaction and one non-spontaneous reaction. State the standard cell potential for each reaction.
   \[
   \text{N}_2\text{O}_5(g) + 2\text{H}^+(aq) + 2e^- \rightleftharpoons \text{N}_2(g) + \text{H}_2\text{O}(l) \quad E^\circ = 1.770 \text{ V}
   \]
   \[
   \text{CuI(s)} + e^- \rightleftharpoons \text{Cu(s)} + \text{I}^-(aq) \quad E^\circ = -0.185 \text{ V}
   \]

7. Identify the oxidizing agent and the reducing agent in a lead-acid battery that is
   - (a) discharging  
   - (b) recharging

8. Rank the following in order from most effective to least effective oxidizing agents under standard conditions.
   \[
   \text{Zn}^{2+}(aq), \text{Co}^{3+}(aq), \text{Br}_2(l), \text{H}^+(aq)
   \]

9. Rank the following in order from most effective to least effective reducing agents under standard conditions.
   \[
   \text{H}_2(g), \text{Cl}^-(aq), \text{Al}(s), \text{Ag}(s)
   \]

10. The ions \text{Fe}^{2+}(aq), \text{Ag}^+(aq), \text{and Cu}^{2+}(aq) are present in the half-cell that contains the cathode of an electrolytic cell. The concentration of each of these ions is 1 mol/L. If the external voltage is very slowly increased from zero, in what order will the three metals Fe, Ag, and Cu be plated onto the cathode? Explain your answer.

Answers to questions highlighted in red type are provided in Appendix A.
11. Write the half-reactions and calculate the standard cell potential for each reaction. Identify each reaction as spontaneous or non-spontaneous.
   (a) \( \text{Zn}(s) + \text{Fe}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Fe}(s) \)
   (b) \( \text{Cr}(s) + \text{AlCl}_3(aq) \rightarrow \text{CrCl}_3(aq) + \text{Al}(s) \)
   (c) \( 2\text{AgNO}_3(aq) + \text{H}_2\text{O}_2(aq) \rightarrow 2\text{Ag}(s) + 2\text{HNO}_3(aq) + \text{O}_2(g) \)

12. Calculate the mass of magnesium that can be plated onto the cathode by the electrolysis of molten magnesium chloride, using a current of 3.65 A for 55.0 min.

13. (a) Describe a method you could use to measure the standard cell potential of the following galvanic cell.
   \( \text{Sn} \mid \text{Sn}^{2+} \text{(1 mol/L)} \parallel \text{Pb}^{2+} \text{(1 mol/L)} \mid \text{Pb} \)
   (b) Why is this cell unlikely to find many practical uses?

14. The two half-cells in a galvanic cell consist of one iron electrode in a 1 mol/L iron(II) sulfate solution, and a silver electrode in a 1 mol/L silver nitrate solution.
   (a) Assume the cell is operating as a galvanic cell. State the cell potential, the oxidation half-reaction, the reduction half-reaction, and the overall cell reaction.
   (b) Repeat part (a), but this time assume that the cell is operating as an electrolytic cell.
   (c) For the galvanic cell in part (a), do the mass of the anode, the mass of the cathode, and the total mass of the two electrodes increase, decrease, or stay the same while the cell is operating?
   (d) Repeat part (c) for the electrolytic cell in part (b).

15. (a) Describe an experiment you could perform to determine the products from the electrolysis of aqueous zinc bromide. How would you identify the electrolysis products?
   (b) Zinc and bromine are the observed products from the electrolysis of aqueous zinc bromide solution under standard conditions. They are also the observed products from the electrolysis of molten zinc bromide. Explain why the first observation is surprising.

16. Use the half-cells shown in a table of standard reduction potentials. Could you build a battery with a potential of 8 V? If your answer is yes, give an example.

17. Suppose you produce a kilogram of sodium and a kilogram of aluminum by electrolysis. Compare your electricity costs for these two processes. Assume that electricity is used for electrolysis only, and not for heating.

18. Research the following information. Prepare a short presentation or booklet on the early history of electrochemistry.
   (a) the contributions of Galvani and Volta to the development of electrochemistry
   (b) how Humphry Davy and Michael Faraday explained the operation of galvanic and electrolytic cells. (Note that these scientists could not describe them in terms of electron transfers, because the electron was not discovered until 1897.)

19. How rapidly do you think that iron would corrode on the surface of the moon? Explain your answer.

20. Reactions that are the reverse of each other have standard cell potentials that are equal in size but opposite in sign. Explain why.

21. Use a labelled diagram to represent each of the following.
   (a) a galvanic cell in which the hydrogen electrode is the anode
   (b) a galvanic cell in which the hydrogen electrode is the cathode

Making Connections

22. A D-size dry cell flashlight battery is much bigger than a AAA-size dry cell calculator battery. However, both have cell potentials of 1.5 V. Do they supply the same quantity of electricity? Explain your answer.

23. (a) Would you use aluminum nails to attach an iron gutter to a house? Explain your answer.
   (b) Would you use iron nails to attach aluminum siding to a house? Explain your answer.
24. Research the aluminum-air battery, and the sodium-sulfur battery. Both are rechargeable batteries that have been used to power electric cars. In each case, describe the design of the battery, the half-reactions that occur at the electrodes, and the overall cell reaction. Also, describe the advantages and disadvantages of using the battery as a power source for a car.

25. Explain why the recycling of aluminum is more economically viable than the recycling of many other metals.

26. Suppose you live in a small town with high unemployment. A company plans to build a smelter there to produce copper and nickel by roasting their sulfide ores and reducing the oxides formed. Would you be in favour of the plant being built, or opposed to it? Explain and justify your views.

27. Many metal objects are vulnerable to damage from corrosion. A famous example is the Statue of Liberty. Research the history of the effects of corrosion on the Statue of Liberty. Give a chemical explanation for the processes involved. Describe the steps taken to solve the problem and the chemical reasons for these steps.

28. (a) Estimate the number of used batteries you discard in a year. Survey the class to determine an average number. Now estimate the number of used batteries discarded by all the high school students in your province in a year.

(b) Prepare an action plan suggesting ways of decreasing the number of batteries discarded each year.

Section Review: 19.1: 1. ox: manganese(IV) oxide, red: zinc 2. Sn(s) → Sn^2+(aq) + 2e^-, red: 2H^+_aq + 2e^- → H_2(g), E°_cell = 0.138 V 3. ox: Cr(s) → Cr^3+(aq) + 3e^-, red: AgCl_2 (s) → Ag(s) + Cl^- (aq), E°_cell = 0.96 V 4. 2Cl^- → Cl_2(g) + 2e^- (b) Cd^2+ + 2e^- → Ca E°_cell = 0.292 V 5. CaCl_2 → Ca + Cl_2 6. Sn^2+(aq) + 2e^- → H_2(g), E°_cell = 0.542 V 7. ox: Sn(s) → Sn^2+(aq) + 2e^-, red: 2H^+_aq + 2e^- → H_2(g), E°_cell = 0.138 V 8. ox: Cr(s) → Cr^3+(aq) + 3e^-, red: AgCl_2 (s) → Ag(s) + Cl^- (aq), E°_cell = 0.96 V 9. (a) 2Cl^- → Cl_2(g) + 2e^- (b) Cd^2+ + 2e^- → Ca E°_cell = 0.292 V 10. (a) cathode: Li^+ → e^- → Li (b) anode: 2Br^- → Br_2(g) + 2e^- (c) 2Li^+ + 2Br^- → 2Li + Br_2 11. direct current: reaction proceeds steadily in one direction 12. reduction (gain of electrons) at cathode of electrolytic cell; electrons come from negative electrode (anode) of battery 13. hydrogen and oxygen 14. hydrogen, not calcium, produced at cathode 15. (a) 0.146 V (b) Cd anode, Ni cathode 16. (a) spontaneous (b) non-spontaneous 17. No (a) spontaneous (b) non-spontaneous 18. (a) spontaneous (b) non-spontaneous 19. 2Cu^+ (aq) → Cu^2+ (aq) + Cu(s), E°_cell = 0.368 V 20. (a) non-spontaneous (b) spontaneous 21. 2.98 g 22. 8.90 min 23. 1.85 A 24. (a) increases by 1.09 g (b) You can use the stoichiometry of the equations. 25. (a) 0.848 V (b) no; conditions are not standard 26. aluminum is more easily oxidized than iron 27. higher levels of salt (an electrolyte) and moisture 28. (a) acidic conditions (b) promotes it 29. 1.229 V 30. (a) overall: CH_4(aq) + 2O_2(g) → CO_2(g) + 2H_2O(l), ox: CH_4(g) + 2H_2O(l) → CO_2(g) + 8H^+_aq + 8e^-, red: O_2(g) + 4H^+_aq + 4e^- → 2H_2O(l) 31. same equation as combustion, but fuel does not burn 32. 0.0452 g 33. oxidation number of Cl increases from 0 to +1 in forming HClO, decreases from 0 to –1 in forming HCl; chlorine undergoes both oxidation and reduction 34. hydrogen and oxygen, but conditions are far from standard

Answers to Practice Problems and Short Answers to Section Review Questions

Practice Problems: 1. (a) oxidizing agent, Cu(II); reducing agent, Zn (b) same as previous

2. (a): Sn(s) → Sn^2+(aq) + 2e^-, red: 2H^+_aq + 2e^- → H_2(g), overall: Sn(s) + 2HCl_2(aq) → Sn^2+(aq) + H_2(g), anode: Sn(s) → Sn^2+(aq) + 2e^-, overall: Sn(s) + 2HCl_2(aq) → Sn^2+(aq) + H_2(g), cathode: (b) Cu^2+ (aq) → Cu(s), overall: Cu^2+ (aq) + 2e^- → Cu(s)

3. (a) ox: I_2(s) → I^-(aq) + 2e^-, red: MnO_2(aq) + 8H^+_aq + 5e^- → Mn^2+ (aq) + 4H_2O(l), overall: 2I_2(s) + 2MnO_2(aq) + 16H^+_aq → 5I^-(aq) + 2Mn^2+ (aq) + 8H_2O(l)

(b) oxidizing agent, MnO_2-, reducing agent, I^- (c) one electrolyte, no barrier

5. ox: 2Br^- → Br_2(g) + 2e^-, red: Cl_2(g) + 2e^- → 2Cl^-(aq), E°_cell = 0.292 V

6. ox: Cu^+(aq) → Cu^2+(aq) + e^-, red: 2H^+_aq + O_2(g) + 2e^- → H_2O_2(aq), overall: Cu^+(aq) + H_2O_2(aq) + 2e^- → Cu^2+ (aq) + 2H^+_aq, E°_cell = 0.542 V

7. ox: Sn(s) → Sn^2+(aq) + 2e^-, red: 2H^+_aq + 2e^- → H_2(g), E°_cell = 0.138 V 8. ox: Cr(s) → Cr^3+(aq) + 3e^-, red: AgCl_2 (s) → Ag(s) + Cl^- (aq), E°_cell = 0.96 V 9. (a) 2Cl^- → Cl_2(g) + 2e^- (b) Cd^2+ + 2e^- → Ca E°_cell = 0.292 V 10. (a) cathode: Li^+ → e^- → Li (b) anode: 2Br^- → Br_2(g) + 2e^- (c) 2Li^+ + 2Br^- → 2Li + Br_2 11. direct current: reaction proceeds steadily in one direction 12. reduction (gain of electrons) at cathode of electrolytic cell; electrons come from negative electrode (anode) of battery 13. hydrogen and oxygen 14. hydrogen, not calcium, produced at cathode 15. (a) 0.146 V (b) Cd anode, Ni cathode 16. (a) spontaneous (b) non-spontaneous 17. No (a) spontaneous (b) non-spontaneous 18. (a) spontaneous (b) non-spontaneous 19. 2Cu^+ (aq) → Cu^2+ (aq) + Cu(s), E°_cell = 0.368 V 20. (a) non-spontaneous (b) spontaneous 21. 2.98 g 22. 8.90 min 23. 1.85 A 24. (a) increases by 1.09 g (b) You can use the stoichiometry of the equations. 25. (a) 0.848 V (b) no; conditions are not standard 26. aluminum is more easily oxidized than iron 27. higher levels of salt (an electrolyte) and moisture 28. (a) acidic conditions (b) promotes it 29. 1.229 V 30. (a) overall: CH_4(aq) + 2O_2(g) → CO_2(g) + 2H_2O(l), ox: CH_4(g) + 2H_2O(l) → CO_2(g) + 8H^+_aq + 8e^-, red: O_2(g) + 4H^+_aq + 4e^- → 2H_2O(l) 31. same equation as combustion, but fuel does not burn 32. 0.0452 g 33. oxidation number of Cl increases from 0 to +1 in forming HClO, decreases from 0 to –1 in forming HCl; chlorine undergoes both oxidation and reduction 34. hydrogen and oxygen, but conditions are far from standard
Knowledge/Understanding

Multiple Choice

In your notebook, write the letter for the best answer to each question.

1. The oxidation number of carbon in a compound cannot be
   (a) +4
   (b) +2
   (c) 0
   (d) +6
   (e) −4

2. Rusting is
   (a) a decomposition reaction
   (b) a combustion reaction
   (c) a redox reaction
   (d) a neutralization reaction
   (e) a double displacement reaction

3. Of the following, the most effective reducing agent is
   (a) Na
   (b) Pb
   (c) Cl−
   (d) H2
   (e) H2O

4. Primary batteries contain
   (a) rechargeable cells
   (b) no cells
   (c) fuel cells
   (d) electrolytic cells
   (e) galvanic cells

5. In an electroplating experiment, the mass of metal plated onto the cathode
   (a) doubles, if the external voltage is doubled
   (b) doubles, if the current is doubled
   (c) depends on the material used to make the cathode
   (d) depends only on the time for which the current flows
   (e) equals the decrease in mass of the electrolyte

6. A fuel cell
   (a) does not form any products
   (b) has a negative cell potential
   (c) uses a spontaneous reaction to generate electricity
   (d) is not very efficient
   (e) produces its own fuel

7. A metal cathode in a cell always
   (a) decreases in mass while the cell is in operation
   (b) conducts electrons out of the cell
   (c) has a positive polarity
   (d) undergoes reduction
   (e) consists of a different metal than the metal anode in the same cell

8. In both a galvanic cell and an electrolytic cell,
   (a) reduction occurs at the cathode
   (b) the cell potential is positive
   (c) the overall reaction is spontaneous
   (d) an external voltage is required
   (e) chemical energy is converted to electrical energy

9. A type of reaction that is always a redox reaction is
   (a) synthesis
   (b) decomposition
   (c) single displacement
   (d) double displacement
   (e) neutralization

10. The sum of the oxidation numbers of all the elements in a compound
    (a) depends on the formula of the compound
    (b) is positive
    (c) is negative
    (d) is zero
    (e) depends on the type(s) of chemical bonds in the compound

11. While a lead-acid battery is being recharged,
    (a) the mass of lead(II) sulfate in the battery is increasing
    (b) the number of electrons in the battery is increasing
    (c) chemical energy is being converted to electrical energy
    (d) no chemical reaction is taking place
    (e) the cell potential is increasing

12. The oxidation number of oxygen
    (a) is always negative
    (b) is usually negative
    (c) is never zero
    (d) is never positive
    (e) is never −1

Answers to questions highlighted in red type are provided in Appendix A.
Determine the oxidation number of
(a) N in N₂O₃
(b) P in H₃PO₇
(c) Si in SiF₆²⁻
(d) each element in (NH₄)₂SO₄

14. Does the fact that you can assign oxidation numbers of +1 to hydrogen and −2 to oxygen in water mean that water is an ionic substance? Explain.

15. (a) Limewater, Ca(OH)₂(aq), turns cloudy in the presence of carbon dioxide. Write a balanced chemical equation for the reaction. Include the states of the substances.
(b) Is this reaction a redox reaction?

16. Balance each of the following half-reactions.
(a) Hg₂²⁺ → Hg
(b) TiO₂ → Ti²⁺ (acidic conditions)
(c) I₂ → H₂IO₆³⁻ (basic conditions)

17. Explain why you cannot use the table of standard reduction potentials in Appendix E to calculate the external voltage required to electrolyze molten sodium chloride.

18. Why is the density of the electrolyte solution in a lead-acid battery greatest when the battery is fully recharged?

19. Some metals can have different oxidation numbers in different compounds. In the following reactions of iron with concentrated nitric acid, assume that one of the products in each case is gaseous nitrogen monoxide. Include the states of all the reactants and products in the equations.
(a) Write a balanced chemical equation for the reaction of iron with concentrated nitric acid to form iron(II) nitrate.
(b) Write a balanced chemical equation for the reaction of iron(II) nitrate with concentrated nitric acid to form iron(III) nitrate.
(c) Write a balanced chemical equation for the reaction of iron with concentrated nitric acid to form iron(III) nitrate.
(d) How are the equations in parts (a), (b), and (c) related?

20. For the following galvanic cell, C(s), I₂(s) | I⁻(aq) || Ag⁺(aq) | Ag(s)
(a) identify the anode, the cathode, the positive electrode, and the negative electrode
(b) write the two half-reactions and the overall cell reaction
(c) identify the oxidizing agent and the reducing agent
(d) determine the standard cell potential

21. State whether the reaction shown in each of the following unbalanced equations is a redox reaction. If so, identify the oxidizing agent and the reducing agent. Balance each equation.
(a) Cl₂O₇ + H₂O → HClO₄
(b) I₂ + ClO⁻ → IO⁻ + Cl⁻ (acidic conditions)
(c) S²⁻ + Br₂ → SO₄²⁻ + Br⁻ (basic conditions)
(d) HNO₃ + H₂S → NO + S + H₂O

22. Determine the standard cell potential for each of the following reactions. State whether each reaction is spontaneous or non-spontaneous.
(a) 2Fe²⁺(aq) + I₂(s) → 2Fe³⁺(aq) + 2I⁻(aq)
(b) Ag(NO₃)₃(aq) + 3Ag(s) → 3AgNO₃(aq) + Ag₃
(c) H₂O₂(aq) + 2HCl(aq) → Cl₂(ℓ) + 2H₂O(ℓ)

Inquiry
23. Predict the products from the electrolysis of a 1 mol/L solution of hydrochloric acid.

24. Suppose you decide to protect a piece of iron from rusting, by covering it with a layer of lead.
(a) Would the iron rust if the lead layer completely covered the iron? Explain.
(b) Would the iron rust if the lead layer partially covered the iron? Explain.

25. When aqueous solutions of potassium permanganate, KMnO₄, and sodium oxalate, Na₂C₂O₄, react in acidic solution, the intense purple colour of the permanganate ion fades and is replaced by the very pale pink colour of manganese(II) ions. Gas bubbles are observed as the oxalate ions are converted to carbon dioxide. If the redox reaction is carried out as a titration, with the permanganate being added to the oxalate, the permanganate acts as both reactant and indicator. The persistence of the purple colour in the solution with the addition of one drop of permanganate at the end-point shows that the reaction is complete.
(a) Complete and balance the equation for acidic conditions.
\[ \text{MnO}_4^- + \text{C}_2\text{O}_4^{2-} \rightarrow \text{Mn}^{2+} + \text{CO}_2 \]

(b) If 14.28 mL of a 0.1575 mol/L potassium permanganate solution reacts completely with 25.00 mL of a sodium oxalate solution, what is the concentration of the sodium oxalate solution?

26. Redox titrations can be used for chemical analysis in industry. For example, the percent by mass of tin in an alloy can be found by dissolving a sample of the alloy in an acid to form aqueous tin(II) ions. Titrating with cerium(IV) ions produces aqueous tin(IV) and cerium(III) ions. A 1.475 g sample of an alloy was dissolved in an acid and reacted completely with 24.38 mL of a 0.2113 mol/L cerium(IV) nitrate solution. Calculate the percent by mass of tin in the alloy.

27. Design and describe a procedure you could use to galvanize an iron nail. Explain your choice of materials.

28. Suppose you build four different half-cells under standard conditions in the laboratory.
   (a) What is the greatest number of different galvanic cells you could make from the four half-cells?
   (b) What is the smallest number of standard cell potentials you would need to measure to rank the half-cells from greatest to least standard reduction potentials? Explain.

29. In a galvanic cell, the mass of the magnesium anode decreased by 3.38 g while the cell produced electricity.
   (a) Calculate the quantity of electricity produced by the cell.
   (b) If the constant current flowing through the external circuit was 100 mA, for how many hours did the cell produce electricity?

30. Calculate the mass of aluminum plated onto the cathode by a current of 2.92 A that is supplied for 71.0 min to an electrolytic cell containing aqueous aluminum nitrate as the electrolyte.

31. An industrial method for manufacturing fluorine gas is the electrolysis of liquid hydrogen fluoride.
\[ 2\text{HF}(\ell) \rightarrow \text{H}_2(\text{g}) + \text{F}_2(\text{g}) \]
If the current supplied to the electrolytic cell is 5000 A, what mass of fluorine, in tonnes, is produced by one cell in one week?

32. Describe how you could build a galvanic cell and an electrolytic cell in which the two electrodes are made of lead and silver. Include a list of the materials you would require.

33. It is possible to use the standard reduction potentials for the reduction of hydrogen ions and the reduction of water molecules to show that the dissociation of water molecules into hydrogen ions and hydroxide ions is non-spontaneous under standard conditions. Describe how you would do this. How is this result consistent with the observed concentrations of hydrogen ions and hydroxide ions in pure water?

**Communication**

34. List all the information you can obtain from a balanced half-reaction. Give two examples to illustrate your answer.

35. (a) If one metal (metal A) displaces another metal (metal B) in a single displacement reaction, which metal is the more effective reducing agent? Explain. Give an example to illustrate your answer.
   (b) If one non-metal (non-metal A) displaces another non-metal (non-metal B) in a single displacement reaction, which non-metal is the more effective oxidizing agent? Explain. Give an example to illustrate your answer.

36. (a) Sketch a cell that has a standard cell potential of 0 V.
   (b) Can the cell be operated as an electrolytic cell? Explain.

37. If a redox reaction cannot create or destroy electrons, how is it possible that the balanced half-reactions for a redox reaction may include different numbers of electrons?
38. (a) A friend in your class has difficulty recognizing disproportionation reactions. Write a clear explanation for your friend on how to recognize a disproportionation reaction.
(b) Write a balanced chemical equation that represents a disproportionation reaction.

39. (a) An electrolytic cell contains a standard hydrogen electrode as the anode and another standard half-cell. Is the standard reduction potential for the half-reaction that occurs in the second half-cell greater than or less than 0 V? Explain how you know.
(b) Will your answer for part (a) change if the hydrogen electrode is the cathode of the electrolytic cell? Explain.

40. Write a descriptive paragraph to compare the reactions that occur in a Downs cell and a chlor-alkali cell. Describe the similarities and differences.

41. One of your classmates is having trouble understanding some of the main concepts in this unit. Use your own words to write an explanation for each of the following concepts. Include any diagrams or examples that will help to make the concepts clear to your classmate.
(a) oxidation and reduction
(b) galvanic and electrolytic cells

Making Connections

42. Black-and-white photographic film contains silver bromide. When exposed to light, silver bromide decomposes in a redox reaction. Silver ions are reduced to silver metal, and bromide ions are oxidized to bromine atoms. The brighter the light that hits the film, the greater is the decomposition. When the film is developed, the parts of the film that contain the most silver metal produce the darkest regions on the negative. In other words, the brightest parts of the photographed scene give the darkest parts of the image on the negative. High-speed black-and-white film uses silver iodide in place of silver bromide. Do you think that silver iodide is more sensitive or less sensitive to light than silver bromide? Explain.

43. The two rocket booster engines used in a space shuttle launch contain a solid mixture of aluminum and ammonium perchlorate. The products of the reaction after ignition are aluminum oxide and ammonium chloride.
(a) Write a balanced chemical equation for this reaction, and identify the oxidizing agent and reducing agent.
(b) The other four engines used in a space shuttle launch use the redox reaction of liquid hydrogen and liquid oxygen to form water vapour. Write a balanced chemical equation for this reaction.
(c) Which of the reactions described in parts (a) and (b) do you think is the more environmentally friendly reaction? Explain.

44. Every year, corrosion is responsible for the failure of many thousands of water mains. These are the pipes that transport water to Canadian homes and businesses. Research and describe the economic, environmental, health, and safety issues associated with rupture and repair of water mains. Describe the methods that are being used to improve the situation.

45. Since the corrosion of iron is such an expensive problem, why do you think that iron is still used for so many purposes?

46. Industrial plants that make use of electrochemical processes are often located close to sources of hydroelectricity. Research and identify an example in Ontario. Write a brief description of what the plant produces and how it produces it.
Appendix A

Answers to Selected and Numerical Chapter and Unit Review Questions

Chapter 1

6. 32 neutrons, 27 electrons
7. (a) 7 (b) 7 (c) 10
   (d) 3− (e) 79Se (f) 2−
   (g) Cr (h) 24 (i) 28
   (j) 21 (k) 3+ (l) 19
   (m) 9 (n) 9 (o) 9
8. (a) SnF₂ (b) BaSO₄ (c) Mg(OH)₂
   (d) CsBr (e) NH₄HCO₃ (f) K₃PO₄
   (g) Fe₂(SO₄)₃
9. (a) sodium hydrogen carbonate (b) iron(II) oxide
   (c) copper(II) chloride (d) PbO₂
   (e) tin(IV) chloride (f) diphosphorus pentoxide
   (g) aluminum sulfate
12. (a) PdCl₂(aq) + 2HNO₃(aq) → Pd(NO₃)₂(aq) + 2HCl(aq)
    (b) Cr(s) + 2HCl(aq) → CrCl₂(aq) + H₂(g)
    (c) 2K(s) + 3H₂O(l) → 2KOH(aq) + H₂(g)
13. (a) single displacement;
    H₂(g) + CaO(s) → Ca(s) + H₂O(g)
    (b) synthesis; 16Ag(s) + S₈(s) → 8Ag₂S₈(s)
    (c) hydrocarbon combustion;
    C₆H₁₂(g) + 6O₂(g) → 4CO₂(g) + 4H₂O(g)
    (d) synthesis; NH₃(aq) + HCl(aq) → NH₄Cl(aq)
    (e) synthesis; 2MgCl₂(aq) + O₂(g) → 2MgO(aq)
14. (a) NaOH(aq) + Fe(NO₃)₃(aq) → NaNO₃(aq) + Fe(OH)₃(s)
    (b) 2Sb(s) + 3Cl₂(g) → 2SbCl₆(s)
    (c) 2Hg(l) + O₂(g) → 2HgO(s)
    (d) NH₃NO₂(s) → N₂(g) + H₂O(l)
    (e) 3Al(s) + 3Zn(NO₃)₂(aq) → 2Al(NO₃)₃(aq) + 3Zn(s)
15. (a) synthesis
    (b) PbO(s) + Cr(s) + 3O₂(g) → PbCrO₄(s)
16. double displacement;
    HCl(aq) + CaCO₃(s) → CaCl₂(aq) + H₂CO₃(aq)
    (the H₂CO₃ then decomposes to form H₂O(l) and CO₂(g))

UNIT 1

Chapter 2

9. 137 10. 77 11. 6.94 u
12. 95% K-39, 5% K-41
13. (a) 2.84 × 10⁻³ mol (b) 0.517 mol
    (c) 8.15 × 10⁻⁵ mol (d) 0.483 mol
    (e) 0.126 mol
14. (a) 7.09 × 10⁻³ mol (b) 1.23 mol
    (c) 8.94 × 10⁻² mol (d) 0.483 mol
    (e) 2.69 mol (f) 9.27 × 10⁻⁴ mol
15. (a) 17.0 g/mol (b) 1.46 mol
    (c) 8.79 × 10⁻³ molecules (d) 3.52 × 10⁻⁴
    (e) 18.0 g/mol (f) 1.58 g
    (g) 8.77 × 10⁻² mol (h) 1.58 × 10⁻³
    (i) 157.9 g/mol (j) 10.5 g
    (k) 6.64 × 10⁻² mol (l) 4.00 × 10⁻²
    (m) 194.2 g/mol (n) 4.98 × 10⁻³ mol
    (o) 3.00 × 10⁻² (p) 2.10 × 10⁻² atoms
    (q) 152.2 g/mol (r) 1.99 × 10⁻¹
    (s) 13.1 mol (t) 1.50 × 10⁻⁶
    (u) 78.0 g/mol (v) 6.66 × 10⁻⁴ g
    (w) 5.14 × 10⁻⁶ (x) 3.60 × 10⁻⁷
16. (a) 354.88 g/mol (b) 74.09 g/mol
    (c) 142.05 g/mol (d) 252.10 g/mol
    (e) 310.18 g/mol (f) 182.90 g/mol
17. (a) 66.7 g (b) 335 g
    (c) 3.75 × 10⁻³ g (d) 1.45 g
    (e) 57.4 g (f) 2.05 × 10⁻² g
18. 21.1 × 10⁻²⁴ atoms
19. 4.22 × 10⁻²⁴
20. (a) 131.29 u (b) 131.29 g
    (c) 2.18 × 10⁻²² g (d) 7.90 × 10⁻²³ u/mol
    (e) 6.02 × 10⁻²³ u/g
21. 3.01 × 10⁻²⁴
22. 6.54 × 10⁻²⁴
23. 4.53 × 10⁻²³
24. 192 g
25. NaCl + AgNO₃ → AgCl + NaNO₃
26. (a) 131 g (b) 380 g
    (c) 4.7 g (d) 4.0 × 10⁻⁵
    (e) 6.4 × 10⁻³ g (f) 78.5 g
27. M = 83.8 g/mol, krypton, Kr(l)
32. (a) 2.65 × 10⁻⁴ mol (b) 118.2 mg
33. (a) 101 mg

Chapter 3

5. 2.64 g
6. (a) 9.93% C; 58.6% Cl; 31.4% F
    (b) 80.1% Pb; 16.5% O; 3.0% H; 3.10% C
7. (a) 6.86 g (b) 1.74 g
8. (a) 63.5% (b) 1.27 × 10⁻² kg
9. 58.8% 10. 62.8% 11. C₄H₅O₄
12. C₂H₂O₂Cl₂
13. (c) C₂H₆
14. C₂H₂O₃
15. Na₂Cr₂O₇
16. HgSO₄
17. (a) Ca₃P₂O₈ (b) Ca₃(PO₄)₂
21. Fe₂(SO₄)·7H₂O
22. (a) 37.50% C; 4.20% H; 58.30% O  
(b) C₆H₄O₂  
(c) C₆H₄O₂
23. 1.37 g CO₂; 1.12 g H₂O
28. (a) 0.87 g/L
29. (a) sodium carbonate heptahydrate  
(b) 54%  
(c) 5.25 x 10⁻⁴ g
30. (b) C₆H₄O₄

Chapter 4

29. (a) 6.02
33. (a)
38. 68.1% C; 13.7% H; 18.1% O
39. (a)
44. (a) 1.48 x 10⁻² mm  
(b) 0.1275 nm  
(c) 0158 nm
UNIT 2

Chapter 5

3. letters—nucleus and all except valance electrons;  
dots—valance electrons
4. (a) KBr  
(b) CaF₂  
(c) MgO  
(d) Li₂O
5. unpaired electrons will most likely be involved in  
bonding, electron pairs most likely not be  
involved in bonding
6. (a) ⋅O::Si::O⋅  
(b) ⋅Br::O::Br⋅  
(c) ⋅Cl::F::  
(d) ⋅F::N::F::

UNIT 2 Review

14. If the compound consists of a metal and a nonmetal,  
it is probably an ionic compound.
18. The diatomic molecules have a different number  
of valance electrons so they have to share a  
different number of electrons to achieve a noble  
gas configuration.
23. short
26. (a) linear  
(b) trigonal planar  
(c) bent
33. number of electrons in the molecule and shape  
of the molecule
35. when a line connecting the two electronegative atoms goes directly through the hydrogen atom

41. LiBr

42. (a) N ← H (b) F ← N (c) I → Cl

43. (a) Cl ← Cl, Br → Cl, Cl → F (b) Si ← Cl, P → Cl, S → Cl, Si–Si

46. ammonium ion is tetrahedral and symmetrical; polarity of bonds cancels; ammonia pyramidal and is polar

UNIT 3
Chapter 7
11. 5.62 g
12. (a) 25 g (b) 225 g (c) 2.5 mol/L
13. 96 mL
14. 1.2 mg NaF; 1.2 ppm
15. 5.67 mol/L
16. (a) 0.427 mol/L (b) 6.3 mol/L
17. (a) 9.89 g (b) 83 g
18. (a) 1.7 mol/L (b) 1.44 mol/L
19. (a) 0.381 mol/L (b) 0.25 mol/L
20. 25.0 g
23. (b) 85 g/100 g water (c) 140 g/100 g water (d) 77°C
24. 390 g
25. 40°C
29. 0.25 ppm; 250 ppb
32. 55.5 mol/L

Chapter 8
11. 0.015 mol/L
12. (a) 0.172 mol/L (b) 0.578 mol/L (c) 0.694 mol/L
13. 1.04 mol/L
14. $K_{\text{aq}} = 0.0667 \text{ mol/L}; \text{Ca}^{2+}_{\text{aq}} = 0.0667 \text{ mol/L};\text{NO}_3^{-}_{\text{aq}} = 0.200 \text{ mol/L}$
16. (a) $\text{Ca}^{2+}_{\text{aq}} = 0.045 \text{ mol/L}; \text{Mg}^{2+}_{\text{aq}} = 0.024 \text{ mol/L}$ (b) $\text{Ca}^{2+} = 1.8 \times 10^3 \text{ ppm}; \text{Mg}^{2+} = 5.8 \times 10^2 \text{ ppm}$
17. 0.014 mol
18. 12.2 g Pb$_3$(PO$_4$)$_2$
20. (b) 0.01057 mol (c) 120.4 g/mol
22. (b) 0.09600%
23. (a) 1.3 L (b) 2.0 g (c) 2.0 mL

Unit 3 Review
16. $3.6 \times 10^{-3}$ g
17. $3.89 \times 10^{-2}$ g
18. $1.94 \times 10^{-3}$ g
19. $2.43 \times 10^{-2}$ mol/L

30. (b) $7.41 \times 10^{-2}$ mol/L
31. (b) 0.364 g
32. (a) 119 g
33. (a) 0.031 mol (b) $3.40 \times 10^{-3}$ mol
34. 2.295 $\times 10^{-3}$ mol/L
38. (a) 0.291 mol/L (b) 0.436 mol/L (c) 0.257 mol/L
41. 5.65 mol
42. (a) 0.420 mol/L (b) 0.840 mol/L
43. $[\text{H}^+] = 0.705 \text{ mol/L}; [\text{OH}^-]$ negligible; $[\text{Ba}^{2+}_{\text{aq}}] = 0.0640 \text{ mol/L}; [\text{Cl}^{-}_{\text{aq}}] = 1.66 \text{ mol/L}$
44. (a) 1.8 mol (b) 1.8 mol (c) 0.90 mol/L
45. (a) 0.212 mol (b) 1.8 g

UNIT 4
Chapter 9
1. (a) fossil fuels (b) wood, plant fermentation products, fossil fuels (c) petroleum
2. bacterial activity, heat, pressure
5. increases
11. (a) $\text{C}_n\text{H}_{2n+2}$ (b) $\text{C}_n\text{H}_{2n}$ (c) $\text{C}_n\text{H}_{2n-2}$
12. (a) alkene (b) alkane (c) alkyne (d) alkane
13. (a) aliphatic (b) aromatic (c) aliphatic (d) aliphatic (e) aromatic
14. (a) alkyne (b) alkene (c) alkyne (d) alkane (e) alkene (cycloalkene)
15. (b) unsaturated, (b) unsaturated, (c) unsaturated, (d) saturated, (e) unsaturated
16. (a) butane (b) ethane (c) 2,3,4-trimethylpentane (d) 4-ethyl-3-methylhexane
17. (a) 2-methylpropene (b) 1-ethyl-2-methylcyclohexane (c) 3-methyl-1-phenylenene (d) trans-3-methyl-2-pentene (e) 3-ethyl-3,4-dimethylhexane (f) ethylbenzene
18. trans-2-heptene and cis-2-heptene
19. (A)—(d); (B)—(f); (C)—(c); (D)—(a)
20. no; 3-methyl-1-cyclobutene
21. oil floats on water, does not dissolve
22. the methyl group would be part of the main chain
23. (a) and (c), (b) and (d) are the same
24. (a) ethylbenzene (b) 1-propyl-3-ethylbenzene (c) 1-ethyl-2-methylbenzene (d) 1,4-dimethylbenzene
Chapter 10

1. (a) tetrahedral, trigonal planar, trigonal planar
   (b) C = O
   (c) non-polar, polar, non-polar

2. (a) polar
   (b) non-polar
   (c) polar
   (d) non-polar
   (e) polar

4. (a) R — OH
   (b) R — NR’
   (c) R — COO — R’
   (d) R — CON — R’

6. (a) amine
   (b) alkane
   (c) alcohol
   (d) ester
   (e) amide
   (f) carboxylic acid

7. (a) hydroxyl
   (b) double bond, amine
   (c) double bond, ester
   (d) triple bond, carbonyl, ether
   (e) chlorine, amide
   (f) carboxyl group, carbonyl group

8. (a) amine
   (b) aldehyde
   (c) ester
   (d) carboxylic acid
   (e) ketone

9. (a) alcohol
10. (a) alkane
11. (a) 1-propanol
    (b) 3-octanol
    (c) 2-hexanamine
    (d) 1-methoxybutane
    (e) 2-propanone
    (f) methyl pentanoate
    (g) 3-methyl-3-hexan
    (h) butanal
    (i) 2-bromopropane
    (j) cyclopentanone
    (k) pentanoic acid
    (l) ethyl propanoate
    (m) 5-ethyl-5,6-dimethyl-3-heptanone
    (n) trans-1-bromo-2-iodo-ethene
12. (a) ethoxyethane, ether
    (b) octanal, aldehyde
    (c) hexanamide, amide
    (d) 3-ethyl-2-hexanol
    (e) 2-methylpentanoic acid
    (f) 1-butynamine, amine
    (g) N-propylpropanamide, amide
13. (a) ethyl alcohol
    (b) methyl alcohol
    (c) formaldehyde
    (d) acetic acid
    (e) acetone
    (f) isopropyl alcohol
15. (a) elimination
    (b) substitution
    (c) addition
    (d) substitution
16. (a) A, ethanamine; B, ethane; C, methoxy methane; D, ethanol; E, ethanoic acid
17. (a) 1-bromopentane + water
    (b) propene + water
    (c) methyl propanoate + water
    (d) ethanoic acid + ethanol
19. (a) propanoic acid + 1-butanol
    (b) cyclobutanol
25. (a) either 2-methylhexanal or pentanal
    (b) N-ethyl-N-methylpentanamide
    (c) 2-methylpropanoic acid
26. 1-butanol, 2-butanol, 2-methyl-1-propanol,
    2-methyl-1-propanol, 1-methoxypropane,
    1-ethoxyethane, 2-methoxypropane
27. butanoic acid, 2-methylpropanoic acid, methyl propanoate, ethyl ethanoate, 1-propyl methanoate,
    2-propyl methanoate (Note: Other isomers are possible
    that contain hydroxyl and carbonyl groups, or alkoxy
    and carboxyl groups, but these are beyond the scope
    of this course.)

Chapter 11

2. Polymers are made of repeating units called monomers.
6. (a) propene, H₂C = CHCH₃
    (b) addition
    (c) polypropylene
8. polyamide; Amino acids are joined by amide linkages.
14. (a) monosaccharide or simple sugar
    (b) glucose
16. (a) ethene, CH₂ = CH₂
    (b) CH₃CHOHCH₂COOH
    (c) CH₂ = CHCH₂CH₃
    (d) NH₂CH₂CH(CH₃)NH₂ + HOOCCH₂COOH
    (e) HOCH₂(benzene)CH₂OH + HOOCCH₂COOH

Unit 4 Review
20. alkenes, alkynes and aromatics do
21. higher
23. grain alcohol
24. ethanoic acid
26. (a) butanoic acid
    (b) methanol
    (c) methyl pentanoate
    (d) 2-butane
    (e) N-methyllethanamine
    (f) 4,5-dimethylheptanal
27. (a) methyl alcohol or wood alcohol
    (b) isopropyl alcohol
    (c) ether
28. (a) 3-ethyl-4-methyl-1-hexene
    (b) methoxypropane
    (c) 3-methyl-1-pentanamine
    (d) 5-ethyl-3,7,9-trimethyl-2-decanol
    (e) butyl propanoate
29. (a) 5-methylcyclohexanoic acid
    (b) N-ethyl-1-butynamine
    (c) 6-ethyl-5-methyl-2-octyne
    (d) butanamide
    (e) 6-ethyl-7-methyl-4-decanone
    (f) 2-ethyl-3-methylcyclohexan
UNIT 5

Chapter 13
8. \([H_2] = 5.6 \times 10^{-4} \text{ mol/L}; [HI] = 1.12 \times 10^{-3} \text{ mol/L}\)
9. \([SO_3] = 0.13 \text{ mol/L}\)
10. 37.4 g
11. \([CO] = [H_2O] = 0.013 \text{ mol/L}; [H_2] = [CO_2] = 0.037 \text{ mol/L}\)
12. \(K_c = 2.7 \times 10^{-4}\)
13. (b) \(1.7 \times 10^{-2}\)
16. 0.26
19. \(1.2 \times 10^{-17} \text{ mol/L}\)

Unit 5 Review
18. \(6.9 \times 10^{-2}\)
20. 0.16
21. \(\frac{[N_{2(g)}][H_2(g)]^3}{[NH_3(g)]^2}\)
22. \(6 \times 10^3\)
24. 3.24
25. \(1.86 \times 10^{-2}\)
26. \(1.3 \times 10^{-2}\)
27. (b) \([PCl_3] = 0.060 \text{ mol/L}; [PCl_3] = 0.38 \text{ mol/L}; [Cl_2] = 0.16 \text{ mol/L}\)
31. (c) \([XO_2] = 0.00985 \text{ mol/L}; [O_2] = 0.992 \text{ mol/L}\)
33. (a) \([CO_2] = 0.0132 \text{ mol/L}\)
(b) \([CO_2] = 0.0132 \text{ mol/L}\)
40. (a) \(K_c = 1.6\)
(b) 0.032 (both CO and H_2O) or 0.064 mol/2 L (both CO and H_2O)

UNIT 6

Chapter 14
18. (a) \(1.0 \times 10^3 \text{ g}\)
(b) 55 mol
(c) \(1.8 \times 10^{-9} \text{ mol/L or about 2 ppb}\)
19. 0.800 mol/L
20. (a) pOH = 4.292
(b) pH = 9.708
(c) \([H_3O^+] = 1.96 \times 10^{-10} \text{ mol/L}\)
25. pH = 12
26. 1 mol
30. (a) \(2.5 \times 10^{-6} \text{ mol/L; 12:1}\)

Chapter 15
1. (a) \(K_a\) for HSO_4^- = 1.0 \times 10^{-2}; \(K_b\) for HSO_4^- = 6.3 \times 10^{-8}
(b) \(K_a\) for HSO_4^- = 1.0 \times 10^{-12}; \(K_b\) for HSO_4^- = 1.6 \times 10^{-7}
6. \(1.4 \times 10^{-1} \text{ mol/L}\)
7. 2.52
8. (a) pH = 2.10; 0.79% dissociation
(b) pH = 2.60; 2.5% dissociation
(c) pH = 3.10; 7.9% dissociation
9. (a) pH = 4.29; 0.078% dissociation
(b) OCl^-, 2.5 \times 10^{-7}
10. pH = 9.10
11. pH = 8.11
12. \(K_a = 1.1 \times 10^{-3}\)
13. \(4.0 \times 10^{-6}\)
17. (b) \(2.6 \times 10^{-10}\)
19. 0.20 mol/L
20. \(1.0 \times 10^{-5}\)
22. 0.1171 mol/L
23. (a) 2.399 mol/L

Unit 6 Review
12. 2.4
13. \([H_3O^+] = 1.7 \times 10^{-3} \text{ mol/L; pH = 2.77; pOH = 11.23}\)
19. (a) \(\frac{[H_3O^+][ClO^-]}{[HClO]}\)
(b) \(\frac{[H_3O^+][HSO_4^-]}{[H_2SO_4]}\)
23. (a) 2.298
25. (a) \(1.6 \times 10^{-5}\)
(b) 11.14
27. 12.3%
31. \([H_3O^+] = 0.0075 \text{ mol/L; pH = 2.12; pOH = 11.88; } [OH^-] = 1.3 \times 10^{-12}\)
32. (b) about 10
33. 1.6%
34. \(3.4 \times 10^{-7}\)
17. (a) $-2657$ kJ
(b) $-1428.4$ kJ/mol; $-47.5$ kJ/g
(c) $4.6 \times 10^2$ kJ

23. (a) CH$_4$(g) + O$_2$(g) → CO$_2$(g) + 2H$_2$O(g);
\[ \Delta H_{\text{comb}} = -802.5 \text{ kJ/mol, or } -50.00 \text{ kJ/g CH}_4 \]
H$_2$(g) + $\frac{1}{2}$O$_2$(g) → H$_2$O(g); \[ \Delta H_{\text{comb}} = -241.8 \text{ kJ/mol, or } -120 \text{ kJ/g H}_2 \]

Unit 7 Review
22. (c) $-0.828$ kJ/g; $0.460$ kJ/g
24. (b) $243$ g
25. (a) $55.7$°C
26. (a) $-46$ kJ/mol
(b) $|\text{calculated } \Delta H| < |\text{actual } \Delta H|$}

28. 3.4 L
29. (a) C$_{12}$H$_{22}$O$_{11}$(s) + 35/O$_2$(g) → 12CO$_2$(g) + 11H$_2$O(l) + $5.65 \times 10^3$ kJ
(b) $-82.5$ kJ
30. $-747.6$ kJ/mol
34. (b) about $-6800$ kJ/mol

Unit 8

Chapter 18
1. (a) Zn(s) + 2AgNO$_3$(aq) → Zn(NO$_3$)$_2$(aq) + 2Ag(s)
(b) $3\text{CoBr}_2$(aq) + $2\text{Al}(s) \rightarrow 3\text{Co(s)} + 2\text{AlBr}_3$(aq)
(c) $\text{Cd}(s) + \text{SnCl}_2$(aq) → $\text{CdCl}_2$(aq) + $\text{Sn}(s)$
2. (a) Zn(s) + 2Ag$^+$ (aq) + 2NO$_3^-$ (aq) → Zn$^{2+}$ (aq) + $2\text{Ag(s)}$
Zn(s) + Ag$^+$ (aq) → Zn$^{2+}$ (aq) + $2\text{Ag(s)}$
(b) $3\text{Co}^{2+}$(aq) + $6\text{Br}^-$ (aq) + $2\text{Al}(s) \rightarrow 3\text{Co}^{3+}$(aq) + $2\text{Al}^{3+}$ (aq) + $6\text{Br}^-$ (aq)
(b) $3\text{Co}^{2+}$(aq) + $2\text{Al}(s) \rightarrow 3\text{Co}^{3+}$(aq) + $2\text{Al}^{3+}$ (aq)
(c) $\text{Cd}(s) + \text{Sn}^{2+}$(aq) + $2\text{Cl}^-$ (aq) → $\text{Cd}^{2+}$(aq) + $2\text{Cl}^-$ (aq) + $\text{Sn}(s)$

3. (a) oxidizing agent: Ag$^+$; reducing agent: Zn
(b) oxidizing agent: Co$^{2+}$; reducing agent: Al
(c) oxidizing agent: Sn$^{2+}$; reducing agent: Cd

4. (a) oxidation half-reaction: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$
reduction half-reaction: $\text{Ag}^+ + e^- \rightarrow \text{Ag}$
(b) oxidation half-reaction: $\text{Al} \rightarrow \text{Al}^{3+} + 3e^-$
reduction half-reaction: $\text{Co}^{2+} + 2e^- \rightarrow \text{Co}$
(c) oxidation half-reaction: $\text{Cd} \rightarrow \text{Cd}^{2+} + 2e^-$
reduction half-reaction: $\text{Sn}^{2+} + 2e^- \rightarrow \text{Sn}$

5. (a) metallic element
(b) non-metallic element
(c) non-metallic element
(d) metallic element

6. (a) Ba = +2; Cl = −1
(b) C = +4; S = −2
(c) Xe = +4; F = −1
7. (a) Ba + 2; H – 1  (f) S 0
(b) Al + 3; C – 4  (g) As + 3; O – 2
(c) K + 1; C + 2; N – 3  (h) V + 5; O – 2
(d) Li + 1; N + 3; O – 2  (i) Xe + 6; O – 2; F – 1
(e) N – 3; H + 1; C + 3; O – 2  (j) S + 2.5; O – 2
8. ClO$_2^-$
9. (a) yes; oxidizing agent: O$_2$; reducing agent: CuH$_6$
    (b) no
(c) yes; oxidizing agent: I$_2$; reducing agent: H$_2$
(d) yes; oxidizing agent: KMnO$_4$; reducing agent: CuCl.
10. (a) yes; Cu undergoes oxidation; Ag$^+$ undergoes reduction.
    (b) no
(c) yes; Mn$^{2+}$ undergoes oxidation; BiO$_3^-$ undergoes reduction.
11. (a) $+5$ in VO$_2$$^+$, VO$_2$$^+$, VO$_3$$^-$, VO$_4$$^{3-}$; $+4$ in VO$_2$, VO$_3$$^+$
    (b) no
12. (a) all three steps
    (b) Step 1: oxidizing agent: O$_2$; reducing agent: NH$_3$
    Step 2: oxidizing agent: O$_2$; reducing agent: NO
    Step 3: oxidizing agent: NO$_2$; reducing agent: NO$_2$
14. (a) I$_2 + 2e^-$ → 2I$^-$
    (b) PbO → Pb$^{4+}$ + 4e$^-$
    (c) AuCl$_4^-$ + 3e$^-$ → Au + 4Cl$^-$
    (d) C$_2$H$_5$OH + H$_2$O → CH$_3$COOH + 4H$^+$ + 4e$^-$
    (e) S$_8$ + 16H$^+$ + 16e$^-$ → 8H$_2$S
    (f) AsO$_2^-$ + 4OH$^-$ → AsO$_3^{2-}$ + 2H$_2$O + 2e$^-$
15. (a) MnO$_2$ + 2Cl$^-$ + 4H$^+$ → Mn$^{2+}$ + Cl$_2$ + 2H$_2$O
    (b) 2NO + 3Sn + 6H$^+$ → 2NH$_3$OH + 3Sn$^{2+}$
    (c) 3Cd$^{2+}$ + 2V$^{2+}$ + 6H$_2$O → 3Cd + 2VO$_3$$^-$ + 12H$^+$
    (d) 2Cr + 6H$_2$O + 2OH$^-$ → 2Cr(OH)$_3^-$ + 3H$_2$
    (e) S$_2$O$_3^{2-}$ + 2NiO$_2$ + H$_2$O + 2OH$^-$ → 2Ni(OH)$_2$ + 2SO$_4^{2-}$
    (f) 2Sn$^{2+}$ + O$_2$ + 2H$_2$O → 2Sn$^{4+}$ + 4OH$^-$
16. (a) 3SiCl$_4$ + 4Al → 3Si + 4AlCl$_3$
    (b) 4PH$_3$ + 8O$_2$ → P$_2$O$_10$ + 6H$_2$O
    (c) I$_2$O$_5$ + 5CO → I$_2$ + 5CO$_2$
    (d) 2SO$_4^{2-}$ + O$_2$ → 2SO$_3^{2-}$
17. (a) 2NO$_2$ + H$_2$O → NO$_2^-$ + NO$_3^-$ + 2H$^+$
    (b) Cl$_2$ + 2OH$^-$ → ClO$^-$ + Cl$^-$ + H$_2$O
18. (a) 2Co$^{3+}$ + Cd → 2Co$^{2+}$ + Cd$^{2+}$
    2Co(NO$_3$)$_3^{3+}$ [aq] + Cd$_{[s]}$ → 2Co(NO$_3$)$_3^{2+}$ [aq] + Cd(NO$_3$)$_2^{2+}$ [aq]
    2Ag$^{+}$ + SO$_2$ + 2H$_2$O → 2Ag$^{+}$ + SO$_4^{2-}$ + 4H$^+$
    2AgNO$_3^{2+}$ [aq] + SO$_2$ [g] + 2H$_2$O[$l$] → 2Ag$_{[s]}$ + H$_2$SO$_4$ [aq] + 2HNO$_3$ [aq]
    (c) Al + CrO$_4^{2-}$ + 4H$_2$O → Al(OH)$_3$ + Cr(OH)$_3$ + 2OH$^-$
    Al$_{[s]}$ + Na$_2$CrO$_4$ [aq] + 4H$_2$O [l] → Al(OH)$_3$ [s] + Cr(OH)$_3$ [s] + 2NaOH [aq]
21. O$_2$ + 2F$_2$ → 2OF$_2$
22. (a) 2P$_4$ + 12H$_2$O → 5P$_3$H$_4$ + 3H$_3$PO$_4$
    (b) reduced
23. (a) 2Al + Fe$_2$O$_3$ → 2Fe + Al$_2$O$_3$
    (b) yes; oxidizing agent: Fe$_2$O$_3$; reducing agent: Al
24. (a) I$_2$ + 10HNO$_3$ → 2HIO$_3$ + 10NO$_2$ + 4H$_2$O
    (b) 31.7 g
27. (a) P$_4$ + 3H$_2$O + 3OH$^-$ → 3H$_3$PO$_2^-$ + PH$_3$
    (c) 2.74 kg
32. (a) C$_2$H$_4$ + H$_2$ → C$_2$H$_6$
    C$_2$H$_6$OH → CH$_3$CHO + H$_2$
33. (a) Na + 1; Al + 3; O – 2; H + 1; C + 4
    (b) NaAl(OH)$_3CO_3$ + 4HCl → NaCl + AlCl$_3$ + 3H$_2$O + CO$_2$
34. (a) 2KClO$_3$ → 2KCl + 3O$_2$
    S + O$_2$ → SO$_2$
    (b) oxidizing agent and reducing agent: KClO$_3$;
    oxidizing agent: O$_2$; reducing agent: S
35. NH$_4^+$ + 2O$_2$ → NO$_3^-$ + H$_2$O + 2H$^+$
36. (b) CaC$_2$ + 2H$_2$O → Ca(OH)$_2$ + C$_2$H$_2$; not redox
    (c) 2C$_2$H$_2$ + 5O$_2$ → 4CO$_2$ + 2H$_2$O; redox

Chapter 19
2. Mg$_{[s]}$ | Mg$^{2+}$ [aq] (1 mol/L) || Cd$^{2+}$ [aq] (1 mol/L) | Cd$_{[s]}$
3. oxidation: NO$_3^-$ + 2H$_2$O$_2$ → NO$_3^-$ [aq] + 4H$^+$ + 3e$^-$
    reduction: I$_2$[s] + 2e$^-$ → 2I$_{-}$[aq]
    overall: 2NO$_3^-$ + 4H$_2$O$_2$(l) + 3I$_2$(s) → 2NO$_3^-$ [aq] + 8H$^+$ + 6I$^-$[aq]
6. spontaneous: N$_2$O$_3$(aq) + 2H$^+$[aq] + 2Ce$^{4+}$[aq] + 2I$_{-}$[aq] →
    N$_2$O$_5$(aq) + 2H$_2$O(l) + Ce$^{3+}$[aq] + 2I$_3$(aq)
    non-spontaneous: N$_2$O$_3$(aq) + 2H$_2$O(l) + 2Ce$^{3+}$[aq] →
    N$_2$O$_5$(aq) + 2H$^+$[aq] + 2Ce$^{4+}$[aq] + 2I$_{-}$[aq] $E^\circ$cell = 1.955 V
7. (a) oxidizing agent: PbO$_2$; reducing agent: Pb
    (b) oxidizing agent: PbSO$_4$; reducing agent: PbSO$_4$
8. Co$^{3+}$[aq], Br$^-$(aq), H$^+$[aq], Zn$^{2+}$[aq]
9. Al$^{[s]}$, H$_2$[g], Ag$^{[s]}$, Cl$^-$(aq)
11. (a) oxidation: Zn$_{[s]}$ → Zn$^{2+}$[aq] + 2e$^-$
    reduction: Fe$^{3+}$[aq] + 2e$^-$ → Fe$^{[s]}$
    cell potential: 0.315 V; spontaneous
    (b) oxidation: Cr$_{[s]}$ → Cr$^{3+}$[aq] + 3e$^-$
    reduction: Al$^{3+}$[aq] + 3e$^-$ → Al$_{[s]}$
    cell potential: –0.918 V; non-spontaneous
(c) oxidation: H$_2$O$_2$(aq) → 2H$^+$[aq] + O$_2$[g] + 2e$^-$
    reduction: Ag$^{[s]}$ + e$^-$ → Ag$^{[s]}$
    cell potential: 0.105 V; spontaneous
12. 1.52 g
14. (a) $E^\circ$cell = 1.247 V
    oxidation: Fe$^{[s]}$ → Fe$^{3+}$[aq] + 2e$^-$
    reduction: Ag$^{[s]}$ + e$^-$ → Ag$^{[s]}$
    overall: Fe$_{[s]}$ + 2Ag$^{[s]}$ → Fe$^{2+}$[aq] + 2Ag$_{[s]}$
    (b) $E^\circ$cell = –1.247 V
17. The cost for Al would be 2.56 times the cost for Na.
Unit 8 Review

13. (a) +3
(b) +5
(c) +4
(d) N −3; H +1; S +6; O −2

14. no

15. (a) Ca(OH)₂(aq) + CO₂(g) → CaCO₃(s) + H₂O(l)
(b) TiO₂ + 4H⁺ + 2e⁻ → Ti²⁺ + 2H₂O
(c) I₂ + 18OH⁻ → 2H₂IO₆³⁻ + 6H₂O + 12e⁻

16. (a) Hg₂²⁺ + 2e⁻ → 2Hg
(b) TiO₂ + 4H⁺ + 2e⁻ → Ti²⁺ + 2H₂O
(c) I₂ + 18OH⁻ → 2H₂IO₆³⁻ + 6H₂O + 12e⁻

17. (a) 3Fe₃⁺ + 8HNO₃(aq) → 3Fe(NO₃)₂(aq) + 2NO(g) + 4H₂O(l)
(b) 3Fe(NO₃)₂(aq) + 4HNO₃(aq) → 3Fe(NO₃)₃(aq) + NO(g) + 2H₂O(l)
(c) 3Fe(s) + 12HNO₃(aq) → 3Fe(NO₃)₃(aq) + 3NO(g) + 6H₂O(l)

19. (a) 3Fe(s) + 8HNO₃(aq) → 3Fe(NO₃)₂(aq) + 2NO(g) + 4H₂O(l)
(b) 3Fe(NO₃)₂(aq) + 4HNO₃(aq) → 3Fe(NO₃)₃(aq) + NO(g) + 2H₂O(l)
(c) 3Fe(s) + 12HNO₃(aq) → 3Fe(NO₃)₃(aq) + 3NO(g) + 6H₂O(l)

20. (b) oxidation: 2I⁻ → I₂ + 2e⁻
   reduction: Ag⁺ + e⁻ → Ag
   overall: 2I⁻ + 2Ag⁺ → I₂ + 2Ag
   (d) 0.264 V

21. (a) no
   Cl₂O₇⁻ + H₂O → 2HClO₄
   (b) yes; oxidizing agent: ClO₄⁻; reducing agent: I₂
   3I₂ + 5ClO₄⁻ + 3H₂O → 6IO₃⁻ + 5Cl⁻ + 6H⁺
   (c) yes; oxidizing agent: Br₂; reducing agent: S₂⁻
   S²⁻ + 4Br₂ + 8OH⁻ → SO₄²⁻ + 8Br⁻ + 4H₂O
   (d) yes; oxidizing agent: HNO₃; reducing agent: H₂S
   2HNO₃ + 3H₂S → 2NO + 3S + 4H₂O

22. (a) −0.235 V; non-spontaneous
   (b) 0.698 V; spontaneous
   (c) 0.418 V; spontaneous

25. (a) 2MnO₄⁻ + 5C₂O₄²⁻ + 16H⁺ → 2Mn²⁺ + 10CO₂ + 8H₂O
   (b) 0.2249 mol/L

26. 20.72%

28. (a) 6
   (b) 3

29. (a) 2.68 × 10⁴ C
   (b) 74.4 h

30. 1.16 g

31. 0.595 t

43. (a) 8Al + 3NH₄ClO₄ → 4Al₂O₃ + 3NH₄Cl
   oxidizing agent: NH₄ClO₄; reducing agent: Al
   (b) 2H₂(g) + O₂(g) → 2H₂O(g)
Appendix B

Supplemental Practice Problems

Chapter 1

1. Label each as either a physical or a chemical property.
   (a) The boiling point of water is 100˚C.
   (b) Chlorine gas reacts violently with sodium metal.
   (c) Bromine has a brown color.
   (d) Sulfuric acid causes burns when it comes in contact with skin.

2. How many significant digits are in the following quantities?
   (a) 624 students
   (b) 22.40 mL of water
   (c) 0.00786 g of platinum

3. Characterize each of the following occurrences as a physical or as a chemical change.
   (a) sugar is heated over a flame and caramelises (turns black)
   (b) blood clots
   (c) a rubber band is stretched until it snaps
   (d) a match burns
   (e) a grape is crushed
   (f) salt is put on the roads in the winter, melting the ice.

4. Name each of the following ionic compounds.
   (a) MgCl₂
   (b) Na₂O
   (c) FeCl₃
   (d) CuO
   (e) AlBr₃

5. Write the chemical formula for each of the following compounds.
   (a) aluminum bromide
   (b) magnesium oxide
   (c) sodium sulfide
   (d) iron(II) oxide
   (e) copper(II) chloride

6. Write the formula for each of the following compounds.
   (a) sodium hydrogen carbonate
   (b) potassium dichromate
   (c) sodium hypochlorite
   (d) lithium hydroxide
   (e) potassium permanganate

7. Name each of the following compounds.
   (a) K₂Cr₂O₇
   (b) NH₄NO₃
   (c) Na₂SO₄
   (d) KH₂PO₄
   (e) Sr₃(PO₄)₂

8. Name each of the following covalent compounds.
   (a) Cl₂O₂
   (b) H₂O
   (c) BF₃
   (d) N₂O₄
   (e) N₂O

9. Write the formula for each of the following compounds.
   (a) tetraphosphorus decoxide
   (b) nitrogen trichloride
   (c) sulfur tetrafluoride
   (d) xenon hexafluoride

10. Balance each of the following skeleton equations.
    Classify each chemical reaction.
    (a) Fe + Cl₂ → FeCl₂
    (b) FeCl₂ + Cl₂ → FeCl₃
    (c) C₂H₅OH + O₂ → CO₂ + H₂O
    (d) Al + H₂SO₄ → Al₂(SO₄)₃ + H₂
    (e) N₂O₃ + H₂O → HNO₃
    (f) (NH₄)₂CO₃ → NH₃ + CO₂ + H₂O

11. Balance the following chemical equation.
    BiCl₃ + NH₃ + H₂O → Bi(OH)₃ + NH₄Cl

12. Balance the equation.
    NiSO₄ + NH₃ + H₂O → Ni(NH₃)₆(OH)₂ + (NH₄)₂SO₄

Unit 1

Chapter 2

    (a) How many protons and neutrons are in each isotope?
    (b) If Ga-69 exists in 60.0% relative abundance, estimate the average atomic mass of gallium using the mass numbers of the isotopes.

14. Rubidium exists as two isotopes: Rb-85 has a mass of 84.9117 u and Rb-87 has a mass of 86.9085 u. If the average atomic mass of rubidium is 85.4678, determine the relative abundance of each isotope.

15. You have 10 mL of isotopically labelled water, ³H₂O. That is, the water is made with the radioactive isotope of hydrogen, tritium, ³H. You pour the 10 mL of tritium-labelled water into an ocean and allow it to thoroughly mix with all the bodies of water on the earth. After the tritium-labelled water mixes thoroughly with the earth’s ocean water, you remove 100 mL of ocean water. Estimate how many molecules of ³H₂O will be in this 100 mL sample. (Assume that the average depth of the ocean is 5 km. The earth’s surface is covered roughly two-thirds with water. The radius of the earth is about 6400 km.)

16. Calculate the molar mass of each of the following compounds.
    (a) Al₂(CrO₃)₃
    (b) C₆H₃SiCl₃ (n-butyltrichlorosilane, an intermediate in the synthesis of silicones)
    (c) Cd[ClO₄]₂·2H₂O (cadmium chlorate dihydrate, an oxidizing agent)

17. How many atoms are contained in 3.49 moles of manganese?

18. How many atoms are there in 8.56 g of sodium?

19. What is the mass of 5.67 × 10²³ molecules of pentane, C₅H₁₂?
20. Consider a 23.9 g sample of ammonium carbonate, \((\text{NH}_4)_2\text{CO}_3\).
   (a) How many moles are in this sample?
   (b) How many formula units are in this sample?
   (c) How many atoms are in this sample?

21. One litre of a certain gas has a mass of 2.05 g at STP. What is the molar mass of this gas?

Chapter 3

22. Pyridine, \(\text{C}_5\text{H}_5\text{N}\), is a slightly yellow liquid with a nauseating odour. It is flammable and toxic by ingestion and inhalation. Pyridine is used in the synthesis of vitamins and drugs, and has many other uses in industrial chemistry. Determine the percentage composition of pyridine.

23. Bromine azide is an explosive compound that is composed of bromine and nitrogen. A sample of bromine azide was found to contain 2.35 g Br and 1.24 g N.
   (a) Calculate the percentage by mass of Br and N in bromine azide.
   (b) Calculate the empirical formula of bromine azide.
   (c) The molar mass of bromine azide is 122 g/mol. Determine its molecular formula.

24. Progesterone is a female hormone. It is 80.2% C, 9.62% H and 10.2% O by mass.
   (a) Determine the empirical formula of progesterone.
   (b) From the given data, is it possible to determine the molecular formula of progesterone? Explain your answer.

25. Potassium tartrate is a colourless, crystalline solid. It is 34.6% K, 21.1% C, 1.78% H, 42.4% O by mass.
   (a) Calculate the empirical formula of potassium tartrate.
   (b) If the molar mass of potassium tartrate is 226 g/mol, what is the molecular formula of potassium tartrate?

26. Menthol is a compound that contains C, H and O. It is derived from peppermint oil and is used in cough drops and chest rubs. When 0.2393 g of menthol is subjected to carbon-hydrogen combustion analysis, 0.6735 g of CO\(_2\) and 0.2760 g of H\(_2\)O are obtained.
   (a) Determine the empirical formula of menthol.
   (b) If each menthol molecule contains one oxygen atom, what is the molecular formula of menthol?

27. Glycerol, \(\text{C}_3\text{H}_8\text{O}_3\), also known as glycerin, is used in products in claim to protect and soften skin. Glycerol can be purchased at the drug store. If 0.784 g of glycerol is placed in a carbon-hydrogen combustion analyzer, what mass of CO\(_2\) and H\(_2\)O will be expected?

28. Calculate the percentage by mass of water in potassium sulfite dihydrate, \(\text{K}_2\text{SO}_3 \cdot 2\text{H}_2\text{O}\).

29. What mass of water is present in 24.7 g of cobaltous nitrate hexahydrate, \(\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}\)?

30. A chemist requires 1.28 g of sodium hypochlorite, NaOCl, to carry out an experiment, but only has sodium hypochlorite pentahydrate, \(\text{NaOCl} \cdot 5\text{H}_2\text{O}\) in the lab. How many grams of the hydrate should the chemist use?

31. A compound was found to contain 54.5% carbon, 9.10% hydrogen, and 36.4% oxygen. The vapour from 0.082 g of the compound occupied 20.9 mL at STP.
   (a) Calculate the empirical formula of the compound.
   (b) Calculate the molecular mass of the compound.
   (c) Calculate the molecular formula of the compound.

Chapter 4

32. Consider the equation corresponding to the decomposition of mercuric oxide.
   \(2\text{HgO(s)} \rightarrow 2\text{Hg(l)} + \text{O}_2(\text{g})\)
   What mass of liquid mercury is produced when 5.79 g of mercuric oxide decomposes?

33. Examine the following equation.
   \(\text{C}_2\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})\)
   (a) What mass of propane, \(\text{C}_2\text{H}_8\), reacting with excess oxygen, is required to produce 26.7 g of carbon dioxide gas?
   (b) How many oxygen molecules are required to react with 26.7 g of propane?

34. Metal hydrides, such as strontium hydride, \(\text{SrH}_2\), react with water to form hydrogen gas and the corresponding metal hydroxide.
   \(\text{SrH}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Sr(OH)}_2(\text{s}) + 2\text{H}_2(\text{g})\)
   (a) What mass of strontium hydride is reacted with 8.03 \times 10^{22} molecules of water, what is the limiting reagent?
   (b) What mass of strontium hydroxide will be produced?

35. Consider the following successive reactions.
   reaction (1): \(\text{A} \rightarrow \text{B}\)
   reaction (2): \(\text{B} \rightarrow \text{C}\)
   If reaction (1) proceeds with a 45% yield and reaction (2) has a 70% yield, what is the overall yield for the reactions that convert A to C?

36. Disposable cigarette lighters contain liquid butane, \(\text{C}_4\text{H}_{10}\). Butane undergoes complete combustion to carbon dioxide gas and water vapour according to the skeleton equation below:
   \(\text{C}_4\text{H}_{10}(\text{l}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})\)
   A particular lighter contains 5.00 mL of butane, which has a density of 0.579 g/mL.
   (a) How many grams of \(\text{O}_2\) are required to combust all of the butane?
   (b) How many molecules of water will be produced?
   (c) Air contains 21.0% \(\text{O}_2\) by volume. What mass of air is required to combust 5.00 mL of butane?
37. If the following reaction proceeds with a 75% yield, how much diborane, \( B_2H_6 \), will be produced when 23.5 g of sodium borohydride, \( NaBH_4 \) reacts with 50.0 g of boron trifluoride, \( BF_3 \)?

\[
NaBH_4(s) + BF_3(g) \rightarrow 2B_2H_6(g) + 3NaF(s)
\]

38. Drinking a solution of baking soda (sodium hydrogen carbonate, \( NaHCO_3 \)) can neutralize excess hydrochloric acid in the stomach in water. A student stirred 5.0 g of baking soda in water and drank the solution, then calculated the size of “burp” expected from the carbon dioxide generated in the following reaction.

\[
NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)
\]

What volume of carbon dioxide will be generated at STP?

39. Examine the reaction below and answer the following questions.

\[
C_2H_6(g) + 11O_2(g) \rightarrow 7CO_2(g) + 8H_2O(g)
\]

(a) if 10.0 L of \( C_2H_6(g) \) at STP are burned, what volume of oxygen gas at STP is required?
(b) if 200 g of \( CO_2 \) are formed, what mass of \( C_2H_6(g) \) was burned?
(c) if 200 L of \( CO_2 \) are formed, measured at STP, what mass of oxygen was consumed?

Unit 2

Chapter 5

40. Draw Lewis structures to represent each of the following atoms.
(a) Mg  
(b) B  
(c) K
(d) C  
(e) Ne  
(f) Al

41. Draw Lewis structures to represent each of the following ions.
(a) \( H^+ \)  
(b) \( K^+ \)  
(c) \( Br^- \)
(d) \( S^{2-} \)  
(e) \( Al^{3+} \)  
(f) \( Mg^{2+} \)

42. Draw Lewis structures to represent each of the following ionic compounds.
(a) KBr  
(b) MgCl_2  
(c) CaO
(d) Mg_3N_2  
(e) Na_2O  
(f) AlBr_3

43. Draw Lewis structures to represent each of the following molecular compounds.
(a) \( I_2 \)  
(b) \( CO_2 \)  
(c) NO
(d) N_2

44. Use Lewis structures to predict the correct formulas for the following.
(a) potassium iodide  
(b) magnesium sulfide  
(c) calcium chloride  
(d) lithium fluoride  
(e) barium chloride  
(f) cesium bromide

45. Determine the \( \Delta EN \) for each of the following pairs or atoms.
(a) carbon and nitrogen  
(b) silver and iodine  
(c) manganese and oxygen  
(d) hydrogen and iodine  
(e) copper and oxygen  
(f) hydrogen and sulfur

46. For each of the pairs of atoms in question 6, state whether a bond between them will be mostly ionic, polar covalent, slightly polar covalent, or non-polar covalent.

47. For each of the following bonds, indicate which will be polar or non-polar. For the polar bonds, use arrows above the symbols to indicate the direction of the polarity.
(a) \( B — F \)  
(b) \( Na — I \)  
(c) \( Si — O \)  
(d) \( N — H \)  
(e) \( O — O \)  
(f) \( Cl — F \)

48. List six pairs of atoms that will have polar covalent bonds between them.

49. Arrange the following bonds in order of decreasing polarity:
hydrogen—nitrogen, calcium—chlorine, nitrogen—nitrogen, magnesium—oxygen, hydrogen—sulfur

50. List the following bonds in order of increasing bond energy.
C — O, C == C, H — H, C == C, Si — H

51. List the bonds in question 50 in order of decreasing length.

52. How do the orders you listed in questions 50 and 51 compare?

Chapter 6

53. Draw Lewis structures of the following compounds.
(a) \( CH_3COOH \)  
(b) \( N_2O \)  
(c) \( SO_4Cl_2 \)  
(d) \( XeO_2F_2 \)  
(e) \( NO_2^- \)  
(f) \( C_2H_2 \)

54. Use VSEPR theory to determine the shape of each molecule in question 53. For part (a), state the shape around the central carbon atom.

55. Which compound(s) in questions 53 has resonance structures?

56. Which of the compounds in question 53 are polar?

57. When the iodide ion is in a solution of iodine, triiodide ion forms. Draw the Lewis structure for \( I_3^- \).

58. Determine the shape of the sulfate, \( SO_4^- \), and sulfite, \( SO_3^- \), ions.

59. The amide linkage that holds amino acids together in proteins creates a rigid structure. Construct a Lewis diagram and determine the shape around the carbon atom and the nitrogen atom in an amide linkage, \( H_2C(O)NH_2 \).

60. Draw Lewis structures for \( CO_2 \), \( NO^+ \), \( CN^- \), \( N_2 \).

State any similarities among these compounds.
61. Draw a Lewis structure for urea, H₂NCO(NH₂). State whether it is a polar molecule.

62. Compare the molecules CH₃F and NH₂F with respect to their
   (a) Lewis structures
   (b) dispersion forces
   (c) hydrogen bonding

63. Determine the shape of the phosphate, PO₄³⁻, and hydrogen phosphate, HPO₄²⁻, ions. Which, if any, of the ions is polar?

Unit 3

Chapter 7

64. How many litres of solution are needed to accommodate 2.11 mol of 0.988 mol/L solute?

65. What volume of 2.00 mol/L hydrochloric acid is needed to react with 36.5 mL of 1.85 mol/L sodium hydroxide?

66. 2.68 L of 2.11 mol/L HCl reacts with 3.17 L of 2.28 mol/L NaOH. How many moles of NaCl are produced by this reaction?

67. Determine the final concentration when 1.50 L of 2.50 mol/L solution is diluted with 3.00 L of solvent. How is this concentration different if 1.50 L of 2.50 mol/L solution is diluted to 3.00 L with solvent?

68. What is the molar concentration of the solution made by dissolving 1.00 g of solid sodium nitrate, NaNO₃, in enough water to make 315 mL of solution?

69. What volume of 4.00 × 10⁻² mol/L calcium nitrate solution, Ca(NO₃)₂(aq), will contain 5.0 × 10⁻² mol of nitrate ions?

70. By the addition of water, 80.0 mL of 4.00 mol/L sulfuric acid, H₂SO₄, is diluted to 400.0 mL. What is the molar concentration of the sulfuric acid after dilution?

71. How many moles of NaOH are in 100.0 mL of 0.00100 mol/L NaOH solution?

72. If a burette delivers 20 drops of solution per 1.0 mL, how many moles of HCl(aq) are in one drop of a 0.20 mol/L HCl solution?

73. What is the mass percent concentration of nicotine in the body of a 70 kg person who smokes a pack of cigarettes (20 cigarettes) in one day? Assume that there is 1.0 mg of nicotine per cigarette, and that all the nicotine is absorbed into the person’s body.

74. Ozone is a highly irritating gas that reduces the lung capability of healthy people in concentrations as low as 0.12 ppm. Older photocopy machines could generate ozone gas and they were often placed in closed rooms with little air circulation. Calculate the volume of ozone gas that would result in a concentration of 0.12 ppm in a room with dimensions of 5.0 m × 4.0 m × 3.0 m.

75. Human blood serum contains about 3.4 g/L of sodium ions. What is the molar concentration of Na⁺ in blood serum?

Chapter 8

76. A student makes a solution by adding 55.0 mL of 1.77 mol/L sodium chloride to 105 mL of 0.446 mol/L calcium chloride, and diluting the solution to 200.0 mL. Determine the concentration of each ion in the solution.

77. What is the total concentration of all the ions in each of the solutions listed below?
   (a) 2.600 mol/L, NaCl
   (b) 1.20 mol/L, Mg(ClO₃)₂
   (c) 10.3 g of (NH₄)₂SO₃ in 420 mL of solution

78. Complete the following reaction by writing a balanced equation. Then write the total ionic equation and net ionic equation for the reaction, and identify the spectator ions.
   CaCl₂(aq) + Cs₃PO₄(aq)

79. Complete the following reaction by writing a balanced equation. Then write the total ionic equation and net ionic equation for the reaction, and identify the spectator ions.
   Na₂S₄(aq) + ZnSO₄(aq)

80. When 25.0 mL of silver nitrate solution reacts with excess potassium chloride solution, a precipitate with a mass of 0.842 g results. Determine the molar concentration of silver ion in the original silver nitrate solution.

81. For each of the following, predict whether a reaction will occur. If it does, write a balanced chemical equation, the total ionic equation, and the net ionic equation, and identify the spectator ions. Assume all the reactions occur in aqueous solution.
   (a) ammonium perchlorate + sodium bromide
   (b) sodium hydroxide and cadmium nitrate

82. Solid iron reacts with aqueous iron(III) chloride to produce aqueous iron(II) chloride. Write the net ionic equation for this reaction.

83. When ammonium sulfide reacts with each of the following substances in aqueous solution, an insoluble sulfide precipitate results. Write a net ionic equation for each.
   (a) zinc chloride
   (b) copper(II) chloride
   (c) manganese(II) chloride

84. Consider the following net ionic equation:
   2H⁺(aq) + CO₃²⁻(aq) → H₂O(l) + CO₂(g)
   Write five balanced chemical equations that result in this net ionic equation.

85. Write the net ionic equation for the reaction between aqueous solutions of barium chloride and sodium sulfate. Be sure to include the state of each reactant and product.
86. Write the net ionic equation for the reaction between aqueous sodium hydroxide and aqueous nitric acid. Be sure to include the state of each reactant and product.

87. What are the spectator ions when solutions of Na₂SO₄ and Pb(NO₃)₂ are mixed?

88. Iron(II) sulfate reacts with potassium hydroxide in aqueous solution to form a precipitate.
   (a) What is the net ionic equation for this reaction?
   (b) Which ions are spectator ions?

89. Write the balanced molecular and net ionic equations for the following reactions:
   (a) Na₃PO₄(aq) + Ca(OH)₂(aq) → NaOH(aq) + Ca₃(PO₄)₂(s)
   (b) Zn(s) + Fe₂(SO₄)₃(aq) → ZnSO₄(aq) + Fe(s)

90. Name each of the following hydrocarbons.
   (a) \( \text{CH}_3\text{CH}==\text{CH}_2\text{CH}_2\text{CH}_3 \)
   (b) \( \text{CH}_3\text{CH}==\text{CH}_2\text{CH}_2\text{CH}2\text{CH}_2\text{CH}_3 \)
   (c) \( \text{CH}_3\text{CH}==\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)
   (d) \( \text{CH}_3\text{CH}==\text{CH}_2\text{CH}_2\text{CH}2\text{CH}_2\text{CH}_3 \)
   (e) \( \text{CH}_3\text{CH}==\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}2\text{CH}_3 \)
   (f) \( \text{CH}_3\text{CH}==\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)

91. Draw condensed structural diagrams for each of the following compounds.
   (a) 2,5-dimethylhexane
   (b) 2-ethyl-5-methylhexane
   (c) 2,3,4-trimethylpentane
   (d) 2,2,3-trimethyl-4-propylpentane
   (e) 3-ethyl-2,4,6-trimethyl-5-propynonane

92. Use each incorrect name to draw the corresponding hydrocarbon. Examine your drawing and rename the hydrocarbon correctly.
   (a) 2-ethyl-3,3-dimethyl-4-propylpentane
   (b) 2,3-dimethyl-3-butylpropane
   (c) 1-ethyl-4-methylbutane
   (d) 2,4-dibutylpentane

93. Write a balanced equation for the complete combustion of 3-ethyl-2,2,5-trimethylheptane.

94. Write two possible, correct equations for the following reaction:
   \( \text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{Cl} \rightarrow \text{UV} \)

95. Name the following compounds.
   (a)
   (b)
   (c)
   (d)
   (e)
   (f)
   (g)
   (h)

96. Examine the following compounds. Correct any flaws that you see in the structural diagrams.
   (a) Is this compound 4-ethyl-2-methylpentane?

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826 MHR • Appendix B
97. Draw condensed structural diagrams for each of the following compounds.
(a) 2-ethyl-1-pentene
(b) 2,6-dimethyl-3-nonene
(c) 2,5-dimethyl-3-hexyne
(d) 2-butyl-3-ethyl-1-cyclobutene
(e) 1-butyl-3-propyl-cyclooctene
(f) 1,3,5-triethyl-2-cyclohexane

98. Name each compound.
(a) CH₃
(b) CH₂═CH—CH₂—CH₃
(c) CH₃—CH₂—CH═CH₂
(d) CH₃—CH₂—CH₂—CH₂—CH₃
(e) CH₂═CH—CH₂—CH₂—CH₃

99. Draw and name the products of each reaction.
(a) CH₃ — C═C — CH₂ — CH₃ + Br₂ →
(b) 1-methylcyclopentene + H₂ →
(c) CH₃(CH₂)₂CH = CH₂ + Cl₂ →
(d) 1,3-dimethylcyclobutene + HCl →

100. Name the following compounds.
(a) CH₂═CH—CH₂—CH₃
(b) CH₃
(c) CH₂═CH—CH₂—CH₃
(d) CH₂═CH—CH₂—CH₃

101. Draw and name the reactants for the following reactions.
(a) ? + ? FeBr₃ → Cl + HCl
(b) ? + ? → NO₂ + H₂
(c) ? + ? → Cl + Br
(d) ? + ? → OH
(e) ? + ? → Br

Chapter 10

102. Identify the type of reaction.
(a) CH₃CH₂OH → CH₂ = CH₂ + H₂O
(b) CH₃CH₂CH₂CH₂OH + HBr → CH₃CH₂CH₂CH₂Br + HOH
(c) CH₃CH₂CH(OH)CH₃ → CH₃CH₂CH = CH₂ + H₂O
(d) CH₃CH₂CH(Br)CH₃ + OH⁻ → CH₃CH₂CH = CH₂ + H₂O + Br⁻
103. Name the compounds.
(a) \[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array}
\begin{array}{c}
\text{CH} \\
\text{CH}
\end{array}
\begin{array}{c}
\text{CH} \\
\text{CH}
\end{array}
\begin{array}{c}
\text{CH} \\
\text{CH}
\end{array}
\begin{array}{c}
\text{CH} \\
\text{CH}
\end{array}
\begin{array}{c}
\text{CH}_3
\end{array}
\]
(b) \[
\begin{array}{c}
\text{OH}
\end{array}
\]
(c) \[
\begin{array}{c}
\text{CH}_2 \\
\text{CH}_2
\end{array}
\begin{array}{c}
\text{CH} \\
\text{CH}
\end{array}
\begin{array}{c}
\text{CH}_3
\end{array}
\]
(d) \[
\begin{array}{c}
\text{OH}
\end{array}
\]

104. Draw a condensed structural diagram for each compound.
(a) 1,3-difluoro-4-methyl-1-pentyne
(b) trans-7,7-dimethyl-1-octene
(c) 2,3,4-trichloropentane
(d) 3-methylcyclopentanol
(e) ethoxy pentane
(f) dichloromethane

105. Draw and name the products of the following reactions.
(a) 3-methyl-5-chlorononane + OH$^-$ →
(b) 4-ethyl-3-octanol + HBr →
(c) 3-nonanol

106. Name the compounds.
(a) \[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array}
\begin{array}{c}
\text{CH} \\
\text{CH}
\end{array}
\begin{array}{c}
\text{CH} \\
\text{CH}
\end{array}
\begin{array}{c}
\text{CH} \\
\text{CH}
\end{array}
\begin{array}{c}
\text{CH}_3
\end{array}
\]
(b) \[
\begin{array}{c}
\text{CH}_2 \\
\text{CH}_2
\end{array}
\begin{array}{c}
\text{CH} \\
\text{CH}
\end{array}
\begin{array}{c}
\text{CH}_3
\end{array}
\]
(c) \[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array}
\begin{array}{c}
\text{CH} \\
\text{CH}
\end{array}
\begin{array}{c}
\text{NH}
\end{array}
\]
(d) \[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array}
\begin{array}{c}
\text{CH} \\
\text{CH}
\end{array}
\begin{array}{c}
\text{NH}_2
\end{array}
\]

107. Write a condensed structural diagram for each compound.
(a) cyclopentanamine
(b) N-butyl-N-ethyl-3-octanamine
(c) 2-ethoxy-2-heptane
(d) methoxy methane
(e) N,N-diethyl-1-hexanamine
(f) 2-butanimine

108. Classify the amines in #18 as primary, secondary, or tertiary.

109. Name the compounds.
(a) \[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array}
\begin{array}{c}
\text{CH} \\
\text{CH}
\end{array}
\begin{array}{c}
\text{CH} \\
\text{CH}
\end{array}
\begin{array}{c}
\text{CH}
\end{array}
\]
(b) \[
\begin{array}{c}
\text{O}
\end{array}
\]
(c) \[
\begin{array}{c}
\text{O}
\end{array}
\]
(d) \[
\begin{array}{c}
\text{O}
\end{array}
\]

110. Explain why the following compounds could not exist.
(a) 3-methyl-3-pentanone
(b) 2-methyl-1-butyne
(c) 3,3-diethyl-2-pentene
(d) 1-methyl propanal

111. Draw a condensed structural diagram of the compounds.
(a) 2,4,5-trimethyl octanal
(b) 3-methyl-2-butanone
(c) 2-ethyl-4,4-dimethyl-3-hexanone
(d) methanal

112. Name the compounds.
(a) \[
\begin{array}{c}
\text{HC} \\
\text{OH}
\end{array}
\]
(b) \[
\begin{array}{c}
\text{O}
\end{array}
\]
(c) \[
\begin{array}{c}
\text{O}
\end{array}
\]
(d) \[
\begin{array}{c}
\text{O}
\end{array}
\]

113. Write reactions for the following.
(a) synthesis of methyl pentanoate
(b) esterification of ethanol and propanoic acid
(c) hydrolysis of butyl butanoate
(d) esterification of 2-propanol and butyric acid
114. Draw a condensed structural diagram for each compound.
(a) N-ethyl-nonamamide
(b) hexanamide
(c) N-methyl propanamide
(d) N,N-dimethyl butanamide

115. Write the reaction, using names and condensed structural diagrams for the following reactions.
(a) acid hydrolysis of N-ethyl hexanamide
(b) base hydrolysis of N,N-dimethyl butanamide
(c) acid hydrolysis of N-propyl 2-methyl-pentanamide
(d) base hydrolysis of 3,3-dimethyl hexanamide

**Chapter 11**

116. Draw the monomers that were used to make the polymer shown here.

\[
\begin{array}{c}
\text{N} \\
\text{H} \\
\text{O} \\
\text{C} \\
\text{O}
\end{array}
\]

117. What is the name of the class of the polymer shown in #116?

118. Was the polymer in #116 an addition or condensation monomer?

119. Sketch three units of the polymer made from the structure shown here.

\[
\text{H}_2	ext{C} \rightarrow \text{CH}
\]

120. Was the polymer you sketched in #119 an addition or condensation polymer?

121. Sketch two units of the polymer formed by a reaction between the following.

\[
n\text{HO} \rightarrow \text{CH}_2-\text{CH}_2-\text{OH} + n\text{HO} \rightarrow \text{CH}_2-\text{CH}_2-\text{C}-\text{OH}
\]

122. What class of polymer did you sketch in #121?

123. Draw the monomer units that were used to make the polymer shown here.

\[
\begin{array}{c}
\text{N} \\
\text{CH}_2-\text{CH}_2-\text{N} \\
\text{CH}_2-\text{CH}_2-\text{C} \\
\text{OH}
\end{array}
\]

124. What class of polymer is shown in #121?

125. Sketch monomer units that could be used to make a polyester. What are the functional groups on the monomer units?

126. Sketch the type of bond that joins amino acids to make proteins.

**Unit 5**

**Chapter 12**

127. (a) Write the overall equation for the following two-step mechanism:
Step 1 \( \text{NO}_2(g) + \text{NO}_2(g) \rightarrow \text{NO}_3(g) + \text{NO}_3(g) \)
Step 2 \( \text{NO}_3(g) + \text{CO}_2(g) \rightarrow \text{NO}_2(g) + \text{CO}_2(g) \)
(b) If Step 1 is slow and Step 2 is fast, which is the rate-determining step?

128. For the equation \( 2\text{H}_2(g) + 2\text{NO}_2(g) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(g) \), a chemist proposes a three-step mechanism. Write Step 2 of this mechanism.
Step 1 \( \text{H}_2(g) + \text{NO}_2(g) \rightarrow \text{H}_2\text{O}(g) + \text{N}_2(g) \)
Step 2 ?
Step 3 \( \text{H}_2(g) + \text{O}_2(g) \rightarrow \text{H}_2\text{O}(g) \)

129. (a) Write the overall equation for the two-step mechanism below.
Step 1 \( \text{O}_3(g) + \text{NO}_2(g) \rightarrow \text{NO}_2(g) + \text{O}_2(g) \)
Step 2 \( \text{NO}_2(g) + \text{O}_2(g) \rightarrow \text{NO}_2(g) + \text{O}_2(g) \)
(b) Identify the reaction intermediates and the catalyst, if any.

130. A chemist proposes the following two-step mechanism:
Step 1 \( \text{NO}_3\text{Cl}(aq) \rightarrow \text{NO}_2\text{Cl}(aq) + \text{Cl}(g) \)
Step 2 \( \text{NO}_2\text{Cl}(aq) + \text{Cl}(g) \rightarrow \text{NO}_2(g) + \text{Cl}_2(g) \)
(a) Write the overall equation for this mechanism.
(b) Identify the rate-determining step if Step 1 is slow and Step 2 is fast.

131. A chemist proposes a three-step mechanism for the reaction
\( \text{Br}_2\text{(aq)} + \text{OCl}_2\text{(aq)} \rightarrow \text{BrOCl}_2\text{(aq)} + \text{BrCl}_2\text{(aq)} \)
Given Steps 2 and 3 below, write the mechanism for Step 1.
Step 1 ?
Step 2 \( \text{Br}(aq) + \text{OCl}_2\text{(aq)} \rightarrow \text{BrOCl}_2\text{(aq)} + \text{Cl}(aq) \)
Step 3 \( \text{Br}(aq) + \text{Cl}(aq) \rightarrow \text{BrCl}_2\text{(aq)} \)

132. (a) Write the overall balanced chemical equation for the following mechanism.
Step 1 \( \text{HOCl}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{HOCl}(aq) + \text{OH}^-(aq) \)
Step 2 \( \text{HOCl}(aq) + \Gamma(aq) \rightarrow \text{HOI}(aq) + \text{Cl}^-(aq) \)
Step 3 \( \text{HOCl}(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l) + \text{Cl}^-(aq) \)
(b) List the reaction intermediates and the catalyst, if any.

133. In the upper atmosphere, ozone decomposes in the presence of ultraviolet radiation. Nitric oxide, NO, is also a part of this process. A chemist proposes the following mechanism for this reaction:
Step 1 \( \text{O}_3(g) + \text{ultraviolet radiation} \rightarrow \text{O}_2(g) + \text{O}_3(g) \)
Step 2 \( \text{O}_2(g) + \text{NO}(g) \rightarrow \text{NO}_2(g) + \text{O}_3(g) \)
Step 3 \( \text{NO}_2(g) + \text{O}(g) \rightarrow \text{NO}_2(g) + \text{O}_3(g) \)
(a) What is the overall equation for this reaction?
(b) Identify the role played by ultraviolet radiation in this reaction.
134. Write the overall equation for the following mechanism:
\[ \text{O}_3(g) \rightarrow \text{O}_2(g) + \text{O} \]
\[ \text{O}_3(g) + \text{O}_3(g) \rightarrow 2\text{O}_2(g) \]

135. Write the missing step in this mechanism for the reaction 2\( \text{NO}_2(g) \) + \( \text{F}_2(g) \) → 2\( \text{NOF}_2(g) \) + \( \text{F}(g) \)

Step 1 \( \text{NO}_2(g) + \text{F}_2(g) \rightarrow \text{NOF}_2(g) + \text{F}(g) \)

Step 2 ?

136. Sketch a potential energy diagram, given the following criteria for a reaction: potential energy of the reactants = 200 kJ; potential energy of the activated complex = 300 kJ; potential energy of the products = 100 kJ. State whether the reaction is exothermic or endothermic.

137. Show how your potential energy diagram for the previous question would be different with the addition of a catalyst, and state the effect on the reactants, the activated complex, the products, and the reaction rate.

138. For the three reactions below, identify the reaction that has the fastest rate and the reaction that has the slowest rate. Assume all reactions take place at the same temperature.

(a) \( \text{2HCl(aq)} + \text{CaCO}_3(s) \rightarrow \text{CaCl}_2(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(l) \)

(b) \( \text{H}_2(g) + \text{I}_2(g) \rightarrow 2\text{HI}(g) \)

(c) \( \text{Na}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{NaCl}(s) \)

Chapter 13

139. For the following reaction at 963 K, \( K_c = 10.0 \): \( \text{CO}_2(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g) \)

State whether or not this system is at equilibrium when reactants and products have the following concentrations: \[ [\text{CO}_2(g)] = 2.0 \text{ mol/L}, \]
\[ [\text{H}_2\text{O}(g)] = 0.10 \text{ mol/L}, [\text{H}_2(g)] = 1.0 \text{ mol/L}, \]
\[ [\text{CO}_2] = 2.0 \text{ mol/L}. \]

140. A chemist places 0.300 mol of \( \text{Br}_2 \) and 0.600 mol of \( \text{Cl}_2 \) into a 3.00 L reaction vessel. At equilibrium at high temperature, 0.045 mol/L of \( \text{Br}_2 \) remain. Calculate \( K_c \) for this reaction.

\( \text{Br}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{BrCl}(g) \)

141. For the equation below, predict the direction in which the equilibrium will shift in response to the changes specified.

\( \text{CO}_2(g) + \text{H}_2\text{O}(g) + \text{energy} \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g) \)

(a) add water and decrease the temperature

(b) add a catalyst and remove carbon monoxide

(c) add hydrogen and water

(d) add carbon monoxide and increase the temperature

142. For the system \( \text{A} + 2\text{B} \rightleftharpoons \text{C} + \text{D} \), 2.00 mol of \( \text{A} \) and 2.00 mol of \( \text{B} \) are placed into a 2.00 L reaction vessel. When the system reaches equilibrium at a certain temperature, \( K_c = 4.00 \times 10^{-5} \). What is \( [\text{C}] \) at equilibrium?

143. For the reaction \( \text{FeSCN}^{2+}(aq) \rightleftharpoons \text{Fe}^{3+}(aq) + \text{SCN}^-(aq) \) at a certain temperature, \( K_c = 9.1 \times 10^{-4} \). Determine the concentrations of each species in a solution in which the initial concentration of \( \text{FeSCN}^{2+} \) is 1.5 mol/L.

144. At 400°C, \( K_c = 50.0 \) for the following reaction:

\( \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g) \)

A chemist places 0.0800 mol of \( \text{H}_2 \) and 0.0800 mol of \( \text{I}_2 \) in a 1.00 L reaction vessel. Calculate the concentration of \( \text{I}_2(g) \) at equilibrium.

145. Determine \( [\text{CO}_2] \) at equilibrium when 2.50 mol of \( \text{CO}_2(g) \) and 2.50 mol of \( \text{H}_2\text{O}(g) \) react in a 1.00 L vessel at a certain high temperature. \( K_c = 0.63 \) for this reaction.

\( \text{CO}_2(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g) \)

146. Consider the equilibrium below.

\( \text{S}_6(s) + 8\text{O}_2(g) \rightleftharpoons 8\text{SO}_2(g) + \text{heat} \)

What is the effect on the concentration of each substance when the equilibrium is altered as follows.

(a) More \( \text{S}_6(s) \) is added.

(b) The temperature is lowered.

(c) The volume of the container is increased.

(d) More \( \text{SO}_2 \) is injected into the system.

147. At 2000 K, the concentration of the components in the following equilibrium system are \[ [\text{CO}_2(g)] = 0.30\text{ mol/L}, [\text{H}_2(g)] = 0.20\text{ mol/L}, \]
\[ [\text{H}_2\text{O}(g)] = [\text{CO}_2(g)] = 0.55\text{ mol/L}. \]

\( \text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{H}_2\text{O}(g) + \text{CO}_2(g) \)

(a) What is the value of the equilibrium constant?

(b) When the temperature is lowered, 20.0% of the \( \text{CO}_2 \) is converted back to \( \text{CO}_2 \). Calculate the equilibrium constant at the lower temperature.

(c) Rewrite the equilibrium equation, and indicate on which side of the equation the heat term should be placed.

148. After 5.00 g of \( \text{SO}_2\text{Cl}_2 \) are placed in a 2.00 L flask, the following equilibrium is established.

\( \text{SO}_2\text{Cl}_2(g) \rightleftharpoons \text{SO}_2(g) + \text{Cl}_2(g) \)

\( K_c \) for this equilibrium is 0.0410. Determine the mass of \( \text{SO}_2\text{Cl}_2 \) that is present at equilibrium.

149. For the equilibrium below, \( K_c = 6.00 \times 10^{-2} \).

\( \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \)

Explain why this value of \( K_c \) does not apply when the equation is written as follows.

\( \frac{1}{2}\text{N}_2(g) + \frac{3}{2}\text{H}_2(g) \rightleftharpoons \text{NH}_3(g) \)

150. A 11.5 g sample of \( \text{I}_2(g) \) is sealed in a 250 mL flask. An equilibrium, shown below, is established as this molecular form of \( \text{I}_2 \) dissociates into iodine atoms.

\( \text{I}_2(g) \rightleftharpoons 2\text{I}(g) \)

\( K_c \) for the equilibrium is \( 3.80 \times 10^{-5} \). Calculate the equilibrium concentration of both forms of the iodine.

Unit 6

Chapter 14

151. A sample of lemon juice was found to have a pH of 2.50. What is the concentration of hydronium ions and hydroxide ions in the lemon juice?
152. What are the concentrations of hydronium and hydroxide ions in a solution that has a pH of 5?
153. What is the pH of a 1.0 × 10^{-5} mol/L Ca(OH)\(_2\)(aq)?
154. What is the pH of a solution in which 2.0 × 10^{-4} mol of HCl are dissolved in enough distilled water to make 300 mL of solution?
155. What is the pH of a solution containing 2.5 g of NaOH dissolved in 100 mL of water?
156. For each of the following reactions, identify the acid, the base, the conjugate base, and the conjugate acid:
   (a) HF(aq) + NH\(_3\)(aq) ⇄ NH\(_4\)\(^+\)(aq) + F\(^-\)(aq)
   (b) Fe(H\(_2\)O\(_6\))\(^3+\)(aq) + H\(_2\)O(l) ⇄ Fe(H\(_2\)O\(_5\))(OH)\(_2\)\(^+\)(aq) + H\(_2\)O\(^-\)(aq)
   (c) NH\(_4\)\(^+\)(aq) + CN\(^-\)(aq) ⇄ HCN(aq) + NH\(_3\)(aq)
   (d) (CH\(_3\))\(_2\)NH\(^+\)(aq) + H\(_2\)O(l) ⇄ (CH\(_3\))\(_2\)NH\(_2\)(aq) + OH\(^-\)(aq)
157. A solution was prepared by mixing 70.0 mL of 4.00 mol/L HCl(aq) and 30.0 mL of 8.00 mol/L HNO\(_3\)(aq). Water was then added until the final volume was 500 mL. Calculate [H\(^+\)] and the final pH.
158. Name the conjugate base and the conjugate acid of HPO\(_4\)\(^2-\). What determines if HPO\(_4\)\(^2-\) will act as an acid or a base?
159. Rewrite each equation below, identify each species as an acid or a base, and draw lines to connect the conjugate acid-base pairs.
   (a) H\(_2\)SO\(_4\)(aq) + OH\(^-\)(aq) ⇄ HSO\(_4\)\(^-\)(aq) + H\(_2\)O(l)
   (b) HSO\(_4\)\(^-\)(aq) + OH\(^-\) ⇄ SO\(_4\)\(^2-\)(aq) + H\(_2\)O(l)
160. Calculate pOH for the following aqueous solutions.
   (a) 3.2 × 10^{-3} mol/L HCl
   (b) 0.0040025 mol/L HNO\(_3\)
   (c) 2.6 × 10^{-4} mol/L Ca(OH)\(_2\)
161. A solution of acetic acid has a pH of 2.4. Is the pH of this solution higher than, lower than, or the same as the pH of a solution of 0.0005 mol/L sulfuric acid?
162. Identify each of the following as an Arrhenius acid/base, a Brønsted-Lowry acid/base, or both.
   (a) Ba(OH)\(_2\)
   (b) HCl
   (c) KOH
   (d) H\(_3\)AsO\(_4\)
   (e) CH\(_3\)COOH
   (f) HClO

**Chapter 15**

163. How many milliliters of sodium hydroxide solution are required to neutralize 20 mL of 1.0 mol/L acetic acid if 32 mL of the same sodium hydroxide solution neutralized 20 mL of 1.0 mol/L hydrochloric acid?
164. How many moles of calcium hydroxide will be neutralized by one mole of hydrochloric acid, according to the following equation?
   \[ \text{Ca(OH)\(_2\)}(aq) + 2\text{HCl(aq)} \rightarrow \text{CaCl\(_2\)}(aq) + 2\text{H}_2\text{O(l)} \]

**Chapter 16**

165. In an experiment, 50.0 mL of 0.0800 mol/L NaOH is titrated by the addition of 0.0500 mol/L HNO\(_3\). What is the hydroxide ion concentration after 30.0 mL HNO\(_3\) solution has been added.
166. A 100 mL volume of 0.200 mol/L HCl was placed in a flask. What volume of 0.400 mol/L NaOH solution must be added to bring the solution to a pH of 7.0?
167. A blood sample has a pH of 7.32. What is the hydronium ion concentration? How can hydronium ions exist in this basic solution?
168. A solution is made by combining 200.0 mL of 0.23 mol/L H\(_2\)SO\(_4\), 600.0 mL of 0.16 mol/L KOH, and 200.0 mL of water. What is the pH of this solution?
169. \(K_a\) for CH\(_3\)COOH is 1.8 × 10\(^{-5}\), and \(K_a\) for HNO\(_2\) is 7.2 × 10\(^{-4}\). When the conjugate bases of these two acids are compared, which has the larger \(K_a\)? What is the value of this larger \(K_a\)?
170. \(K_a\) for hydrazoic acid, HN\(_3\), is 2.80 × 10\(^{-5}\).
   (a) Write the equation for this dissociation of this acid in water.
   (b) What is the \(K_a\) for the conjugate base of this acid?
   (c) Compare the pH of 0.100 mol/L HN\(_3\) with the pH of a sample of the same volume in which 0.600 g of sodium azide, NaN\(_3\), has been dissolved?
171. 10.0 mL of NH\(_3\)(aq), with a concentration of 5.70 × 10\(^{-2}\) mol/L, is titrated to the end point with 2.85 mL of HBr solution. What is the concentration of the HBr solution?
172. 0.250 mol of acetic acid and 0.100 mol of sodium hydroxide are dissolved in enough water to produce 1.00 L of solution. Determine the concentration of the acetate ion, the acetic acid, and the hydronium ion in the solution.
173. The hydroxide concentration of a 0.350 mol/L solution of B, a weak base, is 7.11 × 10\(^{-5}\) mol/L. Find \(K_b\) for B. (The dissociation equation for B is B(aq) + H\(_2\)O(l) ⇄ BH\(^+\)(aq) + OH\(^-\)(aq).)
174. \(K_a\) for formic acid, HCHO\(_2\), is 1.7 × 10\(^{-4}\). Determine the hydronium ion concentration of 0.400 mol/L formic acid.

**Unit 7**
177. ΔH°f of H₁(g) is 25.9 kJ/mol.  
(a) Write the equation that represents this reaction.  
(b) Which has more enthalpy, the elements H₂(g) and I₂(g), or the product HI(g)?  
(c) What does the positive value of ΔH°f indicate about the energy that is needed to break bonds in H₂(g) and I₂(g), compared with the energy released when HI(g) forms?  

178. A 120.0 g sample of water at 30.0°C is placed in the freezer compartment of a refrigerator. How much heat has the sample lost when it changes completely to ice at 0°C?  

179. ΔH° is +106.9 kJ for the reaction  
C(s) + PbO(s) → Pb(s) + CO(g). How much heat is needed to convert 50.0 g of PbO(s) to Pb(s)?  

180. 100 g of ethanol at 25°C is heated until it reaches 75°C. How much heat did the ethanol absorb?  

181. A beaker containing 25 g of liquid at room temperature is heated until the temperature is 5°C. A second beaker containing 50 g of the same liquid at room temperature is heated until it also gains 5°C. Which beaker has gained the most thermal energy? Explain.  

182. An 80.0 g lump of iron at room temperature (23°C) was placed in an insulated container that held 100.0 mL of water at 85°C. What was the final temperature of the iron and water?  

183. A student claimed that a certain ring was pure gold. To test this claim, a classmate first determined that the mass of the ring was 12 g. The classmate then placed the ring in a beaker of hot water until the ring reached a temperature of 62°C. The classmate then removed the ring from the water with tongs and placed into an insulated cup containing 25 mL of water at 20°C. The final temperature of the ring and water was 16.7°C. Was the ring pure gold? Explain your reasoning.  

184. Your hot water heater is not working and you want to take a hot bath. You decide to boil water in a teapot on the stove and pour into the tub. First, you fill the tub with 100 kg of water at room temperature (23°C). You start boiling water on the stove. By the time you get the teapot to the tub to pour the hot water into the tub, the water in the teapot is at 96°C. How much hot water would you have to pour into the tub to bring the water to a temperature of 35°C? (Assume that a negligible amount of heat was lost to the air.)  

Chapter 17  

185. A 20.00 g sample of metal is warmed to 165°C in an oil bath. The sample is then transferred to a coffee-cup calorimeter that contains 125.0 g of water at 5.0°C. The final temperature of the water is 8.8°C.  
(a) Calculate the specific heat capacity of the metal.  
(b) What are three sources of experimental error that occur in this experiment?  

186. Use ΔH°f data to determine the heat of reaction for each reaction.  
(a) 4NH₃(g) + 3O₂(g) → 2N₂(g) + 6H₂O(l)  
(b) 2H₂O(g) + CS₂(g) → 2H₂S(g) + CO₂(g)  
(c) 4NO(g) + 6H₂O(g) → 4NH₃(g) + 5O₂(g)  

187. Use the enthalpies of combustion for the burning of CO(g), H₂(g), and C(s) to determine ΔH° for the reaction C(s) + H₂O(g) → H₂(g) + CO(g).  

188. ΔH°comb for ethene is -337 kJ/mol.  
(a) Write the balanced equation for the complete combustion of ethene in air. Include the heat term in your balanced equation.  
(b) The heat that is produced by burning 1.00 kg of ethene warms a quantity of water from 15.0°C to 85.0°C. What is the mass of the water if the heat transfer is 60.0% efficient?  

189. Determine ΔH° for  
Ca²⁺(aq) + 2OH⁻(aq) + CO₂(g) → CaCO₃(s) + H₂O(l), given the following information.  
CaO(s) + H₂O(l) → Ca(OH)₂(s)  
CaCO₃(s) → CaO(s) + CO₂(g)  
Ca(OH)₂(s) → Ca²⁺(aq) + 2OH⁻(aq)  

190. Calculate the enthalpy of formation of manganese(IV) oxide, based on the following information.  
4Al(s) + 3MnO₂(s) → 3Mn(s) + 2Al₂O₃(s) + 1790 kJ  
2Al(s) + 3/2O₂(g) → Al₂O₃(s) + 1676 kJ  

191. ΔH°comb for toluene, C₇H₈(l), is -3904 kJ/mol.  
(a) Write the equation for the complete combustion of toluene.  
(b) Use the combustion equation and ΔH° values to determine the enthalpy of formation of toluene.  

192. An impure sample of zinc has a mass of 7.35 g. The sample reacts with 150.0 g of dilute hydrochloric acid solution inside a calorimeter. The calorimeter has a mass of 520.57 g and a specific heat capacity of 0.400 J/g°C. ΔH° for the following reaction is -153.9 kJ/mol.  
Zn(s) + 2HCl(aq) → ZnCl₂(aq) + H₂(g)  
When the reaction occurs, the temperature of the solution rises from 14.5°C to 29.7°C. What is the percentage purity of the sample? Assume that the specific heat capacity of the hydrochloric acid is 4.184 J/g°C. Also assume that all of the zinc in the impure sample reacts.
193. An unknown solid was dissolved in the water of a calorimeter in order to find its heat of solution. The following data was recorded:
   - mass of solid = 5.5 g
   - mass of calorimeter water = 120.0 g
   - initial temperature of water = 21.7°C
   - final temperature of solution = 32.6°C
   (a) Calculate the heat change of the water.
   (b) Calculate the heat change caused by the solid dissolving.
   (c) What is the heat of solution per gram of solid dissolved?

194. A 100-g sample of food is placed in a bomb calorimeter calibrated at 7.23 kJ/˚C. When the food is burned, the calorimeter gains 512 kJ of heat. If the initial temperature of the calorimeter was 19°C, what is the final temperature of the calorimeter and its contents?

Unit 8

Chapter 18

195. Identify the redox reactions.
   (a) CCl4 + HF → CF3Cl + HCl
   (b) Al2O3 + 3H2SO4 → Al2(SO4)3 + 3H2O
   (c) CH4 + 2O2 → CO2 + 2H2O
   (d) P4 + 3OH− + 3H2O → PH3 + 3H2PO2−

196. Consider the following reaction.
   S8 + 8Na2SO3 → 8Na2S2O3
   (a) Assign oxidation numbers to all the elements.
   (b) Identify the reactant that undergoes reduction.
   (c) Identify the reactant that is the reducing agent.

197. Find the oxidation number for each element.
   (a) sulfur in HS−, S5−, SO32−, S2O52−, and S4O62−
   (b) boron in B2O32−, BO2−, BO2−, B2H6, and B2O3

198. List the following oxides of nitrogen in order of decreasing oxidation number of nitrogen:
   NO2, N2O4, NO, N2O3, N2O, N2O3.

199. For the following redox reaction, indicate which statements, if any, are true.
   C + D → E + F
   (a) If C is the oxidizing agent, then it loses electrons.
   (b) If D is the reducing agent, then it is reduced.
   (c) If C is the reducing agent, and if it is an element, then its oxidation number will increase.
   (d) If D is oxidized, then C must be a reducing agent.
   (e) If C is reduced, then D must lose electrons.

200. Consider the following reaction.
   3SF4 + 4BCl3 → 4BF3 + 3SCl2 + 3Cl2
   (a) Why is this reaction classified as a redox reaction?
   (b) What is the oxidizing agent in this reaction?

201. The metals Ga(s), In(s), Mn(s), and Np(s), and their salts, react as follows:
   3Mn2+ (aq) + 2Np(s) → 3Mn3+ + 2Np4+ (aq)
   In3+ (aq) + Ga(s) → In(s) + Ga3+ (aq)
   Mn2+ + Ga(s) → no reaction
   Analyze this information, and list the reducing agents from the worst to the best.

202. The following redox reactions occur in basic solution. Balance the equations using the oxidation number method.
   (a) Ti3+ + RuCl32− → Ru + TiO22+ + Cl−
   (b) ClO3→ → ClO2− + Cl−

203. The following redox reactions occur in basic solution. Use the half-reaction method to balance the equations.
   (a) NO2− → NO3− + NO2−
   (b) CrO42− + HSnO2− → CrO32− + HSnO3−
   (c) Al + NO3− → Al(OH)3 + NH3

204. The following redox reactions occur in acidic solution. Balance the equations using the half-reaction method.
   (a) ClO3− + I− → IO3− + Cl−
   (b) Cr2H4 + MnO4− → CO2 + Mn2+
   (c) Cu + SO42− → Cu2+ + SO2

205. The following redox reactions occur in acidic solution. Use oxidation numbers to balance the equations.
   (a) Se + NO3− → SeO2 + NO
   (b) Ag + Cr2O72− → Ag+ + Cr3+

206. Balance each equation for a redox reaction.
   (a) P4 + NO3− → H3PO4 + NO (acidic)
   (b) MnO2 + NO2− → NO3− + Mn2+ (acidic)
   (c) TeO22− + N2O4 → Te + NO3− (basic)
   (d) MnO4− + N2H4 → MnO2 + N2 (basic)
   (e) S2O52− + OC1− → SO42− + Cl− (basic)
   (f) Br2 + SO42− → Br− + SO22− (acidic)
   (g) PbO2 + Cl− → PbCl2 + Cl2 (acidic)
   (h) MnO42− + H2O2 → Mn2+ + O2 (acidic)

207. The following reaction takes place in acidic solution. CH3OH (aq) + MnO4 (aq) → HCOOH (aq) + Mn2+ (aq)
   (a) Balance the equation.
   (b) How many electrons are gained by the oxidizing agent when ten molecules of methanol are oxidized?
   (c) What volume of 0.150 mol/L MnO4− solution is needed to react completely with 20.0 g of methanol?

Chapter 19

208. Consider the galvanic cell represented as Al|Al3+(aq)|[Co4(III)2(II)2]Pt.  
   (a) What is the cathode?
   (b) In which direction do electrons flow through the external circuit?
   (c) What is the oxidizing agent?
   (d) Will the aluminum electrode increase or decrease in mass as the cell operates?
209. (a) Which is a better oxidizing agent in acidic solution, MnO$_4^-$ or Cr$_2$O$_7^{2-}$? From what information did you determine your answer?
(b) Suppose that you have the metals Ni, Cu, Fe, and Ag, as well as 1.0 mol/L aqueous solutions of the nitrates of these metals. Which metals should be paired in a galvanic cell to produce the highest standard cell potential? (Use the most common ion for each metal.)

210. $E^\circ_{\text{cell}}$ for the cell No$|\text{No}_3^+|\text{Cu}^{2+}|\text{Cu}$ is 2.842 V. Use this information, as well as the standard reduction potential for the Cu$^{2+}$/Cu half-reaction given in tables, to calculate the standard reduction potential for the No/No$^+$ half-cell.

211. A galvanic cell is set up using tin in a 1.0 mol/L Sn$^{2+}$ solution and iron in a 1.0 mol/L Fe$^{2+}$ solution.
(a) Write the equation for the overall reaction that occurs in this cell.
(b) What is the standard cell potential?
(c) Which electrode is positive in this cell?
(d) What change in mass will occur at the anode when the cathode undergoes a change in mass of 1.50 g?

212. Predict the products that would be expected from the electrolysis of 1.0 mol/L NaI. Use the non-standard $E$ values for water.

213. Given the half reactions below, determine if the thiosulfate ion, S$_2$O$_3^{2-}$, can exist in an acidic solution under standard conditions.

$$S_2O_3^{2-} + H_2O \rightarrow 2SO_2 + 2H^+ + 4e^- \quad E^\circ = 0.40 \text{ V}$$
$$2S + H_2O \rightarrow S_2O_3^{2-} + 6H^+ + 4e^- \quad E^\circ = -0.50 \text{ V}$$

214. Refer to the table of half-cell potentials to determine if MnO$_2$ can oxidize Br$^-$ to Br$_2$ in acidic solution under standard conditions.

215. A galvanic cell contains 50.0 mL of 0.150 mol/L CuSO$_4$. If the Cu$^{2+}$ ions are completely used up, what is the maximum quantity of electricity that the cell can generate?

216. Determine the standard cell potential for each redox reaction.
(a) IO$_3^-$ + 6ClO$_2^-$ + 6H$^+$ → I$^-$ + 3H$_2$O + 6ClO$_2$
(b) 2Cu$^{2+}$ + Hg$^{2+}$ → 2Hg + 2Cu$^+$
(c) Ba$^{2+}$ + Pb → Pb$^{2+}$ + Ba
(d) Ni + I$_2$ → Ni$^{2+}$ + 2I$^-$

217. A current of 3.0 A flows for 1.0 h during an electrolysis of copper(II) sulfate. What mass of copper is deposited?

218. To recover aluminum metal, Al$_2$O$_3$ is first converted to AlCl$_3$. Then an electrolysis of molten AlCl$_3$ is performed using inert carbon electrodes.
(a) Write the half-reaction that occurs at the anode and at the cathode.
(b) Can the standard reduction potentials be used to calculate the external voltage needed for this process? Explain your answer.

219. Summarize the differences between a hydrogen fuel cell and a dry cell.
### Alphabetical List of Elements

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Math and Chemistry

Precision, Error, and Accuracy

A major component of the scientific inquiry process is the comparison of experimental results with predicted or accepted theoretical values. In conducting experiments, realize that all measurements have a maximum degree of certainty, beyond which there is uncertainty. The uncertainty, often referred to as “error,” is not a result of a mistake, but rather, it is caused by the limitations of the equipment or the experimenter. The best scientist, using all possible care, could not measure the height of a doorway to a fraction of a millimetre accuracy using a metre stick. The uncertainty introduced through measurement must be communicated using specific vocabulary.

Experimental results can be characterized by both their accuracy and their precision.

**Precision** describes the exactness and repeatability of a value or set of values. A set of data could be grouped very tightly, demonstrating good precision, but not necessarily be accurate. The darts in illustration (A) missed the bull’s-eye and yet are tightly grouped, demonstrating precision without accuracy.

**Accuracy** describes the degree to which the result of an experiment or calculation approximates the true value. The darts in illustration (B) missed the bull’s-eye in different directions, but are all relatively the same distance away from the centre. The darts demonstrate three throws that share approximately the same accuracy, with limited precision.

The darts in illustration (C) demonstrate accuracy and precision.

**Random Error**
- Random error results from small variations in measurements due to randomly changing conditions (weather, humidity, quality of equipment, level of care, etc.).
- Repeating trials will reduce but never eliminate the effects of random error.
- Random error is unbiased.
- Random error affects precision, and, usually, accuracy.

**Systematic Error**
- Systematic error results from consistent bias in observation.
- Repeating trials will not reduce systematic error.
- Three sources of systematic error are natural error, instrument-calibration error, and personal error.
- Systematic error affects accuracy.

**Error Analysis**

Error exists in every measured or experimentally obtained value. The error could deal with extremely tiny values, such as wavelengths of light, or with large values, such as the distances between stars. A practical way to illustrate the error is to compare it to the specific data as a percentage.

**Relative Uncertainty**

Relative uncertainty calculations are used to determine the error introduced by the natural limitations of the equipment used to collect the data. For instance, measuring the width of your textbook will have a certain degree of error due to the quality of the equipment used. This error, called “estimated uncertainty,” has been deemed by the scientific community to be half of the smallest division of the measuring device. A metre stick with only centimetres marked would have an error of ±0.5 cm. A ruler that includes millimetre divisions would have a smaller error of ±0.5 mm (0.05 cm or ten-fold decrease in error). The measure should be recorded showing the estimated uncertainty, such as 22.0 ±0.5 cm. Use the relative uncertainty equation to convert the estimated uncertainty into a percentage of the actual measured value.

\[
\text{relative uncertainty} = \frac{\text{estimated uncertainty}}{\text{actual measurement}} \times 100\% 
\]

**Example:**

Converting the error represented by 22.0 ±0.5 cm to a percentage

\[
\text{relative uncertainty} = \frac{0.5 \text{ cm}}{22.0 \text{ cm}} \times 100\% 
\]

\[
\text{relative uncertainty} = 2\% 
\]

**Percent Deviation**

In conducting experiments, it frequently is unreasonable to expect that accepted theoretical values can be verified, because of the limitations of available equipment. In such cases, percent deviation calculations are made. For instance, the standard value for acceleration due to gravity on Earth is 9.81 m/s² toward the centre of Earth in a vacuum. Conducting a crude experiment to verify
this value might yield a value of 9.6 m/s². This result deviates from the accepted standard value. It is not necessarily due to error. The deviation, as with most high school experiments, might be due to physical differences in the actual lab (for example, the experiment might not have been conducted in a vacuum). Therefore, deviation is not necessarily due to error, but could be the result of experimental conditions that should be explained as part of the error analysis. Use the percent deviation equation to determine how close the experimental results are to the accepted or theoretical value.

\[
\text{percent deviation} = \left| \frac{\text{experimental value} - \text{theoretical value}}{\text{theoretical value}} \right| \times 100\%
\]

**Example:**

percent deviation = \left| \frac{9.6 \text{ m/s}^2 - 9.8 \text{ m/s}^2}{9.8 \text{ m/s}^2} \right| \times 100\%

percent deviation = 2%

**Percent Difference**

Experimental inquiry does not always involve an attempt at verifying a theoretical value. For instance, measurements made in determining the width of your textbook do not have a theoretical value based on a scientific theory. You still might want to know, however, how precise your measurements were. Suppose you measured the width 100 times and found that the smallest width measurement was 21.6 cm, the largest was 22.4 cm, and the average measurement of all 100 trials was 22.0 cm. The error contained in your ability to measure the width of the textbook can be estimated using the percent difference equation.

\[
\text{percent difference} = \left| \frac{\text{maximum difference in measurements}}{\text{average measurement}} \right| \times 100\%
\]

**Example:**

percent difference = \left| \frac{22.4 \text{ cm} - 21.6 \text{ cm}}{22.0 \text{ cm}} \right| \times 100\%

percent difference = 4%

**Practice Problems**

1. In Sèvres, France, a platinum–iridium cylinder is kept in a vacuum under lock and key. It is the standard kilogram with mass 1.0000 kg. Imagine you were granted the opportunity to experiment with this special mass, and obtained the following data: 1.32 kg, 1.33 kg, and 1.31 kg. Describe your results in terms of precision and accuracy.

2. You found that an improperly zeroed triple-beam balance affected the results obtained in question 1. If you used this balance for each measure, what type of error did it introduce?

3. Describe a fictitious experiment with obvious random error.

4. Describe a fictitious experiment with obvious systematic error.

5. (a) Using common scientific practice, find the estimated uncertainty of a stopwatch that displays up to a hundredth of a second.

   (b) If you were to use the stopwatch in part (a) to time repeated events that lasted less than 2.0 s, could you argue that the estimated uncertainty from part (a) is not sufficient? Explain.

**Significant Digits**

All measurements involve uncertainty. One source of this uncertainty is the measuring device itself. Another source is your ability to perceive and interpret a reading. In fact, you cannot measure anything with complete certainty. The last (farthest right) digit in any measurement is always an estimate.

The digits that you record when you measure something are called **significant digits**. Significant digits include the digits that you are certain about, and a final, uncertain digit that you estimate. Follow the rules below to identify the number of significant digits in a measurement.

**Rules for Determining Significant Digits**

**Rule 1** All non-zero numbers are significant.
- 7.886 has four significant digits.
- 19.4 has three significant digits.
- 527.266 992 has nine significant digits.

**Rule 2** All zeros that are located between two non-zero numbers are significant.
- 408 has three significant digits.
- 25 074 has five significant digits.

**Rule 3** Zeros that are located to the left of a measurement are not significant.
- 0.0907 has three significant digits: the 9, the third 0 to the right, and the 7.

**Rule 4** Zeros that are located to the right of a measurement may or may not be significant.
- 22 700 may have three significant digits, if the measurement is approximate.
- 22 700 may have five significant digits, if the measurement is taken carefully.

When you take measurements and use them to calculate other quantities, you must be careful to keep track of which digits in your calculations and results are significant. Why? Your results should not imply more certainty than your measured quantities justify. This is especially important when you use a calculator. Calculators usually report results with far more digits than your data warrant. Always remember that calculators do not make decisions about certainty. You do. Follow the rules given below to report significant digits in a calculated answer.
Rules for Reporting Significant Digits in Calculations

Rule 1 Multiplying and Dividing
The value with the fewest number of significant digits, going into a calculation, determines the number of significant digits that you should report in your answer.

Rule 2 Adding and Subtracting
The value with the fewest number of decimal places, going into a calculation, determines the number of decimal places that you should report in your answer.

Rule 3 Rounding
To get the appropriate number of significant digits (rule 1) or decimal places (rule 2), you may need to round your answer.
- If your answer ends in a number that is greater than 5, increase the preceding digit by 1. For example, 2.346 can be rounded to 2.35.
- If your answer ends with a number that is less than 5, leave the preceding number unchanged. For example, 5.73 can be rounded to 5.7.
- If your answer ends with 5, increase the preceding number by 1 if it is odd. Leave the preceding number unchanged if it is even. For example, 18.35 can be rounded to 18.4, but 18.25 is rounded to 18.2.

Scientific Notation
One mole of water, \( \text{H}_2\text{O} \), contains \( 6.02 \times 10^{23} \) molecules. Each molecule has a mass of \( 0.000 \ 000 \ 000 \ 000 \ 000 \ 000 \ 000 \ 000 \ 000 \ 029 \ 9 \) g. As you can see, it would be very awkward to calculate the mass of one mole of water using these values. To simplify large numbers (and clarify the number of significant digits), when reporting them and doing calculations, you can use scientific notation.

Step 1 Move the decimal point so that only one non-zero digit is in front of the decimal point. (Note that this number is now between 1.0 and 9.99999999.) Count the number of places that the decimal point moves to the left or to the right.

Step 2 Multiply the value by a power of 10. Use the number of places that the decimal point moved as the exponent for the power of 10. If the decimal point moved to the right, exponent is negative. If the decimal point moved to the left, the exponent is positive.

\[
6.02 \times 10^{23}
\]

The decimal point moves to the left.

Sample Problem
Using Significant Digits

Problem
Suppose that you measure the masses of four objects as 12.5 g, 145.67 g, 79.0 g, and 38.438 g. What is the total mass?

What Is Required?
You need to calculate the total mass of the objects.

What Is Given?
You know the mass of each object.

Plan Your Strategy
- Add the masses together, aligning them at the decimal point.
- Underline the estimated (farthest right) digit in each value. This is a technique you can use to help you keep track of the number of estimated digits in your final answer.
- In the question, two values have the fewest decimal places: 12.5 and 79.0. You need to round your answer so that it has only one decimal place.

Act on Your Strategy

\[
\begin{array}{c}
12.5 \\
145.67 \\
79.0 \\
+ 38.438 \\
\hline
275.608
\end{array}
\]

Total mass = 275.608 g
Therefore, the total mass of the objects is 275.6 g.

Check Your Solution
- Your answer is in grams. This is a unit of mass.
- Your answer has one decimal place. This is the same as the values in the question with the fewest decimal places.

Practice Problems

Significant Digits
1. Express each answer using the correct number of significant digits.
   a) 55.671 g + 45.78 g
   b) 1.9 mm + 0.62 mm
   c) 87.9478 L − 86.25 L
   d) 0.350 mL + 1.70 mL + 1.019 mL
   e) 5.841 cm × 6.03 cm
   f) 17.51 g
      2.2 cm

Scientific Notation
One mole of water, \( \text{H}_2\text{O} \), contains \( 6.02 \times 10^{23} \) molecules. Each molecule has a mass of \( 0.000 \ 000 \ 000 \ 000 \ 000 \ 000 \ 000 \ 000 \ 000 \ 029 \ 9 \) g. As you can see, it would be very awkward to calculate the mass of one mole of water using these values. To simplify large numbers (and clarify the number of significant digits), when reporting them and doing calculations, you can use scientific notation.

Step 1 Move the decimal point so that only one non-zero digit is in front of the decimal point. (Note that this number is now between 1.0 and 9.99999999.) Count the number of places that the decimal point moves to the left or to the right.

Step 2 Multiply the value by a power of 10. Use the number of places that the decimal point moved as the exponent for the power of 10. If the decimal point moved to the right, exponent is negative. If the decimal point moved to the left, the exponent is positive.

\[
6.02 \times 10^{23}
\]
2.99 $\times$ $10^{-23}$

Figure D.2 The decimal point moves to the right.

Figure D.3 shows how to calculate the mass of one mole of water using a scientific calculator. When you enter an exponent on a scientific calculator, you do not have to enter $(\times 10)$.

Keystrokes

<table>
<thead>
<tr>
<th>Keystrokes</th>
<th>Display</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6 \rightarrow$</td>
<td>6.02 23</td>
</tr>
<tr>
<td>$2 \times$</td>
<td>2.99 $\rightarrow$</td>
</tr>
<tr>
<td>$9 \rightarrow$</td>
<td>17.998</td>
</tr>
</tbody>
</table>

Round to three significant digits and express in scientific notation: $1.80 \times 10^3$ g/mol

Rules for Scientific Notation

Rule 1 To multiply two numbers in scientific notation, add the exponents.

$$(7.32 \times 10^{-3}) \times (8.91 \times 10^{-2})$$

$= (7.32 \times 8.91) \times 10^{(-3)+(-2)}$

$= 65.2212 \times 10^{-5}$

$\rightarrow 6.52 \times 10^{-4}$

Rule 2 To divide two numbers in scientific notation, subtract the exponents.

$$(1.842 \times 10^5 \text{g/mol}) ÷ (1.0787 \times 10^2 \text{g/mol})$$

$= (1.842 ÷ 1.0787) \times 10^((5-2))$

$= 1.707611 \times 10^4 \text{g}$

$\rightarrow 1.708 \times 10^4 \text{g}$

Rule 3 To add or subtract numbers in scientific notation, first convert the numbers so they have the same exponent. Each number should have the same exponent as the number with the greatest power of 10. Once the numbers are all expressed to the same power of 10, the power of 10 is neither added nor subtracted in the calculation.

$$(3.42 \times 10^6 \text{cm}) + (8.53 \times 10^3 \text{cm})$$

$= (3.42 \times 10^6) + (0.00853 \times 10^6 \text{cm})$

$= 3.42853 \times 10^6 \text{cm}$

$\rightarrow 3.43 \times 10^6 \text{cm}$

$$(9.93 \times 10^3 \text{L}) - (7.86 \times 10^1 \text{L})$$

$= (9.93 \times 10^3) - (0.0786 \times 10^1 \text{L})$

$= 9.8514 \times 10^3 \text{L}$

$\rightarrow 9.85 \times 10^3 \text{L}$

Practice problems are given on the following page.

Practice Problems

Scientific Notation

1. Convert each value into correct scientific notation.

(a) 0.000 934
(b) 7 983 000 000
(c) 0.000 000 000 820 57
(d) 496 $\times 10^6$
(e) 0.000 06 $\times 10^4$
(f) 309 72 $\times 10^{-8}$

2. Add, subtract, multiply, or divide. Round off your answer, and express it in scientific notation to the correct number of significant digits.

(a) $(3.21 \times 10^3) + (9.2 \times 10^2)$
(b) $(8.1 \times 10^5) + (9.21 \times 10^2)$
(c) $(1.0101 \times 10^1) - (4.823 \times 10^{-3})$
(d) $(1.209 \times 10^9) \times (8.4 \times 10^3)$
(e) $(4.89 \times 10^{-4}) ÷ (3.20 \times 10^{-2})$

Logarithms

Logarithms are a convenient method for communicating large and small numbers. The logarithm, or “log,” of a number is the value of the exponent that 10 would have to be raised to, in order to equal this number. Every positive number has a logarithm. Numbers that are greater than 1 have a positive logarithm. Numbers that are between 0 and 1 have a negative logarithm. Table D.1 gives some examples of the logarithm values of numbers.

Table D.1 Some Numbers and Their Logarithms

<table>
<thead>
<tr>
<th>Number</th>
<th>Scientific notation</th>
<th>As a power of 10</th>
<th>Logarithm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 000 000</td>
<td>$1 \times 10^6$</td>
<td>$10^6$</td>
<td>6</td>
</tr>
<tr>
<td>7 895 900</td>
<td>$7.859 \times 10^5$</td>
<td>$10^{5.8954}$</td>
<td>5.8954</td>
</tr>
<tr>
<td>1</td>
<td>$1 \times 10^0$</td>
<td>$10^0$</td>
<td>0</td>
</tr>
<tr>
<td>0.000 001</td>
<td>$1 \times 10^{-6}$</td>
<td>$10^{-6}$</td>
<td>–6</td>
</tr>
<tr>
<td>0.004 276</td>
<td>$4.276 \times 10^{-3}$</td>
<td>$10^{-2.3690}$</td>
<td>–2.3690</td>
</tr>
</tbody>
</table>

Logarithms are especially useful for expressing values that span a range of powers of 10. The Richter scale for earthquakes, the decibel scale for sound, and the pH scale for acids and bases all use logarithmic scales.

Logarithms and pH

The pH of an acid solution is defined as $–\log\left[H_3O^+\right]$. (The square brackets mean “concentration.”) For example, suppose that the hydronium ion concentration in a solution is 0.0001 mol/L (10$^{-4}$ mol/L). The pH is $–\log(0.0001)$. To calculate this, enter 0.0001 into your calculator. Then press the [LOG] key. Press the [±] key. The answer in the display is 4. Therefore, the pH of the solution is 4.
There are logarithms for all numbers, not just whole multiples of 10. What is the pH of a solution if \([\text{H}_3\text{O}^+] = 0.004\ 76\ \text{mol/L}\)? Enter 0.00476. Press the [LOG] key and then the \([\pm]\) key. The answer is 2.322. This result has three significant digits—the same number of significant digits as the concentration.

### The Unit Analysis Method of Problem Solving

The unit analysis method of problem solving is extremely versatile. You can use it to convert between units or to solve some formula problems. If you forget a formula, you may still be able to solve the problem using unit analysis.

The unit analysis method involves analyzing the units and setting up conversion factors. You match and arrange the units so that they divide out to give the desired unit in the answer. Then you multiply and divide the numbers that correspond to the units.

### Steps for Solving Problems Using Unit Analysis

#### Step 1
Determine which data you have and which conversion factors you need to use. (A conversion factor is usually a ratio of two numbers with units, such as 1000 g/1 kg. You multiply the given data by the conversion factor to get the desired units for the answer.) It is often convenient to use the following three categories to set up your solution: Have, Need, and Conversion factor.

#### Step 2
Arrange the data and conversion factors so that you can cross out the undesired units. Decide whether you need any additional conversion factors to get the desired units for the answer.

#### Step 3
Multiply all the numbers on the top of the ratio. Then multiply all the numbers on the bottom of the ratio. Divide the top result by the bottom result.

#### Step 4
Check that you have cancelled the units correctly. Also check that the answer seems reasonable, and that the significant digits are correct.

### Practice Problems

#### Logarithms

1. Calculate the logarithm of each number. Note the trend in your answers.
   - (a) 1  (c) 10  (e) 100  (g) 50 000
   - (b) 5  (d) 50  (f) 500  (h) 100 000
2. Calculate the antilogarithm of each number.
   - (a) 0  (c) −1  (e) −2  (g) −3
   - (b) 1  (d) 2  (f) 3
3. (a) How are your answers for question 2, parts (b) and (c), related?
   - (b) How are your answers for question 2, parts (d) and (e), related?
   - (c) How are your answers for question 2, parts (f) and (g), related?
4. (a) Calculate log 76 and log 55.
   - (b) Add your answers for part (a).
   - (c) Find the antilogarithm of your answer for part (b).
Problem

In the past, pharmacists measured the active ingredients in many medications in a unit called grains (gr). A grain is equal to 64.8 mg. If one headache tablet contains 5.0 gr of active acetylsalicylic acid (ASA), how many grams of ASA are in two tablets?

What Is Required?

You need to find the mass in grams of ASA in two tablets.

What Is Given?

There are 5.0 gr of ASA in one tablet. A conversion factor for grains to milligrams is given.

Plan Your Strategy

Multiply the given quantity by conversion factors until all the unwanted units cancel out and only the desired units remain.

<table>
<thead>
<tr>
<th>Have</th>
<th>Need</th>
<th>Conversion factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0 gr</td>
<td>? g</td>
<td>64.8 mg/1 gr and 1 g/1000 mg</td>
</tr>
</tbody>
</table>

Act on Your Strategy

\[
\begin{align*}
5.0 \frac{\text{gr}}{\text{tablet}} \times \frac{64.8 \text{ mg}}{1 \text{ gr}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times 2 \text{ tablets} &= \frac{5.0 \times 64.8 \times 2}{1000} \\
&= 0.648 \text{ g} \\
&= 0.65 \text{ g}
\end{align*}
\]

There are 0.65 g of active ASA in two headache tablets.

Check Your Solution

There are two significant digits in the answer. This is the least number of significant digits in the given data.

Notice how conversion factors are multiplied until all the unwanted units are cancelled out, leaving only the desired unit in the answer.

The next sample problem will show you how to solve a stoichiometric problem.
Therefore, 2.0 g of oxygen are produced by the decomposition of 5.0 g of potassium chlorate. As you become more familiar with this type of question, you will be able to complete more than one step at once. Below, you can see how the conversion factors we used in each step above can be combined. Set these conversion ratios so that the units cancel out correctly.

$$\text{mass } O_2 = \frac{5.0 \text{ g KClO}_3}{122.6 \text{ g KClO}_3} \times \frac{1 \text{ mol}}{3 \text{ mol KClO}_3} \times \frac{3 \text{ mol KClO}_3}{2 \text{ mol KClO}_3} \times \frac{32.0 \text{ g}}{1 \text{ mol O}_2}$$

$$= 1.96 \text{ g}$$

$$= 2.0 \text{ g}$$

**Check Your Solution**

The oxygen makes up only part of the potassium chlorate. Thus, we would expect less than 5.0 g of oxygen, as was calculated.

The smallest number of significant digits in the question is two. Thus, the answer must also have two significant digits.

**Practice Problems**

**Unit Analysis**

Use the unit analysis method to solve each problem.

1. The molar mass of cupric chloride is 134.45 g/mol. What is the mass, in grams, of $8.19 \times 10^{-3}$ mol of this compound?

2. To make a salt solution, 0.82 mol of CaCl$_2$ are dissolved in 1650 mL of water. What is the concentration, in g/L, of the solution?

3. The density of solid sulfur is 2.07 g/cm$^3$. What is the mass, in kg, of a 1.8 dm$^3$ sample?

4. How many grams of dissolved sodium bromide are in 689 mL of a 1.32 mol/L solution?
Table E.1 Useful Math Relationships

\[ D = \frac{m}{V} \]

\[ P = \frac{F}{A} \]

\[ \pi = 3.1416 \]

Volume of sphere \( V = \frac{4}{3} \pi r^3 \)

Volume of cylinder = \( \pi r^2 h \)

Table E.2 Fundamental Physical Constants (to six significant digits)

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>acceleration due to gravity ((g))</td>
<td>9.806 65 m/s²</td>
</tr>
<tr>
<td>Avogadro constant ((N_a))</td>
<td>6.022 14 × 10²³/mol</td>
</tr>
<tr>
<td>charge on one mole of electrons ((\text{Faraday constant}))</td>
<td>96 485.3 C/mol</td>
</tr>
<tr>
<td>mass of electron ((m_e))</td>
<td>9.109 38 × 10⁻³¹ kg</td>
</tr>
<tr>
<td>mass of neutron ((m_n))</td>
<td>1.674 93 × 10⁻²⁷ kg</td>
</tr>
<tr>
<td>mass of proton ((m_p))</td>
<td>1.672 62 × 10⁻²⁷ kg</td>
</tr>
<tr>
<td>molar gas constant ((R))</td>
<td>8.314 47 J/mol·K</td>
</tr>
<tr>
<td>molar volume of gas at STP</td>
<td>22.414 0 L/mol</td>
</tr>
<tr>
<td>speed of light in vacuo ((c))</td>
<td>2.997 92 × 10⁸ m/s</td>
</tr>
<tr>
<td>unified atomic mass ((u))</td>
<td>1.660 54 × 10⁻²⁷ kg</td>
</tr>
</tbody>
</table>

Table E.3 Common SI Prefixes

<table>
<thead>
<tr>
<th>Prefix</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>tera</td>
<td>T</td>
<td>10¹²</td>
</tr>
<tr>
<td>giga</td>
<td>G</td>
<td>10⁹</td>
</tr>
<tr>
<td>mega</td>
<td>M</td>
<td>10⁶</td>
</tr>
<tr>
<td>kilo</td>
<td>k</td>
<td>10³</td>
</tr>
<tr>
<td>deci</td>
<td>d</td>
<td>10⁻¹</td>
</tr>
<tr>
<td>centi</td>
<td>c</td>
<td>10⁻²</td>
</tr>
<tr>
<td>milli</td>
<td>m</td>
<td>10⁻³</td>
</tr>
<tr>
<td>micro</td>
<td>µ</td>
<td>10⁻⁶</td>
</tr>
<tr>
<td>nano</td>
<td>n</td>
<td>10⁻⁹</td>
</tr>
<tr>
<td>pico</td>
<td>p</td>
<td>10⁻¹²</td>
</tr>
</tbody>
</table>

Table E.4 Conversion Factors

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Relationships between units</th>
</tr>
</thead>
<tbody>
<tr>
<td>length</td>
<td>1 m = 10⁻³ km</td>
</tr>
<tr>
<td></td>
<td>= 10⁻⁵ mm</td>
</tr>
<tr>
<td></td>
<td>= 10⁻² cm</td>
</tr>
<tr>
<td></td>
<td>1 pm = 10⁻¹² m</td>
</tr>
<tr>
<td>mass</td>
<td>1 kg = 10³ g</td>
</tr>
<tr>
<td></td>
<td>= 10⁻³ t</td>
</tr>
<tr>
<td></td>
<td>1 u = 1.66 × 10⁻²⁷ kg</td>
</tr>
<tr>
<td>temperature</td>
<td>0 K = −273.15°C</td>
</tr>
<tr>
<td></td>
<td>( T (K) = T (^\circ C) + 273.15 )</td>
</tr>
<tr>
<td></td>
<td>( T (^\circ C) = T (K) − 273.15 )</td>
</tr>
<tr>
<td></td>
<td>mp of H₂O = 273.15 K (0°C)</td>
</tr>
<tr>
<td></td>
<td>bp of H₂O = 373.15 K (100°C)</td>
</tr>
<tr>
<td>volume</td>
<td>1 L = 1 dm³</td>
</tr>
<tr>
<td></td>
<td>= 10⁻³ m³</td>
</tr>
<tr>
<td></td>
<td>= 10⁻¹ mL</td>
</tr>
<tr>
<td>pressure</td>
<td>101 325 Pa = 101.325 kPa</td>
</tr>
<tr>
<td></td>
<td>= 760 mm Hg</td>
</tr>
<tr>
<td></td>
<td>= 760 torr</td>
</tr>
<tr>
<td></td>
<td>= 1 atm</td>
</tr>
<tr>
<td>density</td>
<td>1 kg/m³ = 10³ g/m³</td>
</tr>
<tr>
<td></td>
<td>= 10⁻³ g/mL</td>
</tr>
<tr>
<td></td>
<td>= 1 g/L</td>
</tr>
<tr>
<td>energy</td>
<td>1 J = 6.24 × 10¹⁵ eV</td>
</tr>
</tbody>
</table>